Chapter 2
Polymer Chelating Ligands: Classification, Synthesis, Structure, and Chemical Transformations

Abstract The past few decades were marked by significant achievements in the field of chelating polymer ligands including those of different types of polymers and various chelating fragments. The chelating polymers classification adopted in this book includes, primarily, the method of preparation and structure of the polymer backbone and then its functionality. These ligands provide broad control over the metal chelate distribution and allow to preparing polymeric materials with enhanced stability, tunable solubility in aqueous and organic media, as well as interesting optical, magnetic, and fluorescent properties. This chapter analyzes the synthetic methodologies and spatial structures such chelating polymer polymers as linear, branched, cross-linked, grafted polymers, dendrimers, star and hyperbranched polymers, as well as liquid-crystalline polymers and polymeric films. Special attention is paid to the features of chelating polymer ligand preparation methods: (co)polymerization of chelating monomers, methods of controlled radical polymerization, click chemistry methods, method of cation polymerization, chemical oxidized polymerization, electropolymerization, photo- and microwave-assisted polymerization, cyclopolymerization, asymmetrical polymerization, post-polymerization modification, polycondensation reactions, «green» synthesis, and grafted polymerization. The problems and future prospects of such chelating polymer ligands are outlined.

Chemistry of chelating polymers has reached its peak development in XXI century: keys to the synthesis of a range of new type of CPLs have been found, fine technology of fabrication of such materials as biosensors, medical implants, organic light-emitting diodes (OLED) has been developed, spatial structural organizations of interface boundaries have been basically understood. Thin films give a possibility of direct synthesis of polymers with extremely difficultly compatible functional groups. Using post-polymerization modification (PPM) in combination with click chemistry methods makes it possible to avoid limitations, which would be impossible to achieve otherwise [1]. Polymers are very convenient for fabrication of hybrid materials, because a chain gives a wide range of possibilities for integration of functional groups and active centres of different origins.

G. I. Dzhardimalieva and I. E. Uflyand, *Chemistry of Polymeric Metal Chelates*, Springer Series in Materials Science 257,
https://doi.org/10.1007/978-3-319-56024-3_2

Interaction between MX_n and CPLs is the most-used method of PMC preparation [2–14]. It is important that the possibility of synthesis of PMCs, as well as their physico-chemical properties, can be engineered even at the stage of CPL design. Presently chemistry and synthesis technique of CPL are developed quite well and they continue to improve. Owing to achievements of contemporary polymer chemistry, now there are no considerable difficulties in synthesis of any chelating fragments linked by a polymer chain. Moreover, almost all types and classes of traditional polymers are involved in solutions to these problems (Fig. 2.1) [15].

All three traditional approaches of polymer chemistry are used for creation of the polymers containing chelating fragments:

- homopolymerization, co-polymerization, and grafted polymerization of monomers with chelating nodes;
- polycondensation of respective compounds, which bring to CPL formation;
- PPM of functional groups of polymers for completion of chelating fragments.

The simplest way of producing CPLs is associated with synthesis of new monomers for reactions of polymerization and polycondensation, in which necessary functionalities are included in chemical structure of their monomers. Though these precursors with chelating groups always took a special place among other methods of polymer chelation, due to their simplicity and wide range of reactions with their participation, researchers always encountered with the problems of establishment of the effect of these groups on polymerization rate and conversion, as well as introduction of sufficient number of monomer units in a polymer during copolymerization of multiactive comonomers, etc. However, a potential of this approach is limited,

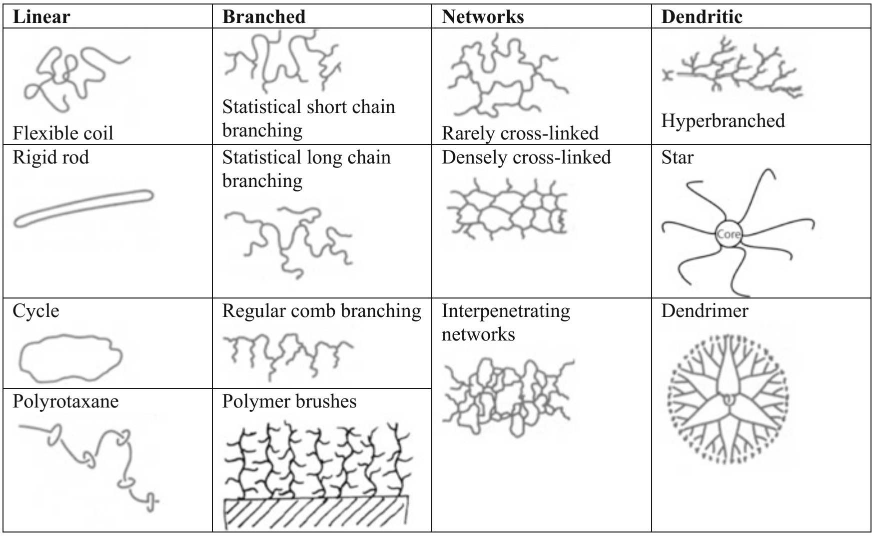


Fig. 2.1 Architecture of macromolecules for CPL design

since, on the one hand, a number of similar monomers is strongly limited, and on the other hand, the (co)polymerization process is accompanied by variety of chemical transformations of these monomers.

Alternative approach is PPM (post-polymerization design) of CPLs of different topology and structure from already known polymers [16, 17], especially, using commercial polymers as backbone [18, 19]. Possibilities of this way are almost infinite: from changing such simple characteristics as composition of a chelating fragment, length of linking bridges (spacers), presence of cross-linkings, etc., to subtler effects, like long-range correlations and gradient structure. Therefore, in frameworks of this approach a wide range of CPLs can be designed, almost without disturbing the main chain of initial polymer.

The developed preparation methods of CPL synthesis are widely used in laboratory practice and in industry, in particular, in production of chelating sorbents.

Increasing needs of science and engineering bring to the forefront the problems of design of principally new «functional» [20–25], «smart» [26–28], «stimuli-responsive shape memory» [29], «self-oscillating» [30], and other materials, using efficient critical technologies meeting demands of «green chemistry» [31–37]. Among them is primary choice of enzymatic catalyst [38–40], reaction medium (supercritical carbon dioxide [41–43], ionic liquids (ILs) [44], water as solvent [45–47]), design of biodegradable polymers [48], etc.

Varying of a polymer chain structure makes it possible to perform «fine tuning» of necessary parameters and properties, thus creating prerequisites for fabrication of materials with desired properties [49–53]. In this respect applying of the principles of constitutional dynamic and adaptive chemistry [54–59] is very promising, especially with usage of molecular dynamic libraries [60] or computer databases of polymers [61]. Chemical structure of macromolecules is widely variable: even a single macromolecule could be considered as a «molecular system», which can change configuration in a wide range, and abnormally low entropy makes it highly sensitive to different impacts.

2.1 Linear, Branched and Network Polymers as Chelating Macroligands

The study of the physico-chemical properties and spatial structure of polymers is one of most promising approaches to solution of the problem of design and directed synthesis of PMC with predetermined properties. In contrast to low molecular weight analogues, polymer ligand is characterized by some features, which make difficult to study its physico-chemical characteristics. This, probably, explains why many CPLs based on synthetic polymers have not been adequately studied. For them three levels of structural organization should be taken into account [62]:

- molecular, which reflects chemical structure of polymer units, their distribution in chain and stereochemical construction of the chains;

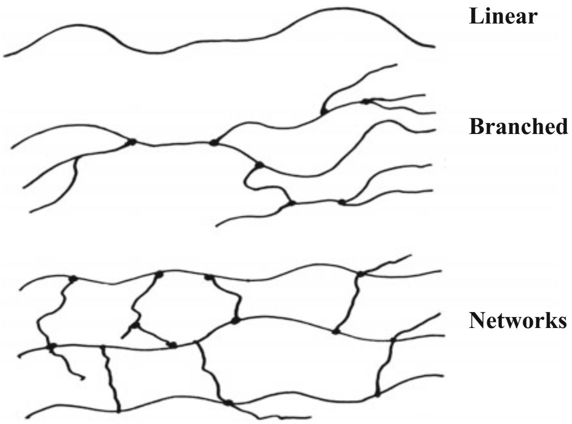


Fig. 2.2 Structure of polymers

- supramolecular, which takes into account intermolecular interactions, degree of ordering and macromolecular packing;
- topological, which characterizes correlation between elements of the structure of polymers (molecular-mass distribution, parameters of 3D structure, etc.)

Among vast variety of topological structures of the polymers [2, 63], the simplest are linear, branched, and network structures (Fig. 2.2).

Most widely for the CPL synthesis free radical polymerization is used, rarely used is ionic polymerization of chelating monomers depending on character of active particles. By a number of types of contributing monomers homopolymerization (one type of monomer) and co-polymerization (two and more types of monomers), resulting in linear or branched polymers, are distinguished. In order to obtain spatially cross-linked polymers, polymerization is carried out in presence of divinyl compounds, for example, divinylbenzene (DVB), *N*,*N*′-methylenebisacrylamide (MBA), etc., or various methods of 3D polymerization are used [64]. Wide use of this technology is stipulated by a possibility of its application for different vinyl monomers, soft conditions of reaction process, often by tolerance to functional groups of monomers, easiness of application in industry, and low cost as compared with other technological processes.

2.1.1 (Co)polymerization of Chelating Monomers

Polymerization begins from breaking of one chemical bonds and creation of others. Break in double bonds leads to decrease in energy of a system and is spontaneous exothermal process ($\Delta G < 0$, $\Delta H < 0$). However, without external impacts (initiators, catalysts, etc.) polymerization usually proceeds slowly. Thus, methacryloylacetone can polymerize slowly at storage at room temperature, however, its polymerization rate is far slower than that of traditional monomers, such as methyl methacrylate (MMA), styrene (St), etc. This is due to strong tendency to transfer of a chain by chelating fragments (for example, by enol form of β-diketonate groups) and low activity of enol radicals as compared to radicals of the chain growth [65].

To increase polymerization rates of chelating type monomers, standard methods are used: chemical action by introduction of different initiators (peroxides, azo-compounds). Thus, benzoyl peroxide (BP) was used in polymerization of monomers containing such chelating fragments as *o*-hydroxyaldehydes (ketones) [66, 67], salicylaldimines [68–70], 8-hydroxyquinolines (HQ) [71–74], etc.

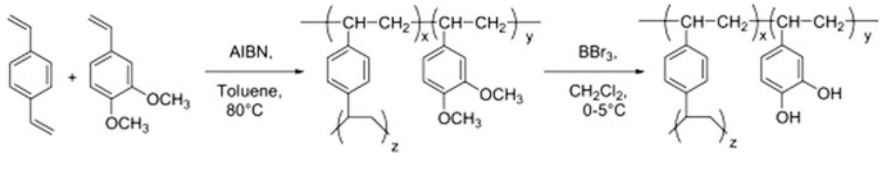
The examples of using 2,2′-azobisiso-butyronitrile (AIBN) are polymerization of monomers with groups 1,4,8,11-tetraazacyclotetradecane (cyclam) [75], HQ [76–79], 2-acrylamidosulphadiazine [80], 2-acrolyl-quinazoline [81], 34-membered monoazacrown ether [82], and also co-polymerization of traditional monomers with chelating monomers 5-vinyl-*m*-phenylene-*m*′-phenylene-32-crown-10 [83], benzo-15-crown-5 derivative [84], acrylamidomethyl-18-crown-6 (acrylamidomethyl-15-crown-5) [85], benzo-12-crown-4 (15-crown-5, 18-crown-6)-acrylamide [86–89], Q-methacrylate [90–92], etc.

These initiators are widely used for synthesis of cross-linked co-polymers. Thus, 2-hydroxy-4-acryloyloxybenzophenone was co-polymerized with DVB in presence of AIBN [93]. Poly(vinylcatechol-*co*-DVB) resins were obtained via suspension polymerization of 3,4-dimethoxystyrene and DVB and toluene as a porogen and the following removal of protection from catechol groups (Scheme 2.1) [94].

Co-polymerization of 4-acetyl acryloyl ethyl acetate and acrylic acid (AA) was performed using AIBN as initiator and MBA as a cross-linking agent [95]. The cross-linked polymers of poly(2-hydroxy-4-acryloyloxybenzophenone) were obtained by free-radical polymerization of 2-hydroxy-4-acryloyloxybenzophenone monomer with DVB cross-linking agent [96].

It should be noted the synthesis of homo- and copolymers of poly(norbornene) containing spiropyran (SP) side groups [97]. Due to the opened merocyanine (MC) form, difficulties in the homopolymerization of SPs were observed, which resulted in low polymerization yields for homopolymers. At the same, copolymers with 10 mol% SP content were obtained in good yield. Also it is important that switching between the apolar SP form and the zwitter-ionic MC form also leads to switchable wettability.

Of considerable interest is also poly(crown ether) bearing dibenzo-24-crown-8 moieties in the polymer backbone prepared using a rotaxanation-protection protocol, including stepwise production via the polymerization of cavity-filled [2] rotaxane and subsequent removal of the axial fragment [98].



Scheme 2.1 Synthesis of porogenic catechol CPL

Values of reactivity coefficients for Q-methacrylate (r_1) and MMA (r_2) found from the Finemann-Ross dependence are 0.76 and 0.52, respectively [90]. When the values r_1 and r_2 are less than 1, azeotropic polymerization takes place, and $r_1 = 0.67$ (which corresponds to the mole fraction of Q-methacrylate in the initial monomer mixture) points to the fact that the formed co-polymer will have the same composition as the initial monomer mixture. When the molar fraction in the monomer mixture is less than 0.67, co-polymer is enriched with units of chelating monomer. The composition of the co-polymer (Table 2.1) illustrates these relationships.

The idea of a character of distribution of co-polymers of a certain molecular weight—polydispersity index (PDI = M_w/M_n), is seen from Table 2.2. The M_w and M_n values change from 13,974 to 19,996 and from 38,071 to 56,950, respectively, while PDI varies from 2.68 to 2.96. Intrinsic viscosity varies from 0.015 to 0.030 dL g^{-1}. These results show that when content of Q-methacrylate decreases in the co-polymers, average molecular weight and viscosity decrease considerably, whereas PDI varies randomly [90].

Table 2.1 Copolymer compositions data and reactivity ratios of copolymers of Q-methacrylate and MMA

Monomer feed composition		Conversion (%)	Composition of Q-methacrylate in copolymer [m_1]	Reactivity ratio	
Q-methacrylate [M_1] mol.	MMA [M_2] mol.			r_1	r_2
1.00	–	–	–	0.76	0.52
0.50	0.50	9.45	0.552		
0.40	0.60	8.86	0.425		
0.30	0.70	8.38	0.336		
0.20	0.80	9.76	0.212		
0.10	0.90	8.40	0.184		
–	1.00	–	–		

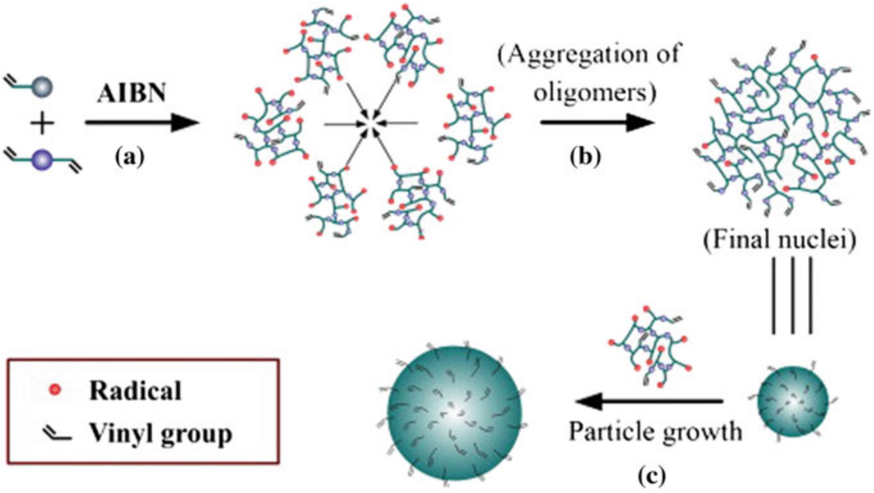
Table 2.2 Average molecular weights and viscosity data for the copolymers Q-methacrylate with MMA

Composition of Q-methacrylate in copolymer	M_n	M_w	PDI	[η], dL g^{-1}
1.00	19,219	56,950	2.96	0.030
0.552	19,966	46,153	2.72	0.023
0.425	15,210	42,356	2.78	0.020
0.336	14,539	39,626	2.73	0.019
0.212	14,210	38,071	2.68	0.016
0.184	13,974	38,102	2.73	0,015
–	14,848	40,146	2.70	0.017

Among other initiators, we shall notice 2,2′-dimethoxy-2-phenyl-acetophenone, which was used for polymerization of diethyliminodiacetate-containing monomers based on ethyl-α-bromomethacrylate and α-chloromethacryloylchloride with diethyl iminodiacetate [99]. Monomers show low homopolymerization activity, which is ascribed to steric effect of *N,N*-disubstituted methacrylamides, in presence of allylamine group they are subjected to the degradation transfer of a chain, while bulky iminodiacetate groups enclose a double bond. Monomers with diethyliminodiacetate groups are co-polymerized with acrylamide (AAm) in water under action of the 2,2′-azobis(*N,N*′-amidinopropane) dihydrochloride initiator. It should also be noted that in this system rate of polymerization and conversion of both monomers are reduced.

Among other kinetic dependencies of polymerization, we shall note that *p*-vinylbenzoylacetone polymerization follows the traditional model of radical polymerization; its rate is proportional to square root from concentration of initiator. The ratio of activities in co-polymerization is $r_1 = 2.56$ for St and $r_2 = 0.32$ for *p*-vinylbenzoylacetone in benzene [100].

Polymerization is carried out in different ways: in bulk, in solution, in suspension. For example, polyacryloylacetone is prepared by polymerization of acryloylacetone in sealed tubes [101]. Initiated polymerization of salicylic acid *O*-carboxyanhydride was performed in block at 140 °C [102]. In this case, rather pure polymer is obtained, and the main difficulty of the process is in removal of polymerization heat. Most CPLs are obtained by polymerization in solution, since it is easier to remove heat and to control composition and structure of the polymers, however, a problem of a solvent removing is raised. A scheme of radical precipitation polymerization can be represented as follows (Scheme 2.2).



Scheme 2.2 Mechanism of particles' formation during precipitation polymerization, including particle nucleation (**a**, **b**) and particle growth (**c**)

The co-polymer PAN-*co*-poly(hexamethylene guanidine hydrochloride), where PAN is polyacrylonitrile, was also obtained by precipitation co-polymerization of acrylonitrile (AN) and modified macromonomer poly(hexamethylene guanidine hydrochloride) in water [103].

During suspension polymerization a monomer exists in form of drops dispersed in water or other liquid. As a result of the reaction, polymer beads are formed with the size from 10^{-16} to 10^{-13} m. Inversion suspension co-polymerization of hydrophilic glycidyl methacrylate (GMA) and iminodiacetic acid (IDA) [104]; suspension radical co-polymerization of 2-methacryloyl amidocysteine, and 2-hydroxyethyl-methacrylate [105, 106] can be considered as examples. The traditional drawback of this method is a necessity in stabilization of suspension and washing of polymers from stabilizers.

Apart from traditional ways of initiation, polymerization of chelating monomers can also take place as a result of radiation initiation. Therefore, γ-radiation polymerization of AA is performed in presence of 2-mercaptobenzimidazole and a cross-linking agent [107]. The CPL with fragments of ethylenediaminetetraacetic acid (EDTA) is obtained via γ-radiation induced template polymerization of AA on polyacrylamide (PAAm) in presence of EDTA-Na_2 and MBA as a cross-linking agent [108]. Hydrogel poly(*N*-(hydroxymethyl) methacrylamide-1-allyl-2-thiourea) is synthesized under action of γ-radiation using ^{60}Co with different radiation doses to change the porosity and cross-linking density of the hydrogels [109, 110].

Control over molecular weight of macromolecules can be realized, as in the case of traditional monomers, using initiators, inhibitors, and other compounds. However, transfer and termination can take place at different stages of a chain growth, therefore macromolecules are polydisperse. A drawback of radical polymerization is a difficulty in control over molecular weight of a polymer, molecular structure, and composition of a co-polymer [111]. Therefore, there was always a necessity in improvement of the process of radical polymerization under soft conditions, so that CPLs with controlled molecular weight, required architecture of macromolecules and low PDI could be obtained.

2.1.2 Chelating Macroligands Obtained by the Methods of Controlled Radical Polymerization

A range of new chemical and biologic methods of polymerization used in large-scale and small-scale polymer production is recently developed [26]. Thus, discovery of «living» controlled radical polymerization (CRP) [112–114] was a serious step in the way of improvement of the technology, because this method provides production of high quality polymers with predetermined structure and molecular weight under conditions typical for radical polymerization. The polymers obtained by that way have narrow PDI and a specified molecular weight. Moreover, the method of CRP gives a possibility of synthesis of polymer molecules of complicated architecture (block-*co*-polymers, star-like and grafted structures), and also a possibility of introduction of chelating fragments in a polymer structure. Thus, the «living» controlled radical co-polymerization is used to obtain polyfunctional block (-*b*-) St-co-MMA polymers with narrow PDI, containing units of 2,2′:6′,2″-terpyridine (tpy) in the side chain [115].

It should be noted the synthesis of «schizophrenic» copolymer (poly[1′-(2-methacryloxyethyl)-3′,3′-dimethyl-6-nitrospiro-(2H-1-benzopyran-2,2′-indoline)]-*b*-PAA) by sequential Cu(0)-mediated «living» CRP at 30 °C in an oxygen-tolerant system followed by hydrolysis of the resulting polymer [116]. The «schizophrenic» micellization behavior of as-prepared copolymer in aqueous solution regulated by light and pH stimuli was vividly demonstrated (Fig. 2.3).

In the ideal «living» polymerization reaction of irreversible chain termination does not happen, all polymer chains begin their growth almost simultaneously (at the initiation rate far higher than the growth rate of a chain). Therefore, PDI is very narrow (<1.5), and growth of polymer chains can be continued at addition of a new portion of a monomer. A decrease in contribution from the reaction of irreversible chain termination can be achieved by decrease in concentration of growing polymer radicals via introduction of mediators of polymerization, which react reversibly with growing polymer radicals, thus converting them into inactive state. Therefore, equilibrium is reached between active and inactive polymer radicals. Without going into details of quite profoundly studied mechanism, we shall notice that, depending on a way of «livening» macromolecules, the following kinds of this method are distinguished:

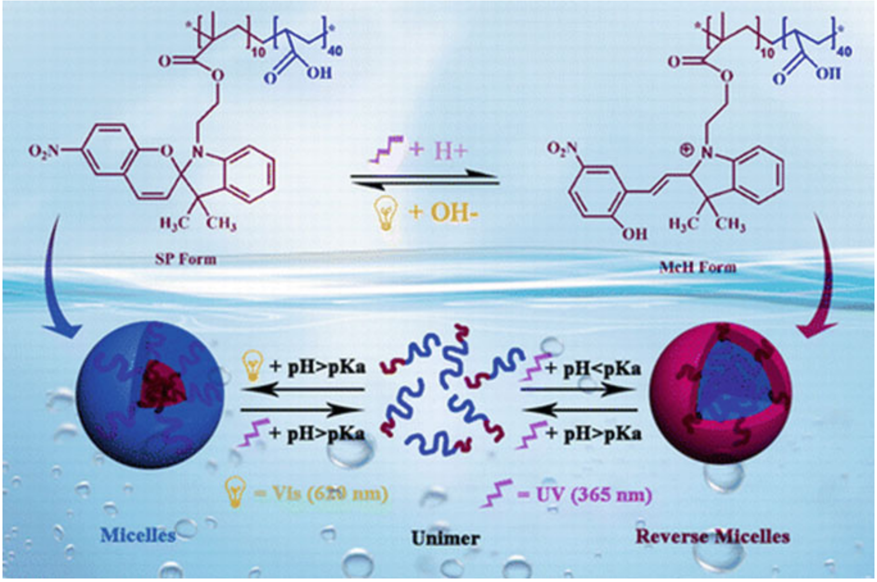


Fig. 2.3 Vividly «schizophrenic» micellization behavior in aqueous system

(1) polymerization with participation of metal complexes, so called Atom Transfer Radical Polymerization (ATRP) [117, 118];
(2) polymerization via reversible addition of a radical and fragmentation of dithioethers, in other words, Reversible Addition Fragmentation Transfer (RAFT) Polymerization [119–123];
(3) polymerization with participation of stable radicals, including nitroxyl groups, which is called Nitroxide Mediated Polymerization (NMP) [124].

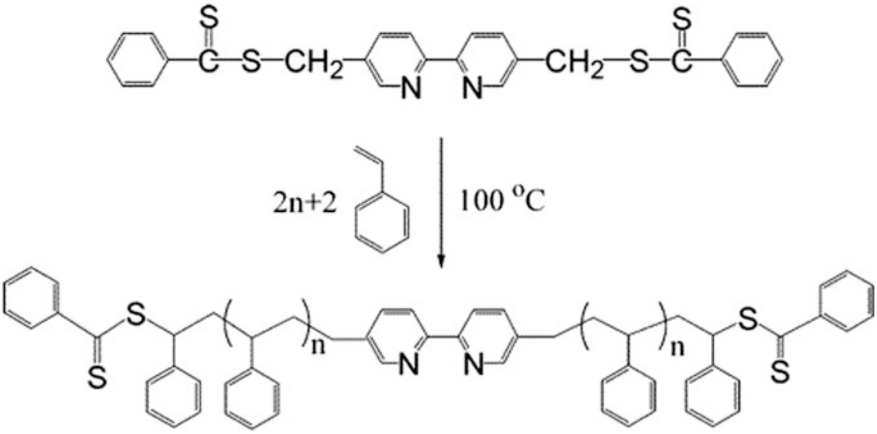
In the most widely spread ATRP method «livening» of macromolecules is due to reversible atom transfer: a macroradical interacts reversibly with a special addition (catalyst, a compound of a transition metal) via redox reaction, alkyl-halide (most often bromide) is used as initiator.

The ATRP of St is performed in presence of 5-(chlorosulfonyl) salicylic acid [125, 126]. Polystyrene (PS) with end-capped HQ groups has been obtained via ATRP with 5-chloromethyl-Q acetate used as initiator. The results point to the fact that polymerization proceeds by the first order by monomer. Molecular weight of the formed polymer increases linearly with consumption of the monomer and displays very narrow molecular-weight distribution (PDI less than 1.2) [127]. Depending on molecular weight, polymers can self-assembly in hollow or solid spheres, or monolayer film with regular pores [128].

Diblock-copolymer with HQ side groups was synthesized by St polymerization using RAFT method in presence of a chain-transfer agent, which was a polymer produced by living controlled polymerization of the monomer being a product of reaction between HQ and 2-hydroxyethylmethacrylate [129]. RAFT co-polymerization of 2-((HQ-5-yl) methoxy) ethyl methacrylate with St or MMA was successfully carried in presence of 2-cyanoprop-2-yl-dithionaphthalenoate. Its kinetic behavior confirms the origin of living polymerization [130]. It is noted application the nonionic amphiphilic brush polymers such as poly(PEO methyl ether vinyl phenyl-*co*-St) trithiocarbonate and poly(PEO methyl ether vinyl phenyl-*b*-St-*b*-PEO methyl ether vinyl phenyl) trithiocarbonate as macro-RAFT agent in the emulsion RAFT polymerization of St, where PEO is poly(ethylene oxide) [131]. PS and poly(*n*-butyl acrylates) with two end tpy groups are obtained via RAFT polymerization using the symmetric bis-tpy-functionalized trithiocarbonate as the chain-transfer agent [132]. Amphiphilic polymers poly(triethyleneglycol methyl ether methacrylate)-*b*-PS with tpy groups randomly distributed along water-soluble block-copolymer have been obtained by RAFT polymerization [133]. Similarly, the PS-*b*-poly(2-hydroxy-5-vinylbenzaldehyde) copolymers are obtained from 2-hydroxy-5-vinylbenzaldehyde using the chain-transfer macroagent PS with the end trithiocarbonate groups [134].

Chelating ligand 2,2′-bipyridine (bpy) with fixed in 5,5′-positions RAFT-agents showed good controlling functions during St polymerization according to the first order kinetics and linear growth of molecular weight with conversion (Scheme 2.3) [135].

The analogous synthetic procedure is applied for synthesis of tpy with one bound RAFT-agent used for controlled co-polymerization of St and *N*-isopropylacrylamide



Scheme 2.3 RAFT polymerization of St using a bpy block with two cross-linked RAFT-agents

(NIPAM) resulted in formation of a polymer with the tpy-chelating end group [136]. The monomer functionalized by benzenedinitrile, 2-methyl-acrylic acid 6-(3,4-dicyano-phenoxy)-hexyl ester, was successfully polymerized via RAFT method. The polymerization has all features of the «living»/CRP: first order kinetics, linear increase of molecular weight with conversion of the monomer, narrow PDI, and successful chain-extension experiments [137]. Also RAFT polymerization was used for production of amphiphilic block-copolymers with chelating oxime group, in which hydrophobic keto-functional blocks self-assemble into micelles in water [138]. Addition of bifunctional alkoxyamine to these solutions brings to cross-linking of the micelles, forming star polymers.

Alternating RAFT copolymerization of *p*-methoxydiethylene glycol-substituted St and *N*-(2-salicylaldehyde-aminoethyl) maleimides leads to well-defined alternating copolymers with narrow polydispersity (PDI < 1.35) [139]. It is interesting that these alternating PMCs show an excellent selective fluorescence «OFF-ON» response to Zn(II) ions by inhibiting the photoinduced electron transfer (PET) effect. At the same time, the initial salicylaldimine monomer almost has no fluorescence response to Zn(II) ions due to the PET process.

RAFT polymerization was used to prepare the well-defined block copolymers based on 2-(acetoacetoxy) ethyl methacrylate (hydrophobic, metal chelating) and 9-anthryl-MMA (hydrophobic, fluorescent) with effective dual chemosensor properties (i.e., amino- and metal-ion sensors) in an organic solvent (chloroform) [140].

The controlled polymerization of commercially available 2-(acetoacetoxy) ethyl methacrylate was performed in presence of such highly efficient chain-transfer agent as 2-cyano-2-propyl dithiobenzoate and AIBN as radical initiator (Table 2.3) [141]. Under determined conditions of the reaction the quantitative conversion of the monomer is really achieved for polymerization time in the interval from 15 to 20 s. The polymerization follows the first order kinetics by the monomer, molecular

Table 2.3 Experimental conditions and molecular characteristics of (acetoacetoxy)ethyl methacrylate homopolymers obtained by RAFT radical polymerization (initiator: AIBN, solvent: ethyl acetate, temperature 60 °C)

$[Monomer]_0/[agent]_0/[AIBN]_0$ (M)	Time (h)	x_p[a]	DP[b]	PDI
5.2/0.271/0.037	20	>0.99	30	1.16
2.6/0.132/0.020	n.d.	0.82	44	1.17
5.2/0.072/0.020	15	>0.99	106	1.16
3.7/0.052/0.007	20	0.96	145	1.15
5.2/0.026/0.005	18	0.39	177	1.13
2.6/0.021/0.004	46	0.85	176	1.13

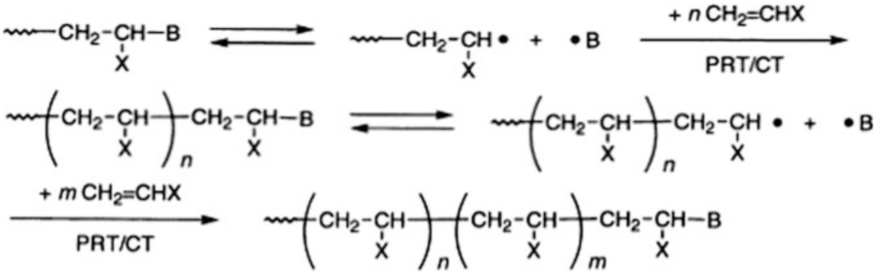
[a] monomer conversion
[b] degree-of-polymerization

weight of the polymers increases linearly with conversion, and final products have monomodal and narrow molecular-weight distribution (apparent PDI < 1.2). These results lead to the assumption that RAFT radical polymerization provides controlled synthesis of CPLs.

A special mechanism of «living» radical polymerization is associated with using of specific initiators, so called iniferters [142]. During inifert-induced «living» radical polymerization a growing radical interacts reversibly with stable or low active radical (stable radicals, spin traps, cobalt porphyrins) with formation of adduct containing labile end group, which is able to split from the end of chain under heating or irradiation (Scheme 2.4).

The iniferter method was used, for instance, for free radical polymerization of acetone oxime acrylate [143].

In the NMP method polymerization is implemented with using of stable, including nitroxyl radicals. Thus, homo-telechelic macroligands with chelating tpy-4′-yl units at the ends of a chain are obtained by NMP of St using bis-tpy-functionalized NMP initiator [144]. The NMP method was also used to obtain amphiphilic water-soluble block-copolymer of poly(sodium-styrenesulfonate) (PSS) and 5-(4-acryloyloxyphenyl)-10,15, 20-tritolylporphyrin) [145]. Polymers with M_w higher than 60,000 containing up to 10 mol% of chelating tpy units were successfully obtained by NMP method via



Scheme 2.4 Mechanism of iniferter-induced «living» radical polymerization

co-polymerization of MMA with a monomer containing a tpy fragment. The PDI occurred lower than 1.3, though it is well known that tpy interacts with a stationary phase during gel chromatography and broadens polydispersion [146]. Interaction between a primary produced benzylchloride-functionalized initiator with 2,6-di (2-pyridyl)-4-pyridone in presence of potassium carbonate was used to fabricate a tpy-containing initiator for NMP, which was successfully applied for controlled bulk St polymerization, resulted in production of chelating macroligand based on PS. It should be noted that the remained nitroxide groups at the end of PS can be replaced by a tpy-containing maleimide with formation of telechelic bis-tpy-functionalized PS [147].

The synthesized free-radical TEMPO-based (TEMPO is (2,2,6,6-tetramethylpiperidin-1-yl) oxyl, or (2,2,6,6-tetramethylpiperidin-1-yl) oxidanyl) initiators containing dibenzo-24-crown-8 and bis(*m*-phenylene)-32-crown-10 were used for production of PS with the end crown ether fragments and narrow PDI [148, 149].

Presently many research groups improve these methods of synthesis of polymers in order to obtain CPLs with determined beforehand molecular weight, polydispersion, topology of a chain, which also contain necessary functional groups in predetermined sites of the chain. The aforementioned methods are now essential in CRP, though many variants and combinations of them exist. We shall resume that possibilities of CRP are as follows: narrow PDI, control over the rate of polymerization, topology of macromolecules, microstructure of a chain, and composition homogeneity of copolymers, and also controlled functionality of macromolecules.

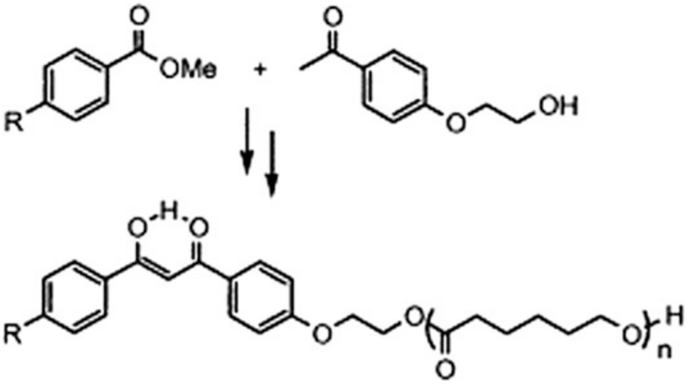
2.1.3 ROMP as a Method of Production of Chelating Polymers

An interesting method of CPL production is ring-opening metathesis polymerization (ROMP) [150]. This method, in particular, was applied to obtain chelating polymers with tpy and carbazole (Cz) groups in side chain [151, 152], porphyrin (Pp) copolymers, and long-chained alkyl norbornene using Grubbs initiator [153]. Dibenzoylmethane (dbm) initiators with one or two alcohol groups are used for creation of poly(ε-caprolactone) (PCL) macroligands with chelating fragments at the end or in the middle of a chain with low PDI ~1.1 (Scheme 2.5) [154].

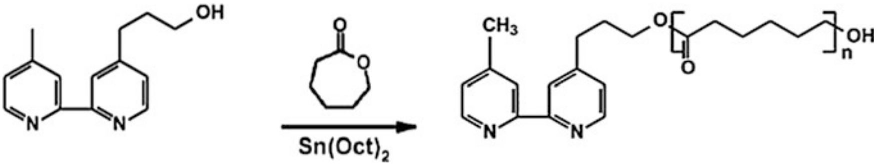
Mono and bis(hydroxyalkyl)-bpy were used as ROMP initiators of ε-caprolactone and DL-lactide, catalyzed by tin octoate (Scheme 2.6) [155].

Hydroxypropyl-tpy macroligand was used as initiator of polymerization of ε-caprolactone with hydrogen-bound (H-bound) end groups (Scheme 2.7) [156, 157].

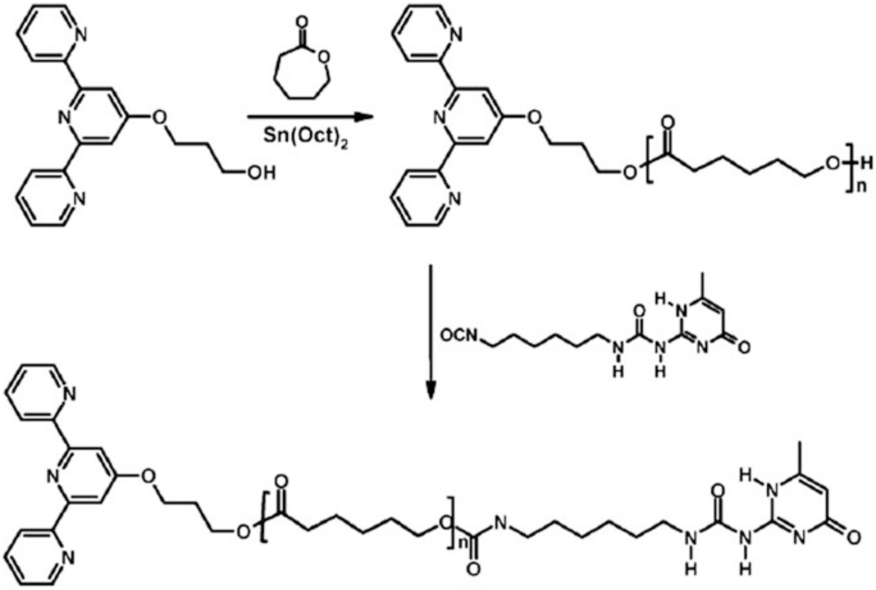
Instead of tin octoate aluminum alkoxide can be used as a catalyst of ROMP with contribution from polymer initiators (Scheme 2.8) [158].



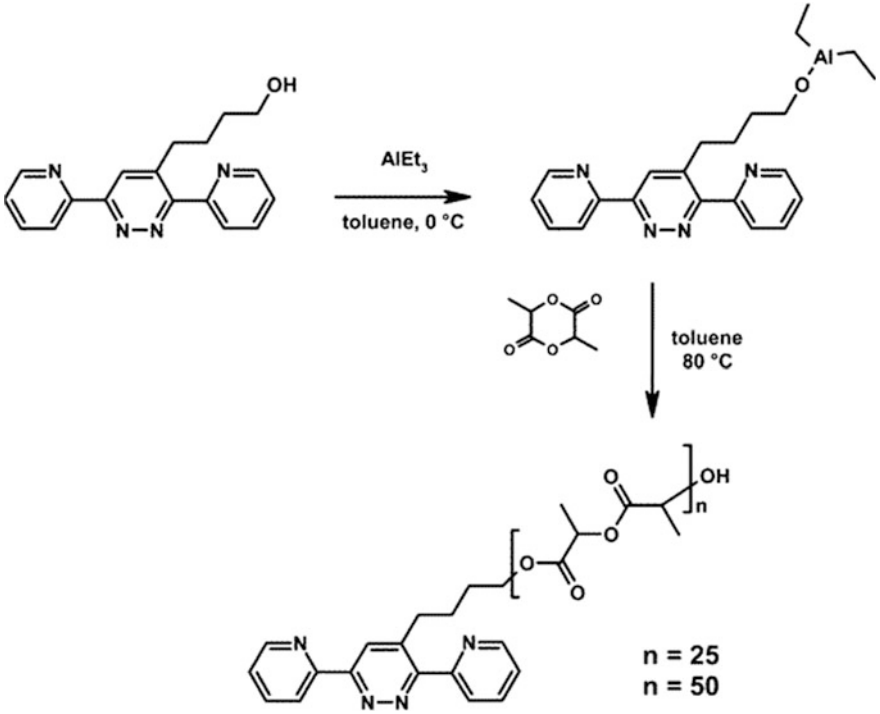
Scheme 2.5 Synthesis of CPL with dbm fragments



Scheme 2.6 Synthesis and chelation of bpy-containing PCL ligand using tin octoate as a catalyst



Scheme 2.7 Synthesis of PCL with tpy-chelating fragments



Scheme 2.8 Schematic representation of synthesis of poly(L-lactide)-based 3,6-di(2-pyridyl) pyridazine (DPP) chelating ligand

The cross-linked crown ether polymers with sulfur-ether group were obtained by ROMP from 3-thiopentyl glycidyl ether and diethylene glycol bisglycidyl ether with Na, $NaOCH_2CH_2OCH_2CH_2OH$, or BuLi as a catalyst, respectively [159].

2.1.4 Click Chemistry Methods in Synthesis of Chelating Polymers

One of the methods of control over topology of the formed CPLs is using of «click chemistry», simple in realization of reactions, which proceed stereospecifically and with high yield in easily removed solvents, with formation of easily separated side products [160, 161]. The Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC) is the premier example of a click reaction [162]. The majority of studied click reaction is based on the 1,2,3-triazole as a stable linkage to connect two components. In particular, 1,4-functionalized 1,2,3-triazoles are versatile ligands with wide set of donor sites for metal chelation, including N3, N2 and C5 (Fig. 2.4).

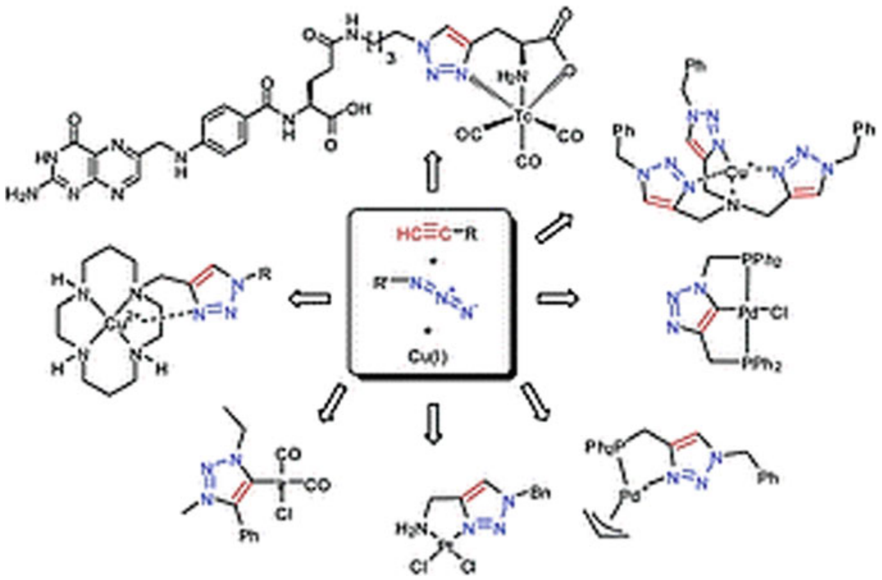


Fig. 2.4 Examples of metal coordination with participation of 1,4-functionalized 1,2,3-triazoles

Click polymerization was successfully used for synthesis of a range of Pp-containing polymers with triazole rings served as spacers. Polyaddition of Pp-containing dialkyne and 1,4-diazidobenzene is initiated either simple heating, or by Cu(I)-catalyst, bringing to polymers with relatively high molecular weight. The polymer obtained by thermally induced click polymerization has unimodal molecular-weight distribution and moderate PDI after long time of reaction up to 170 h. As compared to the metal-free click polymerization, growth rate of the molecular weight in Cu(I)-catalyzed click polymerization decreases, which results in relatively low molecular weight of the produced polymer [163].

2.1.5 *Method of Cation Polymerization in Chemistry of Chelating Macroligands*

Ionic polymerization proceeds via heterolytic mechanism and is initiated by ions (anions or cations). They particularly play in this case a role of active centers. Vinylcatechol monomers can be polymerized in presence of tin tetrachloride (5-vinyl-1,3-benzodioxol, 3,4-dimethoxystyrene, 6-vinyl-1,4-benzodioxane, 4-vinyl-1,3-benzodioxol) or lithium butyl (5-vinyl-1,3-benzodioxol, 2,3-dimetoxy-St, 6-vinyl-1,4-benzodioxane) with formation of polymers with molecular weights up to 95,000 [164]. N,N′-bis(vinyloxyethyl) thiuramdisulphide homopolymers are also obtained by the reaction of cation polymertization [165].

Vinyl polymers with macrocyclic side crown ether chain are synthesized via anion polymerization of derivatives of α-(alkoxy-methyl) acrylates with 13–17 cyclic units. Counter-cation in the polymerization system predetermines a polymer yield and its stereo-regularity [166].

2.1.6 *Chemical Oxidized Polymerization in the Chemistry of Chelating Polymers*

Recently synthesis of PCL by chemical oxidized polymerization is widely studied [167]. Thus, linear Pp-thiophene copolymers are synthesized via polymerization of Pp bound in 5,15-positions with tetrathiophene or bithiophene fragments in presence of $FeCl_3$ as an oxidizer [168].

Copolymers containing IDA were obtained via polymerization of MMA and chelating monomer, GMA-IDA, with potassium persulfate as initiator [169]. Oxidized copolymerization of 8-aminoquinoline and *o*-anisidine with using of ammonium persulfate as oxidizer brings to pure and uniform particles of the copolymer of several microns in size [170]. Polymerization yield and intrinsic viscosity of a copolymer depend strongly on the ratio of monomers (Fig. 2.5). In particular, the yield decreases in geometric progression from 64 to 16% as the content of aminoquinoline increases from zero to 100%, thus pointing that 8-aminoquinoline is inhibitor to oxidized polymerization of *o*-anisidine. It should be noted that 8-aminoquinoline shows higher homo-polymerization activity than two others chelating nitrogen heterocyclic amines, i.e. pyrimidylamine [171] и pyridylamine [172]. Intrinsic viscosity of 8-aminoquinoline and *o*-anisidine copolymers, and DP change, depending on content of 8-aminoquinoline in a complicated way.

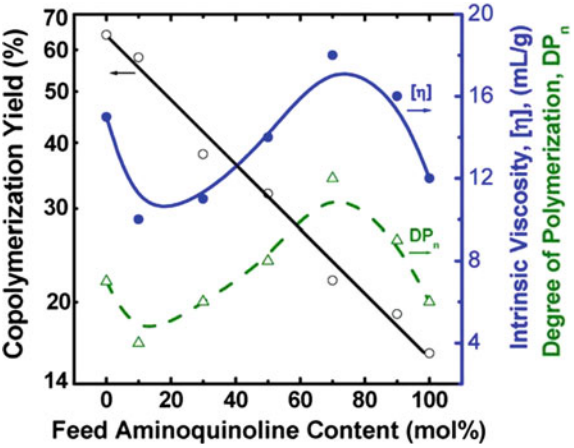


Fig. 2.5 A change of yield of copolymerization, intrinsic viscosity, and medium degree-of-polymerization $[(DP)_n]$ in polymers of 8-aminoquinoline/o-anisidine on content of 8-aminoquinoline

In the case of poly(*o*-phenylenediamine) (PPD) obtained using ammonium persulfate as an oxidizer, yield of a polymer depends on presence of metal ions in the reaction mixture, which can react as oxidizing reagents and/or catalysts [173]. In this case ladder polymers were obtained.

The initial rate of homogeneous polymerization of 2-methacryloyloxyethyl phosphorylcholine as betaine monomer with potassium peroxydisulfate at 40 °C corresponds to the equation $V = k[\text{activator}]^{0.98}[\text{monomer}]^{1.9}$, and the total activation energy of polymerization is 12.8 kcal mol^{-1} [174]. Copolymers of aniline and *o*-aminoacetophenone of different compositions were obtained via chemical oxidized co-polymerization using two different methods (emulsion and inverse emulsion copolymerization) with two different oxidizers (ammonium persulfate and BP) [175]. Poly(2-aminobenzoic acid) and poly(2-aminobenzoic acid-*co*-aniline) are synthesized via chemical polymerization in 1 M aqueous solution of hydrochloric acid [176, 177]. Poly(1,8-diaminonaphthalene) in form of microparticles is obtained by chemical oxidized polymerization of 1,8-diaminonaphthalene in presence of $(NH_4)_2S_2O_8$ [178]. Poly(2,6-diaminopyridine) was synthesized via interphase polymerization, in which solid $(NH_4)_2S_2O_8$ was quickly added to solution containing 2,6-diaminopyridine [179]. Morphology of thus obtained poly(2,6-diaminopyridine) is characterized by spherical microparticles with average diameter 1 μm, which is smaller than that of poly(2,6-diaminopyridine) obtained by homogeneous polymerization. Chemical interphase oxidized polymerization for synthesis of poly(1-amino-5-chloroanthraquinone) particles in nitrobenzene solution is performed with CrO_3 used as oxidizer in aqueous phase in air [180].

Copolymers of *o*-aminobenzylamine and different amounts of aniline are obtained in diluted solution of hydrochloric acid using ammonium persulfate as oxidizer [181]. Nanoparticles with properties of semiconductors are synthesized by oxidized copolymerization of 8-aminoquinoline and 2-ethylaniline [182]. Fine particles of the copolymers 8-aminoquinoline and *o*-phenetidine are synthesized via chemical oxidized polymerization in three aqueous media. Copolymer nanoparticle size decreases monotonically with increasing the content of 8-aminoquinoline from 5 to 100 mol%. A special feature of this method is fabrication of semiconductor nanoparticles without a stabilizer by incorporation of 8-aminoquinoline groups with positively charged quaternary ammonium groups adjusted to sulfone groups. Both molecular weight and bulk electric conductivity reach maximum values at content of 8-aminoquinoline 5 mol%, and yield of polymer and bulk electric conductivity are maximum at minimal temperature of polymerization 5 °C [183].

The PPD microrods are produced with iron chloride used as an oxidizer [184]. In contrast to electrochemical polymerization, which has some limitations, such as low efficiency and uniform shape of the formed film, chemical oxidized polymerization under action of $(NH_4)_2S_2O_8$ or $FeCl_3$ allows production with high yield of microparticles of poly(1,8-diaminonaphthalene) with high molecular weight [185]. Conducting nanofibrils of poly(1-amino-5-chloroanthraquinone) have been successfully synthesized by interphase chemical oxidized polymerization [186]. The nanofibrils show maximal yield 64.8%, their aspect ratio is 67 (diameter 30 nm, length 2 μm), and bulk electric conductivity 6.2×10^{-3} S cm^{-1}, when 1-amino-5-chloroanthraquinone monomers oxidize CrO_3 in combined medium consisting nitrobenzene and 250 mmol L^{-1} of $HClO_4$ in solution.

Depending on conditions of reaction of chemical oxidation, PPD are formed as powders, colloid dispersions, thin films, or composites [187].

Polythiophenes containing oligo (ethylene glycol) spacers and crown ethers are synthesized by copolymerization of 3-methyl tetra (oxyethylene)oxy-4-methylthiophene and 3-(((2-aminobenzo-18-crown-6-ethyl) triethoxy) oxy)-4-methylthiophene in presence of $FeCl_3$ solution [188]. Thiophene monomers containing *meso*-tet raphenyl-Pp units bound via alkyl spacers, and also *meso*-3,5-*ditert*-butyl-tetra phenyl-Pp units, bound via tetra (ethylene glycol) spacers, were copolymerized in presence of 3-dodecylthiophene using $FeCl_3$ as an oxidizer [189, 190]. Studies in this field are intense.

2.1.7 Chelating Macroligands Obtained by the Methods of Photo- and Microwave-Assisted Polymerization

Series of copolymers poly(methacryloyl-2-oxy-1,2,3-propanetricarboxylic acid-*co*-*exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic acid), poly(methacryloyl-2-oxy-1,2,3-propanetricarboxylic acid-*co*-hydrogenethyl-*exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalate), and poly(methacryloyl-2-oxy-1,2,3-propanetricarboxylic acid-*co*-α-ethoxy-*exo*-3,6-epoxy-1,2,3,6-tetrahydrophthaloyl-5-fluorouracil) were obtained from the respective monomers via photopolymerization at 25 °C for 48 h [191, 192]. M_n of the synthesized polymers was in the range from 9400 to 14,900, and PDI—1.2–1.4.

Interest in application of microwave irradiation in polymer synthesis and modifications constantly increases [193]. Especially active the method of microwave irradiation is recently applied in step-growth polymerization, open-chained polymerization, and radical polymerization [194, 195]. It is often used also in «green» synthesis of CPLs. Thus, using microwave irradiation, the CPL were obtained by condensation of thymol and guanidine with formaldehyde in 2 M hydrochloric acid with the 1:1:2 molar ratios of the reacting monomers for 15 min [196], and also dianhydride of 3,3′,4,4′-benzophenonetetracarboxylic acid, 4,4′-diaminodiphenylmethane and 4,4′-oxydianiline [197]. It is noted using of microwave irradiation for the production of phthalocyanine (Pc) polymer by the reaction of tetranitrile monomer with 4,4′-[pyridine-2,6-diylbis(methyleneoxy)] diphthalonitrile [198], different polyamidoamines (PAMAM) [199], including optically active ones containing hydantoin and thiohydantoin in the main chain [200], and also dithia-bridged polymeric Pc containing a substituted thiophenylamine Schiff base [201]. Functionalization of polychloromethylstyrene (PCS) by 2-aminothiophenyl-*S*-acetic acid was performed under action of microwave irradiation [202].

Also microwave-assisted enzymatic polymerizations should be noted, which combine advantages of microwave heating and enzymatic catalysis, the field rather well studied in synthesis of CPL [203].

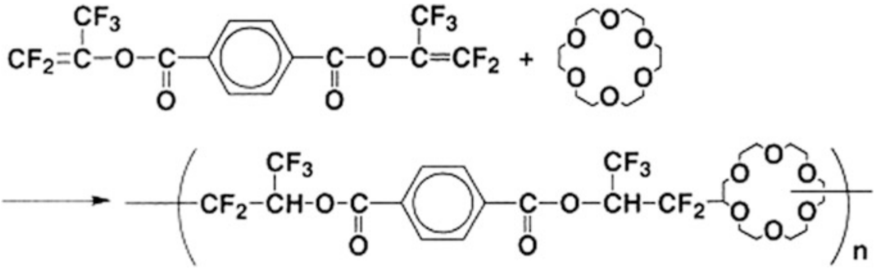
2.1.8 Cyclopolymerization for the Production of Chelating Macroligands

Derivatives of poly(phenyl acetylene) with crown ether units in the main chain are obtained by cyclopolymerization of the 1,14-bis(4′-ethynylphenoxy)-3,6,9,12-tetraoxatetradecane and 1,17-bis(4′-ethynylphenoxy)-3,6,9,12,15-pentaoxaheptadecane using Rh(nbd)BPh_4 (nbd—norbornadiene) as the catalyst [204].

Pc polymer is formed by the reaction of polytetracyclomerization of *o*-bis [3-(3,4-dicyanophenoxy) propyloxy] benzene synthesized via interaction of 4-nitrophthalonitrile with o-bis[(3-hydroxypropyl) oxy] benzene [205].

π-Conjugated polymers containing units of dithiafulvene and bpy are obtained by the cycloaddition polymerization of aldothioketene derivative from 5,5′-diethinyl-bpy [206]. Radical polyaddition of bis (α-trifluoromethyl-β,β-difluorovinyl) terephthalate with 18-crown-6 gives soluble fluorine-containing polymers containing crown ether units in the main chain and $M_n = 5.5 \times 10^4$ with unimodal PDI (Scheme 2.9) [207].

Stable porous organic polymers containing functional units of catechol with tunable porosities (560–1050 m^2 g^{-1}) and degrees of functionalization are synthesized using the strategy of Co-catalyzed acetylene trimerization [208].



Scheme 2.9 Preparation of fluorine-containing polymers containing crown ether units in the main chain

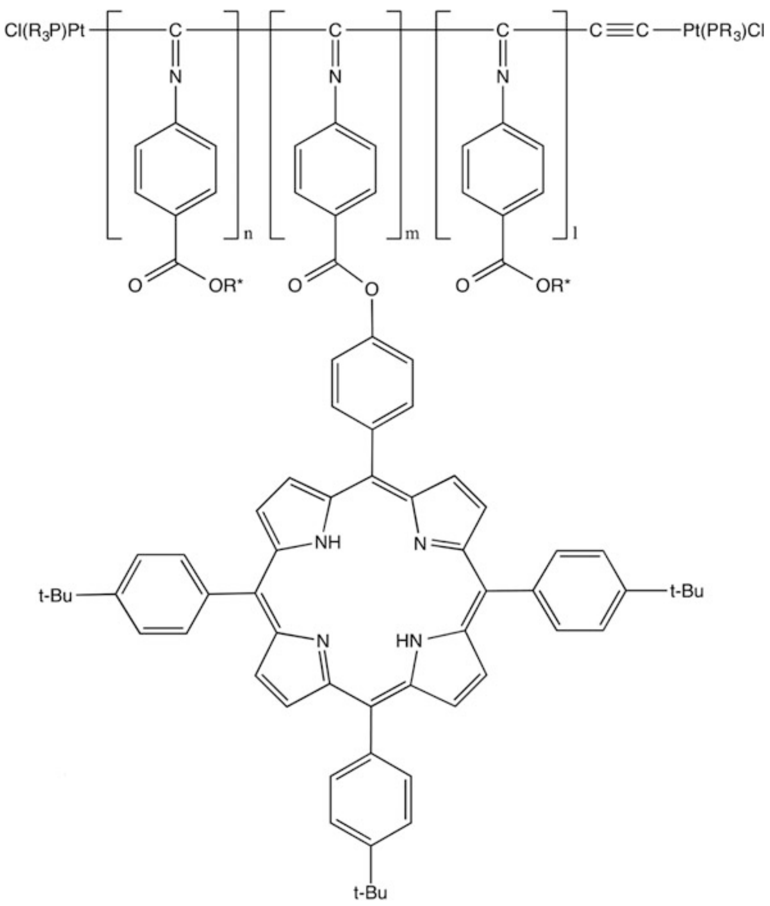
2.1.9 Asymmetrical Polymerization in Synthesis of Chelating Polymers

Recently great attention is paid to production of chiral CPLs [209]. For example, chiral poly(L-lactides) with end tpy groups are obtained by controlled coordination polymerization [210]. Asymmetrical anion homopolymerization of *N*-4′-benzo-15-crown-5-maleimide for production of optically active polymers has been performed with chiral anion initiator consisting of metal-organic compound (*n*-butyl lithium, diethyl zinc) and chiral ligand ((–)-sparteine), (S,S)-(1-ethylpropylidene)-bis(4-benzyl-2-oxazoline) [211].

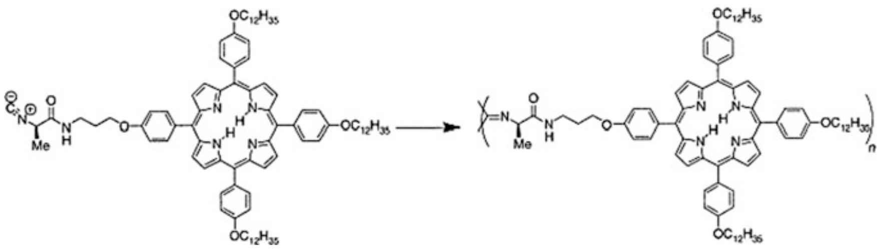
Optically active PAAm containing amino acid fragment poly [*N*-methacryloyl-L-leucine methyl ester] with controlled M_n and relatively narrow PDI (<1.3) has been obtained using initiating system methyl-2-bromopropionate/CuBr/tris(2-dimethylaminoethyl) amine [212]. Acetylene monomers containing salicylidene Schiff-base groups as well as Schiff base and hydroxyl groups are polymerized with the catalyst $[(nbd)RhCl]_2/Et_3N$ with formation of polymers with high molecular weights ($M_n = 2.6–7.2 \times 10^5$) and high yields (75–97%) [213]. The polymers form helical structures with a predominantly one-handed screw sense. The same catalyst $[(nbd)RhCl]_2/Et_3N$ is used for polymerization of acetylene monomers, containing Schiff base and the amino group, (*S*)-*N*-(4-ethynylbenzylidene)-1-phenylethanamine, (*R*)-*N*-(4-ethynylbenzylidene)-1-phenylethanamine, *N*-(4-ethynylbenzylidene)-1-phenylethanamine, (*R*)-*N*-(4-ethynylbenzyl)-1-phenylethanamine and (*R*)-*N*-(4-ethynylbenzyl)-1-phenylethanamine with formation of polymers with lower molecular weight (M_n = 9000–60,000), but the same high yield (85–97%) [214]. The polymers also have helical structures with a predominantly one-handed screw sense.

Asymmetrical polymerization of 4′-isocyanatobenzo-18-crown-6 in presence of chiral initiator of lithium amide salt and (*S*)-(2-methoxymethyl) pyrrolidine was used to produce 4′-isocyanatobenzo-18-crown-6 with end units of (S)-(2-methoxy methyl) pyrrolidine [215]. The polymer has a positive Cotton effect (240–350 nm), and in its main chain a single-coil partial helix is formed, which does not change under action of adverse factor, chiral compound of L-phenylalanine $HClO_4$. *Cis*-transoidal 4-ethynylbenzo-15-crown-5 was polymerized with $Rh(nbd)BPh_4$ [216]. Analysis of chiral optical properties of the polymer allows it to be recommended as thermally sensitive material.

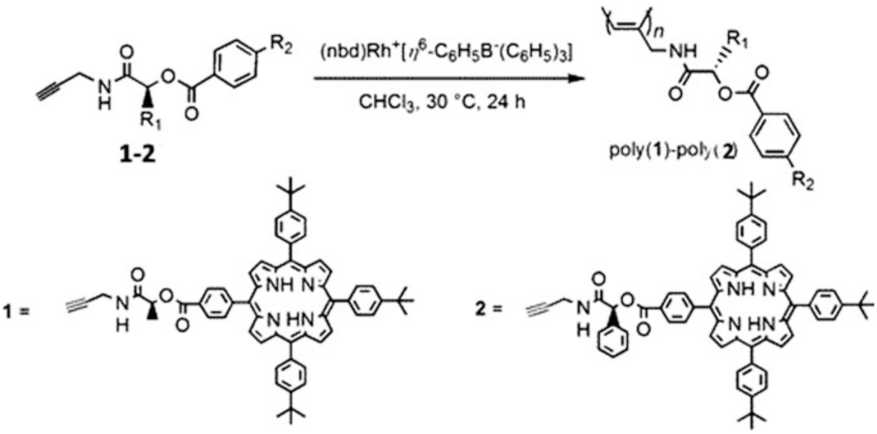
Copolymerization of monomers containing different chiral and Pp units results in formation of artificial helical polyisocyanides containing enantiopure groups [217].



The similar approach was used in design of helical nanorods based on polymers with fixed Pp [218]. In this case, Ni(II)-catalyzed polymerization of isocyanide monomers containing chiral Pp brings to respective polymers (Scheme 2.10), Pp units of which are in four clearly defined stacks which run in parallel to the polymer axis.



Scheme 2.10 Synthesis of Pp-containing polymers



Scheme 2.11 Preparation of Pp-containing polymers based on poly(*N*-propargylamine)

Another polymer matrix was used for production of chiral poly(*N*-propargylamines) containing Pp groups (Scheme 2.11) [219]. Molecular weights of the polymers are 17,000 and 24,000 with *cis*-content 85 and 78%, respectively, displaying highly stereo-regular structures with considerable optical activity.

Cyclopolymerization of diacetylene monomers in presence of rhodium catalyst was used to produce poly(phenylacetylenes) with cavities of different sizes formed by crown ethers placed in elementary units [220]. The polymers have helical structure with single-coil macromolecules prevailing. Formation of «guest-host» complexes with achiral compounds brings to chiroptical changes based on the fluctuation in the main chain conformation. The polymers with chiral main chain cross-linked alternately with (*R*,*R*)-salen (where salen—*N*,*N*′-bis(salicylidene)ethylenediamine) and 1,4-dioctyloxybenzene, using the Pd-catalyzed C–C cross-coupling as the key stage of the reaction [221]. The polymers are soluble in standard solvents and work as

Fig. 2.6 Polymers with chiral main chain cross-linked alternately with (*R*,*R*)-salen and 1,4-dioctyloxybenzene, as highly selective «OFF-ON» fluorescent chemosensors on Zn(II) ion, and enantioselective recognition of (*R*)- and (*S*)-imines under action of polymer complexes

selective «OFF-ON» fluorescent chemosensors on Zn(II) ion (Fig. 2.6). The obtained Zn(II) polymeric chelates have strong chiral recognition with respect to (*R*-) and (*S*)-1-phenyl-*N*-[(pyridine-2-yl) methylene] ethanamines under ambient conditions.

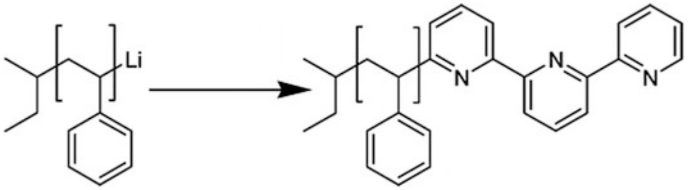
2.1.10 Chelating Macroligand Preparation via Post-polymerization Modification

PPM is the most widely used method of CPL synthesis [222, 223]. The method is based on chemical interactions between reactive functional groups contained in a polymer matrix or preliminary incorporated in the polymer with respective organic compounds in direction of completion of chelating fragments. These reactions lead to a change in chemical composition of a polymer, but do not disturb its main chain. The PPM method gives a possibility to obtain different CPL structures based on polymer matrices, for example, of syndiotactic PS [16]. However, one of the main drawbacks of this method is presence of different side processes, and a necessity of removal of unlinked components.

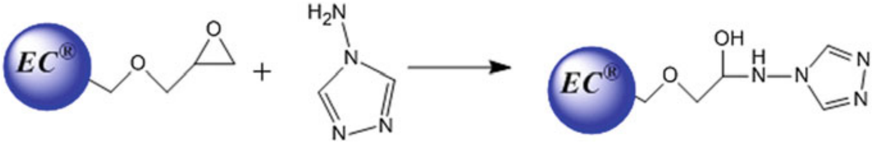
PPM as a method of introduction of functional groups into ready reactive polymer precursors is considered as highly effective synthetic strategy for design of materials with predetermined properties [17], and also of complicated polymer topologies based on multifunctional cyclic polymers [224]. PPM of block-copolymers attracts keen attention beginning from fundamental synthesis, correlation between structure and properties, and to practical applications [225]. The formed block-copolymers with modified side chain preserve properties attributed to a parent block-copolymer, while incorporated into the side chain functionalities provide control over properties of a materials, and hence, their applications.

Thus, polyacrylic acid (PAA) was chemically modified with 1,2,4,5-tetrahydroxybenzene or benzene-1,2,4,5-tetrol via Minisci reaction. Degree of modification reached the highest value 55% under the following optimal conditions: temperature 70–80 °C, time 4 h and the ratios of the reagents 1.25 [226].

The method of nucleophilic incorporation of the lithium PS living chains to 6-position of the pyridine ring with the following termination and oxidized rearomatization was applied to perform end functionalization of the polymer. In order to prevent two living chains coupling via addition to the same bpy, or tpy unit, excess of pyridyl-containing compounds is used, which makes it possible to produce polymers consisting of 77–93% only singly end-functionalized chains [227].

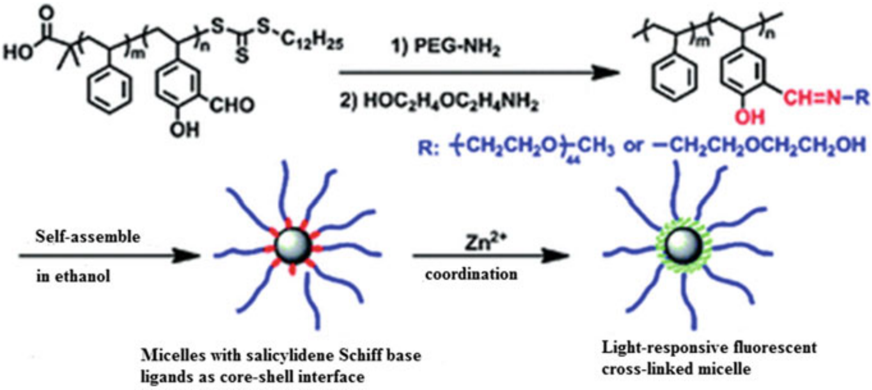


The commercial polymer Eupergit® C, which consists of epoxy-activated polymers formed from hydrophilic AAm with allyl glycidyl (epoxide) groups was modified by aminotriazole [228].



The polymer ligand having tpy as a fixed group has been obtained by Williamson etherification reaction between 4′-hydroxy-tpy and commercial PCS [229]. Interaction of monoamine-functionalized poly(ethylene glycol) (PEG) and 2-(2-aminoethoxy) ethanol with PS-*b*-poly(2-hydroxy-5-vinyl benzaldehyde) via aldehyde-amine condensation brings to amphiphilic block-copolymers containing fixed salicylidene-Schiff base with precise structure. This polymer can self-assemble in ethanol in micelles with salicylidene-Schiff base on the core-shell interface (Scheme 2.12) [134].

Interaction between *meso*-tetracarboxyporphyrin (mTCPP) and PEG-diamine brings to Pp-cross-linked hydrogel for fluorescence-guided monitoring and surgical resection (Fig. 2.7) [230].



Scheme 2.12 Synthesis and self-assembly PMC based on salicylidene-Schiff base

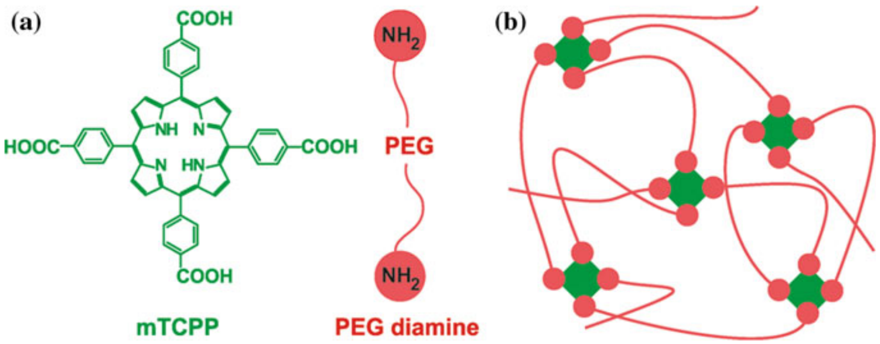
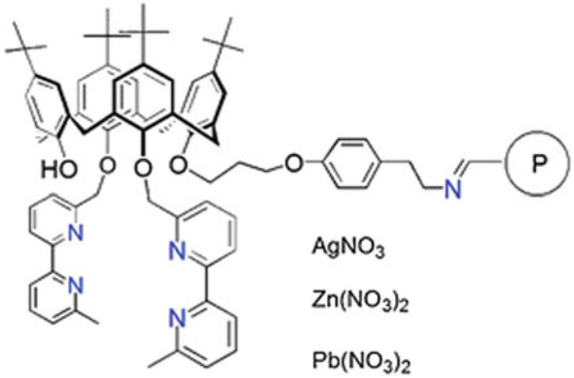


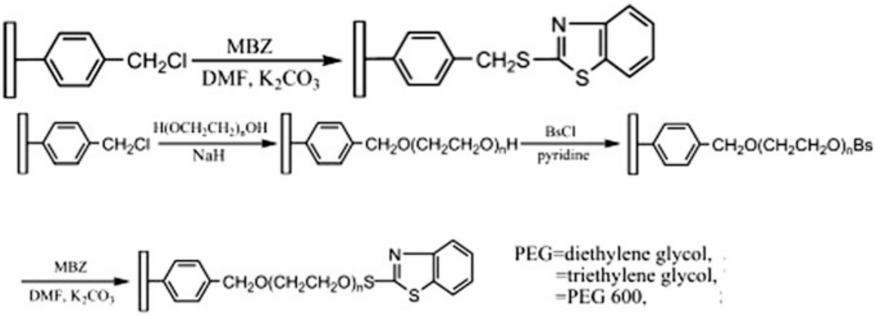
Fig. 2.7 Pp-cross-linked hydrogels. **a** mTCPP (green) structure and PEG-diamine (red); **b** schematic image of hydrogel

Benzaldehyde Wang resin was used for production of fixed calixarene-bpy ligands [231].



3D ordered macroporous cross-linked PS with 2-mercaptobenzothiazole groups incorporated in walls of pores directly or via arms of hydrophilic spacer to the polymer backbone is obtained (Scheme 2.13). Arms of the hydrophilic spacer are PEG chains with three different lengths. It is important that 3D ordered structure is well preserved after functionalization. Density of 2-mercaptobenzothiazole groups is 0.052 mmol m^{-2} [232, 233].

The reaction of condensation of sodium salt of pentane-1,3-dione and PCS in dichloromethane brings to β-diketone-functionalized resins [234]. Poly(chloromethylstyrene-*co*-divinylbenzene) (PCD) is chemically modified via alkylating by pyridylazo-α-naphthol in presence of phase transfer catalyst [235]. Poly(GMA) beads with average size 350 μm were treated by iminodiacetonitrile, and then by hydroxylamine to produce amidoxime fragments [236]. The series of amine-functionalized



Scheme 2.13 Preparation of CPLs containing 2-mercaptobenzothiazole groups

resins with ethylenediamine (en), *N*,*N*-dimethylethylenediamine, *N*,*N*-diisopropylethylenediamine, 2-methoxyethylamine, diethylenetriamine (dien), tris(2-aminoethyl) amine, triethylenetetramine (trien) was obtained by chemical modification of terpolymer from glycidyl methacrylate-*co*-ethylenedimethacrylate (GL) (20 mol%), St (77 mol%) and DVB (3 mol%) [237]. The reaction of nucleophilic substitution between benzyl chloride groups of PCD microspheres and 5-amino salicylic acid brings to CPL such as PS-salicylic acid [238]. Such examples are numerous.

2.1.11 Polycondensation Reactions as a Way to Chelating Polymers

Polycondensation reaction is based on ability of phenols, amines, and other compounds to interact with aldehydes, ketones, and their derivatives in presence of alkali or acid catalysts, which results in polymer preparation, accompanied by formation of low molecular weight products. Polycondensation is carried out in melt, solution, or on interface. Depending on structure and ratio of initial components taking part in the polycondensation, CPLs of linear, branched or spatial configuration can be obtained [239, 240]. As a rule, a mixture of products of condensation forms due to synthesis. Besides, this way of CPL production has drawbacks, in particular, ambiguity of structure of produced polymers, poor reproducibility of the synthesis products, low capacity of CPL, and limited possibility of changing character of the functional groups during synthesis. Polycondensation proceeds stepwise, at that intermediates are stable, i.e. polycondensation can be stopped at any stage. The resulting low molecular weight products of reaction can be reacted with intermediates, stimulating their decomposition (hydrolysis, aminolysis, acidolysis, etc.). Therefore, low molecular weight products should be removed from the reaction medium.

Polycondensation of bifunctional compounds called linear, and polycondensation of compounds having three or more functional groups is called a three-dimensional. Thus, condensation of 2,4-dihydroxybenzophenone, oxamine and formaldehyde in various ratios in the presence of an acid catalyst led to terpolymers [241].

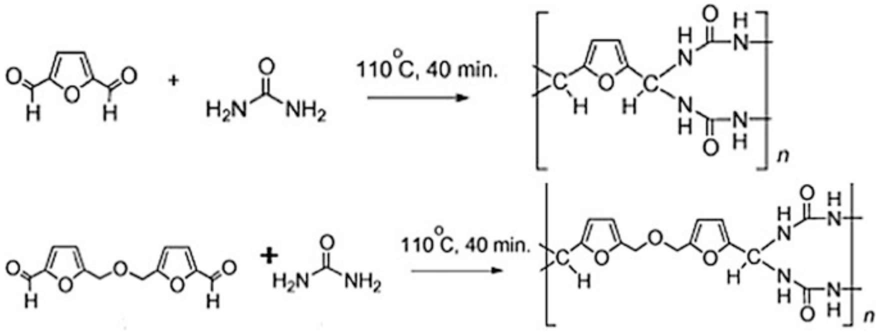
It should note polycondensation in melt carried out without solvents, heating monomers at the temperature by 10–20 °C higher than the melting point (softening temperature) of polymers (usually 200–400 °C). The process begins in the inert gas medium and is finished in vacuum. For example, condensation of 2,5-diformylfuran or 5,5′-oxydimethylenebis(2-furaldehyde) with carbamide at 110 °C by melting of the solid mixture gives a crystalline polymer with 90% yield (Scheme 2.14) [242].

Kinetics of synthesis of polyesters based on 1,4-naphthalene di(carboxylic acid) and hydroquinone diacetate via polycondensation in melt is studied. In particular, the polycondensation obeys the second order kinetics independently on whether it is catalyzed or not. To describe kinetics at the initial stage, a system of twelve differential equations was derived with four different rate constants [243].

For polycondensation in solution a solvent is used, which can also serve as an absorbent of low molecular weight product. Thus, method of polycondensation in solution of 2,5-bis(mercapto-acetichydrazide)-1,3,4-thiadiazole with 4,4′-biphenic, 3,3′-azodibenzoyl or 4,4′-azodibenzoyl dichlorides was used for synthesis of interesting class of poly hydrazides containing 1,3,4-thiadiazole fragment in the main chain [244].

Interphase polycondensation takes place on the interface of gases, solutions, or two immiscible liquids, and provides production of polymers with high molecular weight. We should also notice mechano-chemical synthesis of salicylic acid-formaldehyde CPLs [245].

Various polycondensation reactions are used for the synthesis of CPL, among them catalyzed cross-coupling reactions (particularly, Sonogashira [246–248], Suzuki [247, 249, 250], Heck [247], Buchwald-Hartwig [251], Wittig [252], Williamson [253], Stille [254, 255], and also Horner-Wadsworth-Emmons condensation [256]).



Scheme 2.14 Condensation of 2,5-diformylfuran or 5,5′-oxydimethylenebis(2-furaldehyde) with carbamide

It should be noted the use of condensation reactions for the synthesis of such interesting class of CPL as a polymeric SPs [257]. Thus, waterborne polyurethane containing SP groups is prepared by polycondensation of isophorone diisocyanate, polytetrahydrofuran glycol, dimethylol propionic acid, 1,4-butanediol, trimethylolpropane and 1-(2-hydroxyethyl)-3,3-dimethylindolino-6′-nitrobenzopyrylospiran [258]. The dispersion and film showed a very good photochromic effect.

A series of alternating copolymers of SP and flexible spacers is synthesized by Suzuki polycondensation [259]. These polymers can be transformed into the corresponding protonated form of the red alternating MC polymer in quantitative yield by direct acidification or pulsed ultrasound. At the same time deprotonation of MC polymer occurs upon the addition of a base resulting in the blue form of polymer. Suzuki polycondensation is also used for production of the main-chain conjugated copolymers based on alternating SP and 9,9-dioctylfluorene units [260]. It is important that the reaction conditions are optimized to obtain copolymers with appreciably high molecular weight up to $M_w \approx 100{,}000$. Ultrasound-induced isomerization of SP to the corresponding MC form yields a deep-red solution.

The combination of microwave-assisted synthesis and Suzuki-Miyaura polycondensation leads to a mechanochromic, alternating SP-based copolymer that allows the reproduction of molecular mass distributions [261]. Several parameters such as microwave power, temperature, stoichiometry, and ligand are screened, leading to molecular weights up to $M_w \sim 174{,}000$. Embossing films of SP-based copolymer yields the colored MC copolymer that undergoes a thermally facilitated back reaction to SP-based copolymer.

2.1.12 «Green» Synthesis of Chelating Macroligands

Recently in synthesis of CPL, like in all chemical syntheses, ecology problems receive much attention, which is realized via «green chemistry» principles, implemented by displacement of ecologically hazardous substances by more safe materials, enhancing product biodegradation cycles, using of catalysts and renewed resources for safety improvement and efficiency of polymer chemistry [34–39, 262]. Different biocatalytic syntheses can serve as examples of this approach [40]. Thus, the phenol ligand, 4-(phen-5-yliminomethyl)-phenol, was subjected to biocatalytic polymerization by Hematin [263]. Typical is increase in molecular weight with increase in conversion, though accompanied by simultaneous broadening of PDI. The drawback of this process is inability of the reaction product to recommence a living process with addition of a fresh portion of monomer. A polymer is formed exclusively due to reaction of square termination of the growth radicals.

Hemoproteins encapsulated in reversible micelles were used as catalysts of polymerization of *o*-phenylenediamine in presence of hydrogen peroxide. During catalysis of polymerization with hemoproteins in water, only trimers were formed. It is interesting to notice that macromolecules synthesized in presence of hemoglobin in reversible micelles are linear or trapezoid [264]. Linear PAMAM are obtained via polymerization of ethyl acrylate and *N*-methyl-1,3-diaminopropane in a solvent medium in presence of lipase catalyst produced by *Candida Antarctica* [39]. Depending on conditions of reaction, lipase catalyzes polymerization of monomers or formation of Michael adduct. Lipase has high selectivity in the reaction of polymerization and provides polymer production for biomedical application. Enzymatic oxidation of *o*-phenylenediamine with cytochrome C as a catalyst is carried out in organic media [38]. Polyphenols with molecular weight 1000–3000 and containing 0.94–0.59 mol kg^{-1} hydroxyl groups are synthesized via reaction of phenol, catechol, and pyrogallol catalyzed by horseradish peroxidase [265]. When adding *tetra*-butyl-ammonium bromide to buffer to obtain convenient and ecologically pure system, enzymatic polymerization of phenol is more effective: the maximum conversion of phenol can reach 99.1% [266]. The catalyzed by lipase polycondensation of L-malic acid, adipic acid and 1,8-octanediol in organic media is performed using Novozym 435 as a biocatalyst [267]. M_w increases from 3200 to 16,600 as the reaction time increases from 6 to 48 h at the temperature 70 °C and remains relatively constant as the reaction time goes on increasing to 72 h.

A series of di-acids (succinic, glutaric, adipic, and sebacic acid) and diols (1,4-butanediol, 1,6-hexanediol, and 1,8-octanediol) were used for lipase-catalyzed polycondensation [268]. Synthesis of PPD is performed using a catalyst similar to oxidase in presence of cerium nanodioxide [269]. The polymer showed unique morphology, conductivity, and photoluminescence due to control over pH of the solution during synthesis (Fig. 2.8).

A combination of enzymatic polycondensation and click chemistry was used for production of grafted copolymers (Scheme 2.15) [270]. Aliphatic polyester containing fixed azide groups were obtained via enzymatic polycondensation in

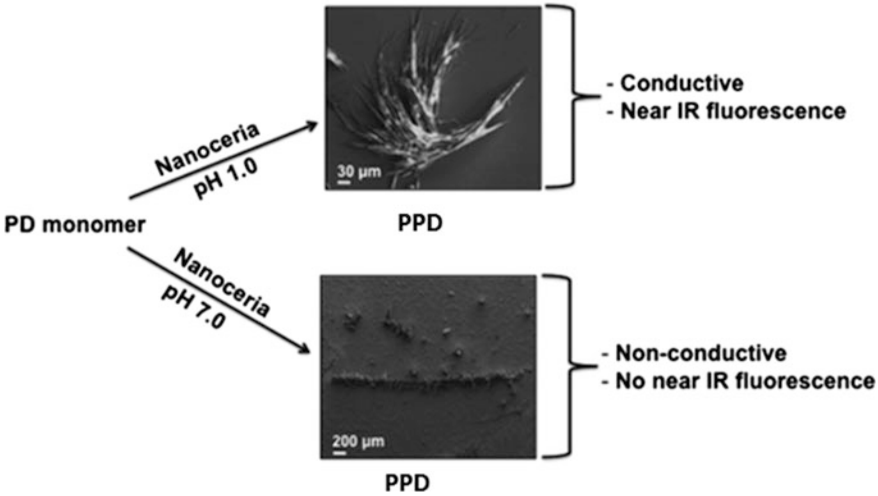
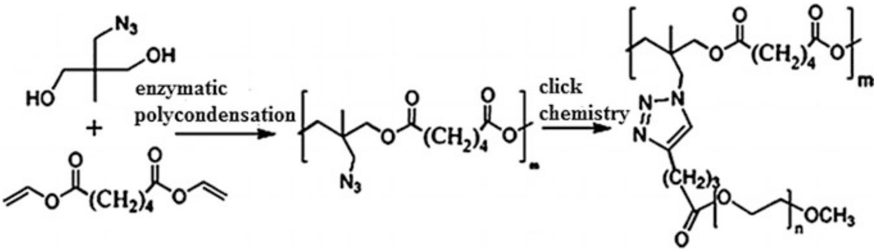


Fig. 2.8 The effect of pH synthesis on morphology, conductivity, and photoluminescence of PPD in presence of cerium nanodioxide



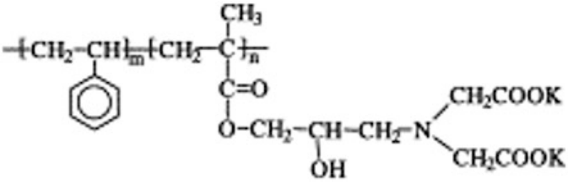
Scheme 2.15 An example of a combination of enzymatic polycondensation and click chemistry for production of CPLs

presence of lipase from *Candida Antarctica of B type.* Grafting to N_3-functional polyether was made quantitatively at room temperature using click reaction CuAAC with monoalkyne-functional PEO, $M_n = 750$. Moreover, both, enzymatic polycondensation and click reaction were successfully carried out sequential in one reactor:

Enzymatic synthesis of CPL was developed with account for different types of reactions, including open-chained polymerization, polycondensation, the combination of open-chained polymerization and polycondensation, and chemoenzymatic polymerization [271].

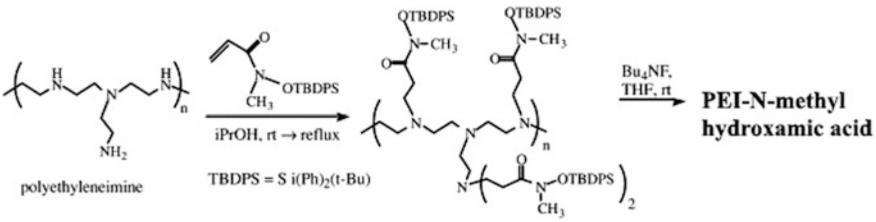
Among demands of «green chemistry» is primary choice of reaction medium, which is safe from ecological point of view. In this regard the majority of studies were performed with water used as a solvent [45–47]. Water-soluble polymers attract a great interest due to their potential application for environment protection, for removal of polluting substances, in biomedicine, etc. Among irrefutable advantages of water-soluble polymers is the fact that their application does not cause pollution of environment, and this is not associated with using of toxic, flammable and explosive solvents [272].

The water-soluble poly(St-*co*-GMA-IDA) is formed during interaction of St with chelating vinyl monomer GMA-IDA [273].



Water-soluble polyethylene imine (PEI) containing *N*-methyl hydroxamic acid chelating groups was synthesized (Scheme 2.16) [274].

Sulfonate-functionalized water-soluble conjugated polymer containing bpy units in main chain as receptors of transition metal ions was obtained by Sonogashira reaction. This polymer can be easily solved in water (5 mg mL^{-1}) and in some



Scheme 2.16 Synthesis of water-soluble PEI containing *N*-methyl hydroxamic acid

polar organic solvents, such as methanol [275]. Anion water-soluble polyfluorene bpy-derivative polymer with side sulfonate groups in position 9 of the fluorine units is developed [276].

CPLs are obtained by one-step synthesis under soft conditions [268] via copolymerization of thiosemicarbazide and formaldehyde in water solution. Water-soluble aminosulfonate-phenol-salicylic acid-formaldehyde polymer with narrow PDI range is synthesized via reaction between phenol, sodium sulfanilate, salicylic acid and formaldehyde [277]. Dianhydride reacts with diazacrown ethers with formation of water-soluble EDTA-diazacrown ether polymers [278]. Also water-soluble polymer drug-form produced via the reaction of vinylpyrrolidone (Vp) and *N*-vinyl-*N*-glycidyl-γ-aminobutyric acid with acetylsalicylic acid is interesting [279]. Readily available and highly effective material for determination of rare earth metals based on a polymer containing amino groups for water solubility and thiourea groups for metal chelation was synthesized [280].

Using radical polymerization, the water-soluble polymers, poly-(2-acrylamido-glycolic acid) [281], and CPLs containing sulfonic acid groups [282] are obtained.

Tripyridyl-Pp monomer, 5-[4-[2-(acryloyloxy) ethoxy] phenyl]-10,15,20-tris(4-pyridyl)-Pp monomer is copolymerized with AAm to obtain hydrophobically linked water-soluble polymer [283]. Water-soluble π-conjugated polymers containing 5,5′-bpy or 6,6′-bpy units in π-conjugated main chain are obtained as scaffolds for macromolecular chelation of metal [284]. A possibility to adapt fluorescence quenching conjugated polymers under action of nitrogen oxide NO and its partial reduction with addition of Cu(II) ions in the system acetonitrile-water is considered for fluorescent detection of NO (Fig. 2.9).

Another important solvent in green chemistry of polymers is supercritical carbon dioxide [43]. Thus, following the strategy of green chemistry, gradient copolymer poly(1,1,2,2-tetrahydroperfluorodecyl acrylate-co-acetoacetoxyethyl methacrylate) successfully synthesized by RAFT in supercritical CO_2 with good control over M_n and composition [42, 285].

Ionic liquids, being a new class of solvents, which possess interesting properties, such as high ionic concentration, nonvolatility, good thermal stability and inflammability are of certain interest for green chemistry. As a typical example, we note polyhydrazides obtained by direct polycondensation of dihydrazides with benzofuro

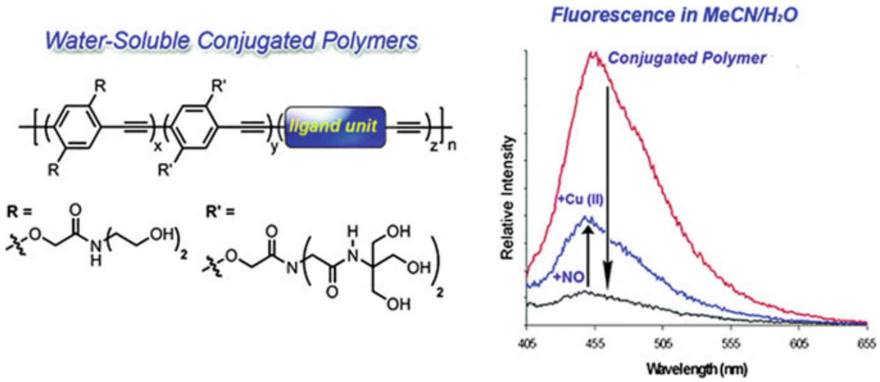


Fig. 2.9 Structure of conjugated polymers with bpy units in the main chain and change in intensity of their fluorescence at adding NO and Cu(II) ions

[2,3-b]-benzofuran-2,9-dicarboxylic acid in ILs and triphenyl phosphite (condensing agent) without any additional components (Il can act as a solvent or as a catalyst) [286].

Undoubted advantage of green chemistry is using of biodegraded polymers [48]. Thus, biodegrading poly(anhydride-ester) was synthesized by polycondensation in melt of acetylated monomer for production of a polymer prodrug [286]. The polymer consists of alkyl chains linked by ester bonds in aromatic fragments, in particular, salicylic acid, an active component of aspirin. Incorporation of this compound, having remedy properties ascribed to salicylic acid, and easiness of metabolism, into the polymer chain gives a polymer prodrug, which can have different potential applications (for example, at inflammatory bowel decease).

Hydrolytically and microbiologically degraded poly (EDTA-*co*-lactose) with linked carboxyl groups of high molar weight (132,000) was obtained via polycondensation of EDTA anhydride and lactose [287]. Also biodegraded polyamides containing α-amino acid should be noted [288].

Biodegraded poly(anhydride-esters) containing EDTA in the main chain and linked antimicrobial groups (for example, carvacrol, thymol or eugenol) are synthesized via polymerization in solution [289]. For these polymers hydrolytic degradation in vitro ends after 16 days, bringing to release of free antimicrobial drugs and EDTA. There polymers are completely decomposed in components, which are biologically relevant and provide a possibility of increasing shelf life of consumer goods in food and personal care manufacturing using antimicrobial and antioxidizing approach.

In other biodegraded poly(anhydride-esters) based on salicylic acid and diglycolic acid the bioaccessibility of salicylic acid was dependent on several factors, including solubilization rate, macroscopic erosion of the powdered polymer, and hydrolytic cleavage of the anhydride bonds [290].

Cross-linked, biodegraded cytocompatible polyesters based on salicylic acid were produced from melt condensation for localized and steady supply of salicylic acid [291].

The improved strategy of PAMAM synthesis for biomedical application is also worthy of notice: catalysis using green biocompatible salts of alkali-earth metals [292]. Outstanding results should be expected in this direction in the nearest future.

2.2 Grafted Polymerization in Chelation of Macroligands

There are many problems, to solve which it is necessary to transport a chelating fragment to the surface or near-the-surface layer of a polymer, for example, in catalysis [293]. Fixing chelating units on a polymer surface decreases considerably diffusion limits of chelation processes, and mobility of grafted chains diminishes role of spatial problems during chelation of MX_n. In many cases this purpose is achieved by the grafted polymerization techniques.

According to recommendations of IUPAC, grafted macromolecules are considered to be the macromolecules with one or more types of blocks linked to the main chain, so that these side chains have constitutional or configuration characteristics different from those of the main chain and randomly distributed. They are used as CPLs since the end of 1960s. A number of potential applications of the grafted polymers are presently substantially broadened due to development of CRP technique. Graft-copolymers containing a great number of side chains can display worm-like conformations, compact molecular packing and substantial effects of end chains due to their limited and closely fitting structures [294–298].

2.2.1 *Specifics of Grafted Polymerization*

The main approaches to synthesis of grafted copolymers are based on well-known methods: chemical (free-radical polymerization, ATRP, ROMP, iniferter-induced polymerization), radiation, photochemical, plasma-induction, enzymatic grafting, polycondensation reaction, etc. Grafting has noticeable advantages as compared with other methods of CPL synthesis due to several reasons, including easy and controlled incorporation of grafted chains with high density and their exact localization on the surface without changing properties of a polymer substrate. Moreover, rigid fixation of grafted chains on a polymer surface prevents them from delamination and guarantees long-term chemical stability of the integrated chain, in contrast to physically bound polymer chains [299].

The grafted polymers are most often obtained in two principal ways: «grafting-from» and «grafting-through» [300]. However, development of click chemistry has brought to appearance of the third approach «grafting-to» (Fig. 2.10) [301].

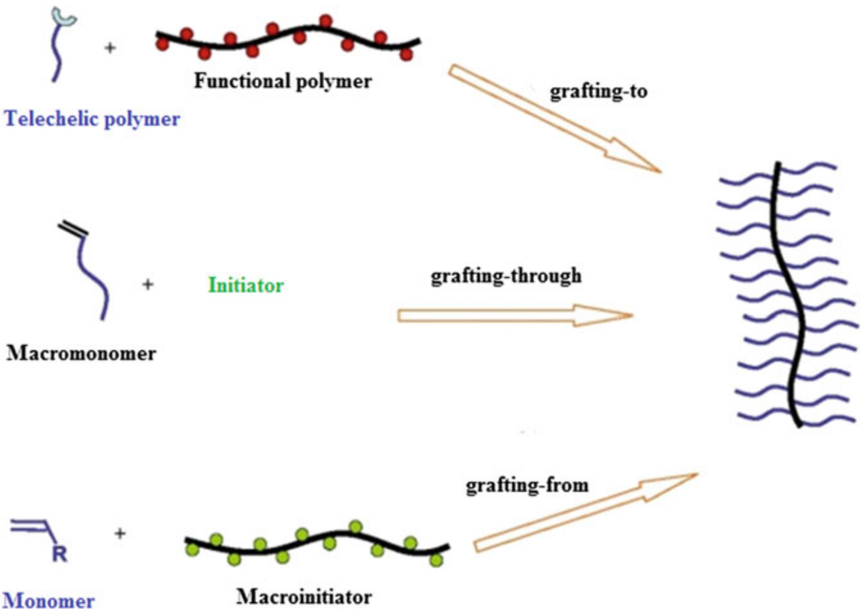
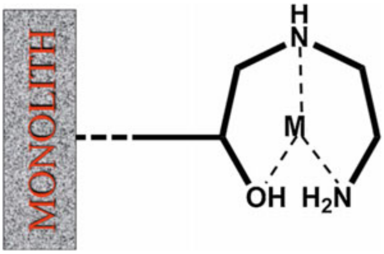


Fig. 2.10 Schematic presentation of «grafting-from», «grafting-through», and «grafting-to» processes

The main demand to successful «grafting-from» reaction is preliminary obtained macromolecule with distributed initiating active centers. In other words, in the «grafting-from» method a macromolecular matrix is modified to integrate active centers capable of initiating the grafted polymerization [21, 295, 296, 302].

Commercial polymers are widely applied as polymer carriers in the «grafting-from» polymerization processes: polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC), PCD, etc. [18, 19]. Thus, the methods of PE surface modification by grafting are compared (flame treatment, crown discharge, plasma and high energy radiation, initiators and polymer grafting, chemical and photochemical treatment, halogenation) [303], and the PE modifying methods using grafting in solution, melt, solid state grafting, other methods [304]. There is an interesting usage of grafting for surface functionalization of latexes for their following application in biotechnology [305]. Simple devices have been designed [306] for adsorption and metal ion concentration, which contain different chelating monolithic polymers, for example, poly(butyl methacrylate-*co*-ethylene dimethacrylate) monoliths with photo-grafted, en-modified GMA.



Production of polymers with grafted chelating fragments is carried out in two ways: one-stage, which includes grafted polymerization of chelating monomers to a polymer substrate, and two-stage, which supposes production of grafted multi-functional groups with their following completion up to a chelating fragment. The «grafting-from» method provides production of polymers with very different chelating fragments, for example, en, diethylenediamine, trien [307–309], 2,2′-dipyridilamine [310], thiol [311], amidoxime [312–314], sulfonic acid [315], iminodiethanol [316, 317], di-2-propanolamine and 3-amino-1,2-propandiol [316], IDA [318–320], *N*-methylglucamine [316, 321], 2,3-diaminonaphthalene [322], catechol [323], β-diketones [324, 325], salicylic acid [326, 327] and acetyl salicylic acid [328], *N*-acylsalicylamides [329], Pp [330], crown ethers having a variety of donor-atoms (thia- and azacrown ethers, crown ethers with oxygen atoms) [331, 332], anthranilic acid [333], etc.

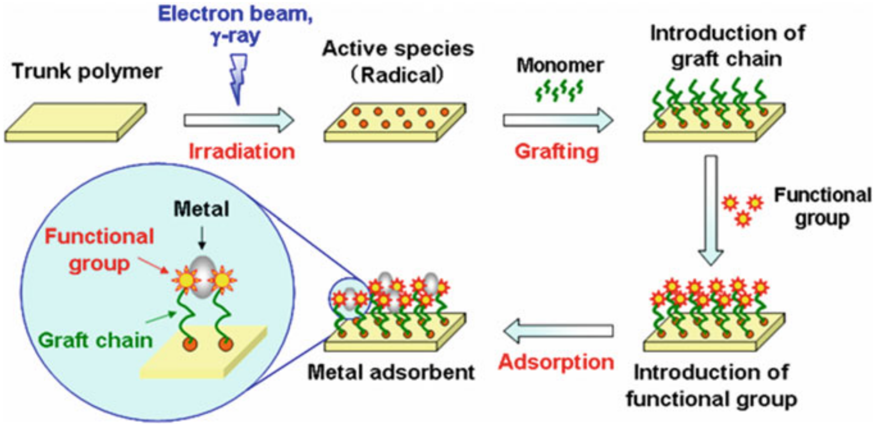
Surface modification of polymers is initiated by free radicals formed from an initiator and transferred to a polymer matrix for interaction with a monomer with grafted copolymers forming. Examples of directly generated free radical formation are redox reactions with participation of peroxides and persulfates. Free-radical active centers are generated by direct oxidation of a polymer matrix by ions of some transition metals (cerium, chromium, vanadium, cobalt). Thus, polymer flocculant (cross-linked copolymer PAAm-xanthate with grafted sodium gluconate) was synthesized in aqueous solution using cerium-ammonium nitrate (initiator of the reaction) and epichlorohydrin (cross-linking agent) [334]. The same initiator was used for grafting diaminomaleonitrile on PVC in nitrogen atmosphere in aqueous nitric acid [335]. The grafted copolymerization of AN to PVA microspheres was performed using cerium-ammonium sulfate as initiator. The grafted PAN was converted into poly(amidoxime) by the reaction with hydroxylamine hydrochloride [336]. Redox-potential of metal ions is an important factor, which determines efficiency of grafting. In general case metal ions with low oxidation potential are preferred as efficiency of grafting is concerned. Using metal chelates in grafting is not very suitable, but has some advantages. There are compounds, which can give free radicals upon heating, which are transferred to a polymer chain (for example, azo-compounds, peroxides, hydroperoxides, peroxide diphosphates, etc.). Apart from the aforementioned initiators, BP and AIBN are very effective in grafting reactions. Preliminary chemical treatment (for example, ozonation, diazotization, xanthantion) of polymeric matrix can generate free radicals, which initiate the grafted polymerization process. We shall also notice formation of secondary free radicals, which initiate the grafted polymerization process, for example, CO_2^-, $C_2O_4^-$, etc. [296].

When performing grafted radical polymerization, first polymer monolayers form, as a result, catching of a double-bond on a surface is kinetically impeded at once after covering of the surface by polymer chains, due to which amount of the grafted polymer on the surface is limited and does not exceed 1.5 mg m^{-2} [337]. Polymerization on grafted self-assembled monolayers (SAM) allows controlled decoration of the surface by macromolecules [338]. Using of SAM in grafting attracted much attention due to their stability, reliability, and perfect control over orientation of functional groups.

More rarely free radical grafting in melt is used. In this case a mixture of polymer matrix, monomer and initiator is heated to high temperature, so that grafting proceeds in the melt. Thus grafted polymerization of *p*-(met) acryloyloxybenzoic acids on isotactic PP was performed [339]. Grafted polymerization of *p*-acryloyloxybenzoic acid has no effect on formation of both forms of α (monoclinic) PP, while *p*-metacryloyloxybenzoic acid brings to α_2 form. β-Crystalline (hexagonal) modification forms in PP-grafted(-*gr*-)-poly(acryloyloxybenzoic acid) at 185 °C; β-form was not observed in the grafted copolymers of poly(methacryloyloxybenzoic acid).

Radiation grafted polymerization is widely used as CPL synthesis technique [340]. Especially efficient is using the radiation-grafted materials (nanogels and microgels, hydrogels, fibers and monoliths, as well as membranes and brushes) for separation and purification, including environmental remediation, biotechnology, water production, chemical industry, and biomedicine categories [341]. General scheme of the grafted chelating adsorbent production can be represented as follows:

Preparation scheme of graft adsorbent



Irradiation of macromolecules can cause their homolytic splitting and, therefore, brings to formation of free radicals on a polymer surface. A medium is important in this case, for example, if irradiation is performed in air, peroxides can be formed on a polymer surface. Lifetime of free radicals depends on origin of a polymer matrix. Grafting is performed in three ways: (a) preliminary irradiation; (b) peroxidation, and (c) simultaneous irradiation technique [342, 343]. In the method of preliminary irradiation, a polymer matrix is first irradiated in vacuum or in presence of inert gas for free radical formation. The irradiated polymer matrix is then treated by a monomer in liquid or gaseous state or solution in appropriate solvent. This method, in particular, was applied to obtain chelating porous sheets for using in solid-state extraction [344]. First vinyl monomers containing epoxy-groups were radiation-grafted to PE-based porous sheets, and then the epoxy-groups were converted into IDA chelating fragments. The chelating porous sheets with density of IDA groups 2.1 mol kg^{-1} were cut into discs of 13 mm in diameter in order to fit an empty cylindrical cartridge with a capacity 6 mL. The similar procedure of preliminary irradiation of a polymer-substrate was applied for grafting GMA on preliminary irradiated PP fibers then followed by dien amination [345].

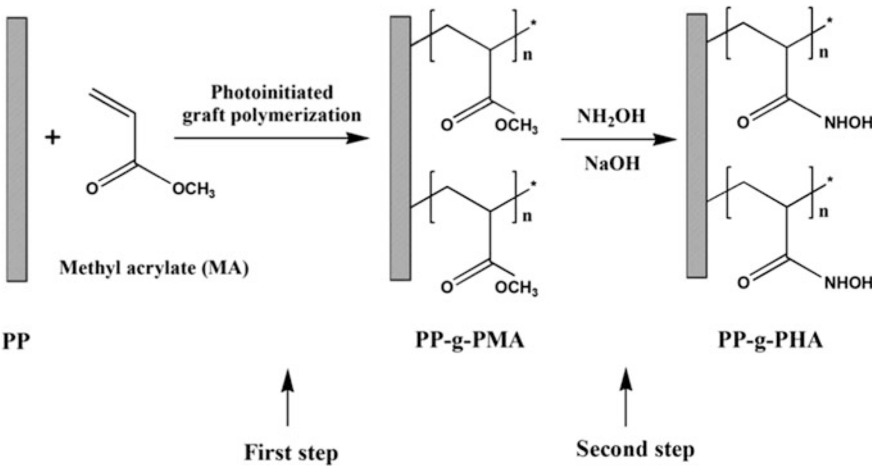
In the peroxidase grafting method, the initial polymer is subjected to irradiation with high energy in presence of air or oxygen with formation of hydroperoxides or diperoxides depending on nature of a polymer matrix and irradiation conditions. Stable peroxy products are then treated by a monomer at high temperature, at which peroxides are decomposed into radicals, which initiate the grafting process. An advantage of this method is that the intermediate peroxide products can be stored for a long time before involvement in the grafting process.

And finally, in the simultaneous irradiation method a polymer and monomers are irradiated simultaneously with formation of free radicals and the following linking. Thus, PVA aqueous solutions containing different amount of EDTA were subjected to γ-irradiation with ^{60}Co source to produce PVA-EDTA hydrogels. It occurs that content of EDTA in the hydrogel matrix is far lower than in the initial mixture [346].

The two-stage method of production of grafted siderophore-mimetic CPLs on PP surface has been developed: photo-initiated grafting poly(methacrylate) (PMA) with the following transformation into poly(hydroxamic acid) (Scheme 2.17) [1].

Photo-initiation was also used for grafting GMA on PE films followed modification at 80 °C of grafted films by disodiumimino diacetate [347]. Photo-grafting such chelating monomer as 2-acrylamidoglycolic acid, 3-sulfopropylmethacrylate, and 2-acrylamido-2-methyl-1-propanesulfonic acid on poly(ester sulfonic) membranes was performed without photoinitiator [348].

Surface modification using plasma or glow-discharge includes three possible methods: plasma treatment, plasma polymerization, and plasma-induced grafted polymerization [349, 350]. Thus was, for example, immobilized tetraphenyl-Pp on a plasma-treated PP [351]. Plasma treatment or glow discharge treatment can change properties of a surface of a polymer-substrate by integration of some polar groups, such as hydroxyl and amino groups. Thus, amino groups generated by



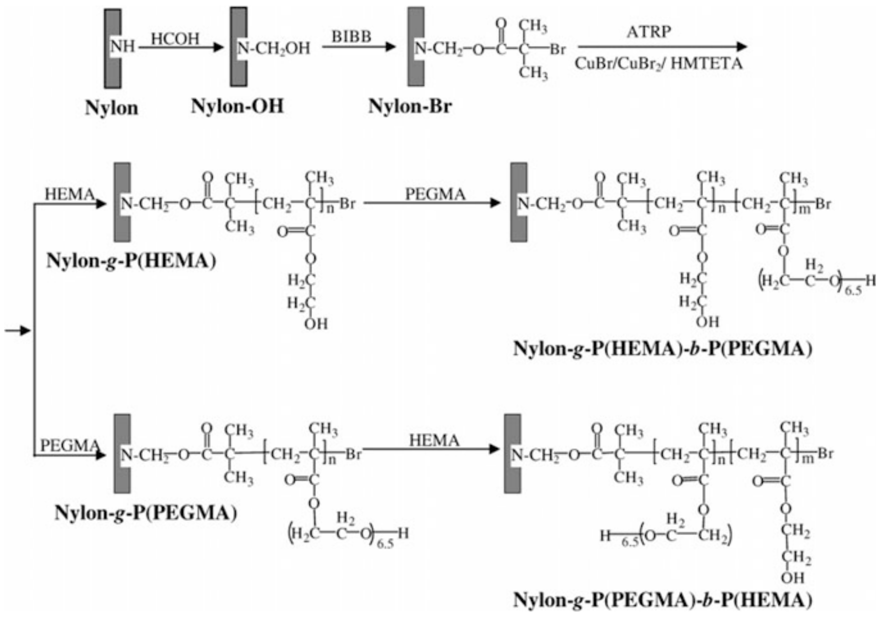
Scheme 2.17 Schematic diagram of production of PP-*gr*-poly(hydroxamic acid) using two-stage surface grafting

ammonia plasma, initiate open-chained polymerization of *N*-carboxyanhydride of γ-stearyl-L-glutamate on PP microporous membranes [352] . Also plasma-initiated grafted polymerization of benzo-18-crown-6-acrylamide should be noted [353].

2.2.2 Controlled Grafted Polymerization

The vast majority of the recent years' studies considering synthesis of grafted CPLs are focused on using CRP technologies, such as NMP, RAFT, and most often, ATRP [354–356]. Using CRP makes it possible to easily control molecular weight of the grafted chains, which, in turn, control a grafted layer thickness. Probably, the simplest way to achieve it is to control polymerization duration, experimentally this can be realized by a simple periodical removal of samples from reaction as necessary. Thus, very thin uniform layers (just several nanometers in thickness) can be obtained using slow polymerization methods and short times of growth, though thickness ~500 nm is possible. Gradient in thickness is also formed by slow feeding of a polymerization solution (monomer and a catalyst in a solvent) in container with a substrate [357]. Control over thickness can be also achieved by addition of free (non-bound) initiator, and allows achievement of high conversion, at that molecular weight is determined by the [monomer]/[initiator] ratio.

The ATRP method has some advantages for production of well-defined grafted polymers, among which are simplicity of initiator synthesis, fair control over a polymer growth, «living» character of the grafting process and a possibility to carry out a reaction in ecologically safe solvents under fair control [296]. Many different classes of grafted polymers are obtained by ATRP method, including hydrophobic,



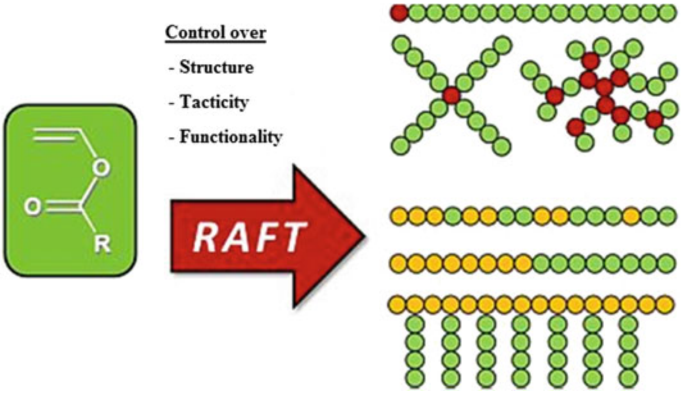
Scheme 2.18 Diagram representing activation and surface-initiated ATPRs on a nylon membrane, where HEMA is hydroxyethyl methacrylate, PEGMA is poly(ethylene glycol methacrylate), and BIBB is 2-bromoisobutyrate bromide

hydrophilic, charged (cation and anion), stimuli-responsible (pH and temperature), biocompatible, cell-adhesive, antimicrobial, and chemically active (for PPM or cross-linking) [355]. The method of surface-limited ATPR provides access to user's database of hybrid materials based on polymers for special applications [358]. CPLs are obtained by grafting poly(GMA) on bead PCD using surface-initiated ATRP, and the following reaction of epoxy groups with IDA [359]. Using ATRP method, 2-hydroxyethylmethacrylate and poly(ethylene glycol methacrylate) were grafted on a nylon-membrane surface (Scheme 2.18). Formed grafted homopolymers can interact in the following copolymerization reactions with formation of polyfunctional grafted diblock-copolymers [360].

ATRP was successfully used for the surface-initiated grafted polymerization, but it has one serious drawback, sensitivity to oxygen of Cu(I) complexes usually used for polymerization. This sensitivity requires thorough deoxygenation of solvents and polymerization containers. Therefore, a version of ATRP was developed, called Activators ReGenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGETATRP), which substantially decreases sensitivity to oxygen by introduction of excess reducing agent in a reaction [361]. This approach has two important advantages as compared to conventional ATRP: it provides improved oxygen enduring and considerable decrease in concentration of a catalyst from heavy metals [362].

Electrochemically-induced ATRP (eATRP) is also developed for production of IDA-functionalized poly(GMA) grafted to carbon fibers for detection of nano-nickel from baths for chemical nickel-plating [363].

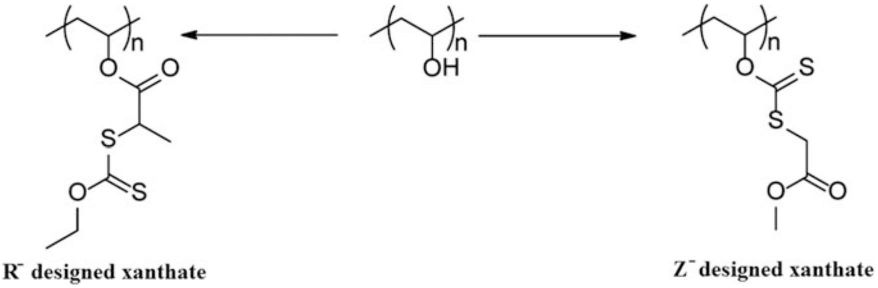
The only demand to multifunctional RAFT grafting from a macro-initiator is a possibility of radical transfer of atoms along a polymer chain. Initiating active centers can be incorporated by copolymerization [364]; they can be integral part of the first polymer [365] or can be included in PPM reactions [366]. If each active center along a polymer matrix contributes to formation of one of the branches, then a number of chains grafted to a macromolecule can be controlled by a number of active centers. Though a number of grafted chains can be regulated, there can still be a difference in lengths of each grafted chain due to kinetic and steric effects. The key feature of RAFT polymerization is a possibility of obtaining grafted polymers, for example, poly(vinyl esters) by chain extension of macroRAFT-agents containing polyfunctional fragments [367]:



The most often used macroRAFT-agent for this purpose is *O*-ethyl xanthate-terminated PEG. An example of using a macroRAFT-agent obtained using PPM by xanthate of a polymer preliminary produced by the RAFT method is fabrication of PVA-*gr*-polyvinyl acetates using R- and Z-approaches (Scheme 2.19) [368].

Alternative approach is that, in which macroRAFT-agent (poly 2-((2-ethylxanthatepropanoyl) oxy) ethyl methacrylate) is obtained by linking chain transfer xanthate agents to each monomer unit of poly(2-hydroxyethyl methacrylate) obtained by ATRP method. RAFT polymerization of vinyl acetate [369], or consequent polymerization of Vp and vinyl acetate [370] in presence of synthesized macroRAFT-agent provide production of polyfunctional polymers (Fig. 2.11).

The «grafting-from» method was successfully applied to obtain some chiral grafted polymers [371–374]. These polymers include, for example, helical polyacetylene polymer matrix with side poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) chains [375].



Scheme 2.19 Strategy for the R- and Z-designed PVA combs

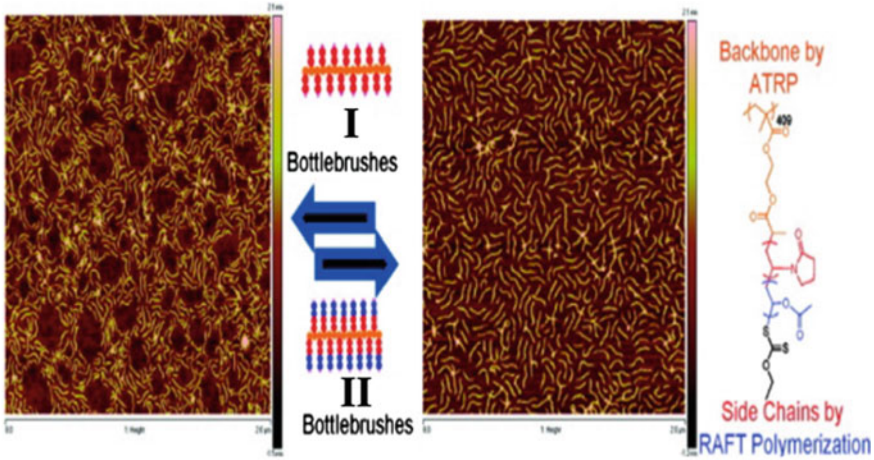


Fig. 2.11 Grafted polymers synthesized by RAFT polymerization from ATRP-obtained macroxanthate, where **I** is poly(Vp) and **II** is poly(Vp)-*b*-poly(vinyl acetate)

Recently easily available method of grafted polymerization from a polydopamine (PDA) coating layer has been developed [376]. First a PDA layer is applied to virtually any surface, independently on functional groups present on the surface, which can form surface-bound radicals under sunlight. Therefore, the PDA layer can serve as a photo-inducing layer for initiation of radical grafted polymerization of any monomer (Fig. 2.12). The special features of this method are the possibility of spatial control over architecture of the grafted polymer chains (pattern, gradient) and use of a vast grafting area with ultrasmall amount of a monomer solution (thin polymer layer).

Unusual strategy of creation of functionally grafted pseudo-semi-interpenetrative network structures is developed by the reaction of bifunctional linear polymers cross-linking with multifunctional dendritic cross-linking units placed in the ends of chains of linear polymers. The obtained materials have pseudo-semi-interpenetrative structure [377], in which a linear polymer is fixed by a network structure.

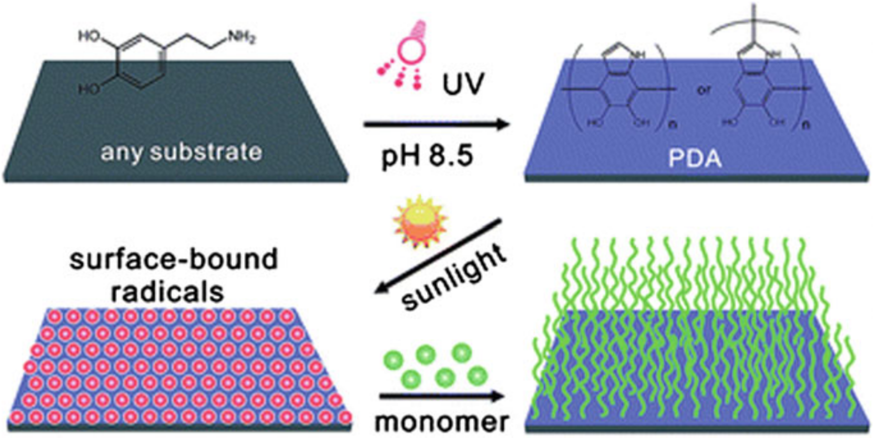


Fig. 2.12 Grafted polymerization of thin layers

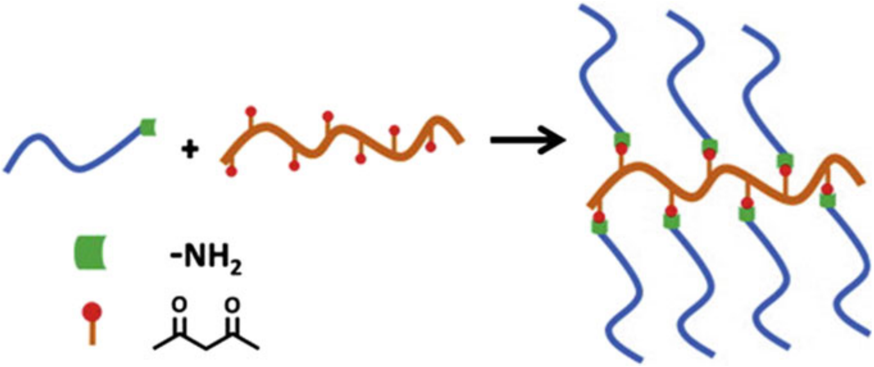
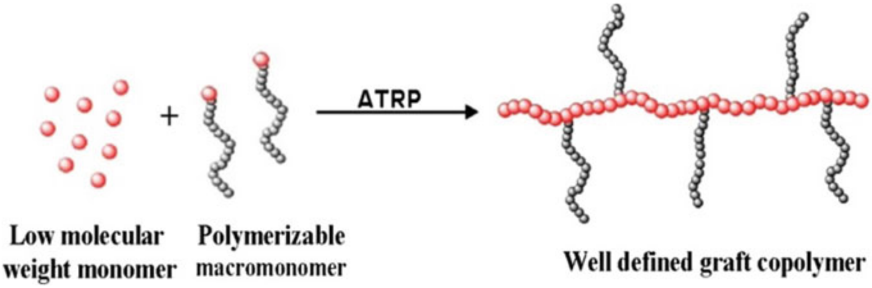


Fig. 2.13 Condensation of grafted ligand

We shall notice using reaction of polycondensation for production of grafted CPLs (Fig. 2.13) [378]. In this case a polymer-substrate poly [(2-acetoacetoxy) ethyl methacrylate] with β-keto ester groups along a chain is obtained by RAFT polymerization and is introduced into reaction of polycondensation with PEG monomethyl ether with end NH_2-groups. By varying the initial molar ratio between a polymer-substrate and a polymer with end NH_2-groups, grafted polymers with varied graft density can be obtained.

The «grafting-through» (or macromonomer method) is one of the simplest ways of synthesis of grafted polymers with well-defined side chains [379, 380].



This method enables to introduce macromonomers, which are prepared by another process of controlled polymerization into matrix obtained by CRP method. Thus, for example, macroRAFT-agents of a chain transfer, α-norbornenyl-functionalized poly (*t*-butyl acrylates) were obtained by RAFT method and then polymerized by ROMP method using Grubbs catalyst (Fig. 2.14) [381].

Combination of controlled polymerization processes allows control over polydispersion, functionality, composition of a copolymer, a matrix length, length of grafted chains, and a distance between them by changing a molar ratio between a

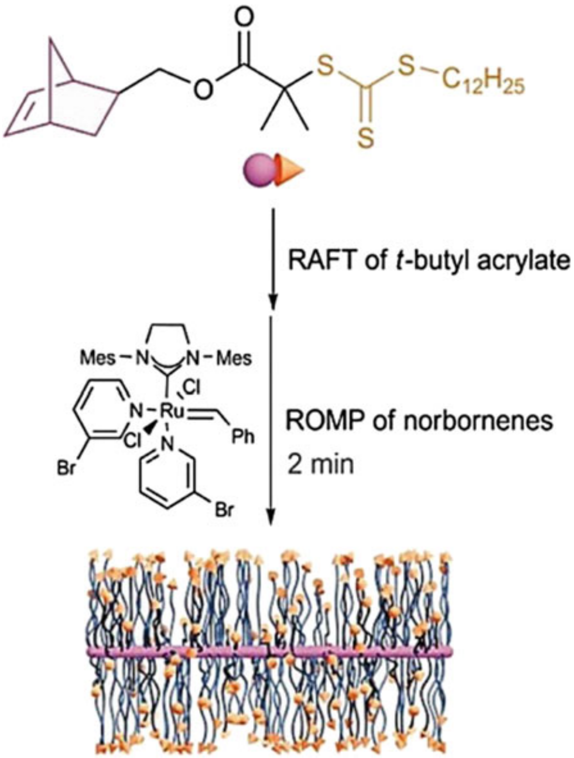
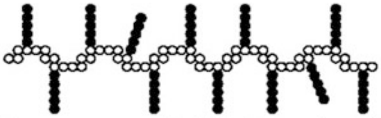
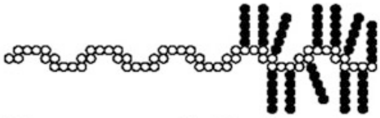


Fig. 2.14 Grafted polymerization by combination of RAFT and ROMP methods

monomer and a macromonomer and relationships of reactivity values of both. The grafted chains can be homogeneously or heterogeneously distributed depending on the relations between reactivity of end functional groups on a macromonomer and a low molecular weight monomer; this has a significant effect on physical properties of materials.



Homogeneous distribution of grafts

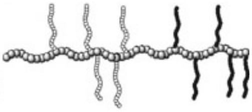


Heterogeneous distribution of grafts

A series of segmented poly(alkyl methacrylate)-*gr*-poly(D-lactide)/poly(dimethylsiloxane) terpolymers with different topology were prepared using «grafting-through» and CRP techniques [382]. At that, two ways of synthesis were used: one-step approach, in which methacrylate monomer (MMA or butyl methacrylate) was copolymerized with the mixture of poly(D-lactide) and poly(dimethylsiloxane) macromonomers, another one was two-stage approach, in which a grafted copolymer containing one macromonomer was chain-extended by copolymerization of the second macromonomer and low molecular weight methacrylate monomer. Topology of the grafted terpolymers prepared in different combinations of two approaches can be schematically presented as:

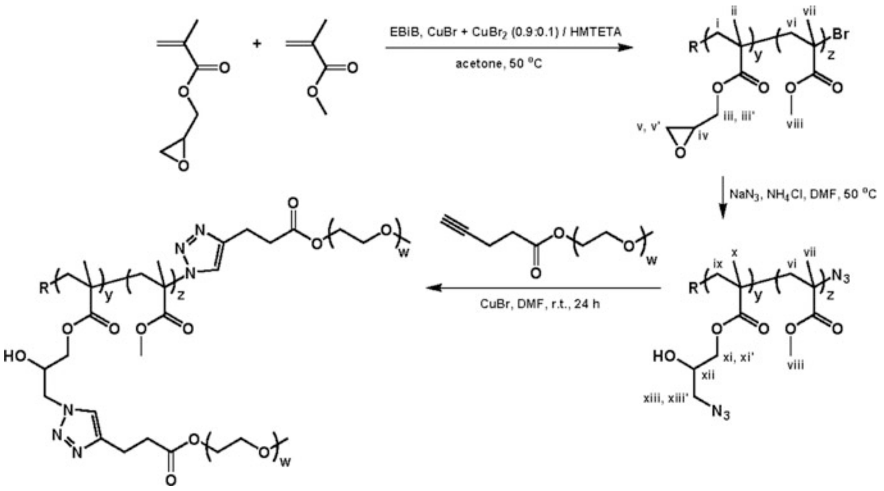
Gradient "palm tree"

Symmetrical gragient



Successive gradients

Grafting becomes more efficient way for production of grafted copolymers as different methods of click chemistry have appeared [301, 383]. This approach called «grafting-to» includes such click reactions as thiol-based additions, activated ether coupling, azide-alkyne cycloadditions, some Diels-Alder reactions, and also non-aldol carbonyl chemistry, for example, oximes, hydrazones, and amides formation [384]. Thus, a polymer-substrate with glycidyl butyrate units obtained by ATRP method is modified by sodium azide for preparation of a suitable for «grafting-to» copolymer using click chemistry (Scheme 2.20). The reaction of click-type with high yields results in the formation of a co-polymer with 1-hydroxy-2-azido functional groups with high yields, which are additionally functionalized for a second via a click reaction at room temperature. 1,3-Dipolar cycloaddition of PEO methyl ether pentynoate catalyzed by CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine gives grafted polyfunctional polymers with PEO hydrophilic side chains [385].



Scheme 2.20 Click reactions in grafted polymerization

«Grafting-to» approach is used for preparation of star-shaped molecules of weakly and densely grafted polymers [386]. The «grafting-to» technique assumes using a main chain with functional groups, which are randomly distributed along the chain. Formation of a grafted polymer follows the reaction of coupling between the functional matrix and end groups of the reactive grafted chains. These coupling reactions make possible chemical modification of a polymer matrix. General mechanisms of reactions used for synthesis of these copolymers include free-radical polymerization, anion polymerization, ATRP [387, 388], ring-opening polymerization (ROP) [389, 390], ROMP [391] and living polymerization technique. Copolymers prepared using the «grafting-to» method often used the technique of anion polymerization. This method including the coupling reactions of electrophilic groups of a polymer matrix and growing centers of anion living polymer would be impossible without generation of a polymer matrix having reactive groups. High yield of the chemical reaction called atom transfer nitroxide radical coupling chemistry is typical of the «grafting-to» polymerization method.

We shall focus on production of CPLs for gadolinium contrast agents using «grafting-to» strategy. For example, copolymers of activated ester monomer, pentafluorophenyl acrylate, and oligoethylene glycol methyl ether acrylate were prepared and modified with the chelating ligand 1-(5-amino-3-aza-2-oxypentyl)-4,7,10-tris (*tert*-butoxycarbonylmethyl)-1,4,7,10-tetraazacyclododecane for chelation with Gd (III) [392]. We shall notice synthesis of macrocyclic [393] and amylose-containing [394] grafted polymers by the «grafting-to» method.

Optically active grafted polymers based on helical polyacetylenes were produced using combination of ATRP, catalytic polymerization and click chemistry (Fig. 2.15) [395]. Strategy of obtaining grafted polymers consists of four main steps: (1) synthesis by ATRP method of alkynyl terminated poly(NIPAM) as one click-reagent for using as side chains in grafted polymers; (2) synthesis by catalytic polymerization of helical copolymer acting as helical polymer substrate; (3) synthesis of azido-functionalized copolymer by transformation of bromide groups into azide for production of the second click-reagent, and (4) synthesis of optically active grafted polymers by click reaction. The grafted polymers can self-assemble in aqueous solution forming core/shell structured nanoparticles having optical activity and thermal sensitivity.

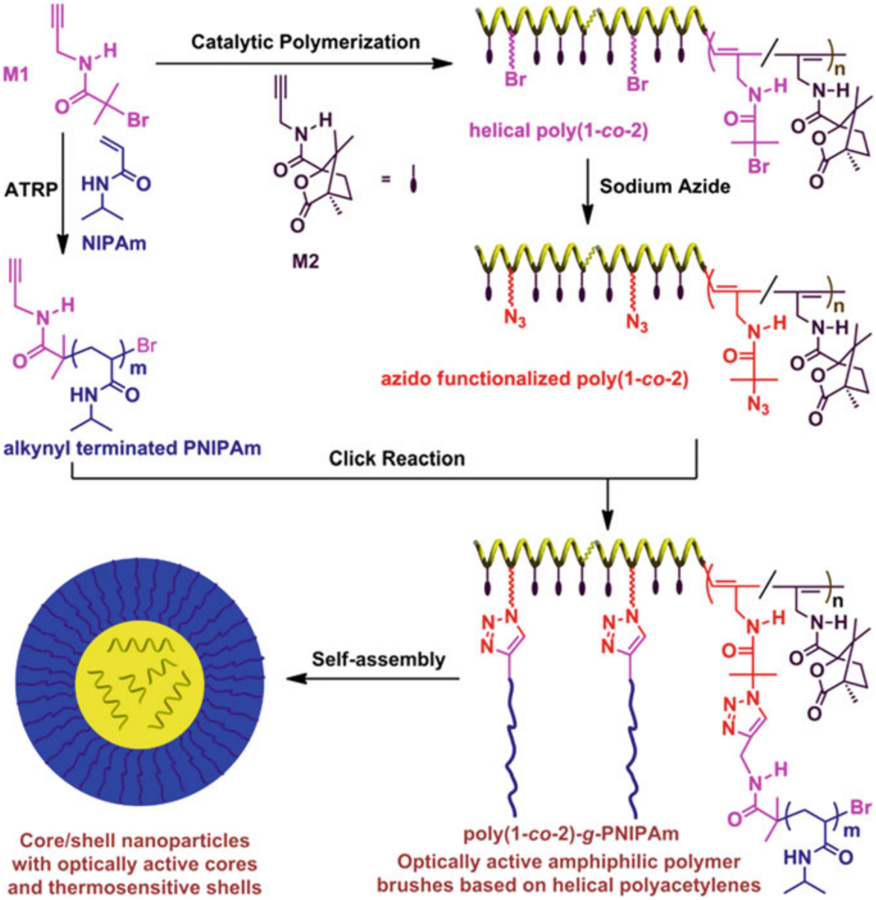


Fig. 2.15 Scheme of production and self-assembly of thermally-responsible amphiphilic polymers based on helical polyacetylenes

2.2.3 Macromolecular «Brushes»

The distinctive physical properties of grafted polymers are attributed to three interconnected parameters, such as grafting density (σ), molecular weight of the grafted chains, and quality of a solvent. The most fundamental and easily measured property of a grafted polymer is its height (H), which is determined by hydrodynamic radius (R_g) of polymer covering a particle and increasing as repulsion forces between particles increase. The main statements of theoretical and experimental approaches for description of spatial structure of grafted chains are derived from the idea that depending on density of a polymer grafting, fixed chains gain so called mushrooms or brushes configurations on the solution/substrate interface (Fig. 2.16). At that, their mutual transitions are possible, depending on different factors [396].

In a good solvent, where a surface is «inert», height of a grafted chain is determined by balance of monomer-monomer repulsion (or osmotic pressure of the monomers), which advances heightening of a grafted chain, and stretching of entropy of the chains, which promotes decrease in height. Grafting density is a number of ends of grafted chains per unit surface area of a substrate, and is expressed by equation

$$\sigma \equiv \frac{1}{(D/\alpha)^2} \tag{2.1}$$

where D is a distance between grafting points in units of monomer size. If α is very small, chains are efficiently isolated from each other and act independently: there is no additional osmotic pressure caused by the chains to stretch them away from the surface, and the chains form isolated islands or «mushrooms».

Size of isolated chains in a good solvent is determined by Flori radius:

$$R_F \sim \alpha N^{3/5} \tag{2.2}$$

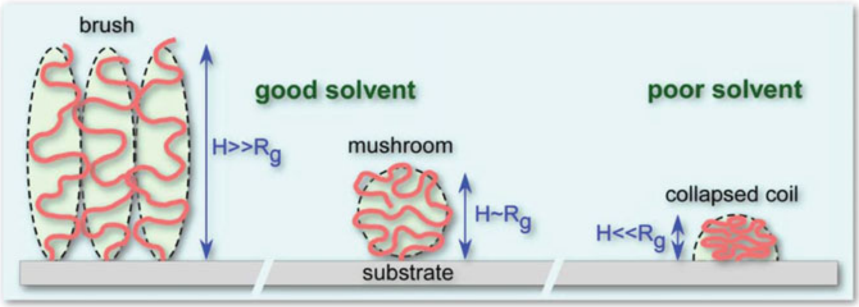


Fig. 2.16 Schematic representation of conformations of surface-linked polymers in the brush regime (on the left) and in the mushroom regime (on the right) in good diluter. Also conformations of surface-linked polymers in a bad solvent are shown

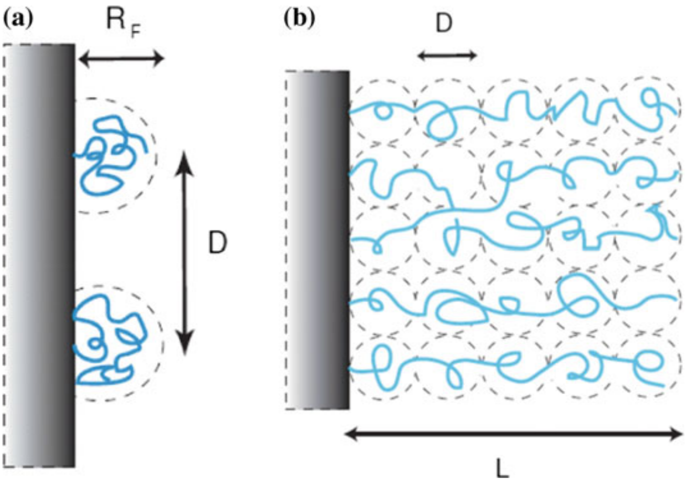


Fig. 2.17 **a** Scheme of chains grafted by the ends to inert substrate swelling in solvent at D distance between the grafting points. Distance between the grafting points is far more than the radius $R_F \sim aN^{3/5}$, so that these chains are isolated from each other and form mushrooms on the surface. **b** Scheme of Alexander-de-Gennes solvated brushes

so that if tethered dilutedly, size of a single-chain mushroom is R_F. Critical grafting density (σ^*), which makes a boundary between the mushroom and the brush regimes, is grafting density, at which mushrooms begin to touch each other, or if distance D between graftings is approximately equal to R_F (Fig. 2.17a).

The equations, which connect height of the grafted chains (H), polymerization degree (DP) and grafting density (σ) based on the Flori theory, are as follows:

$$H \propto DP\sigma^n$$
$$\sigma = h_d \rho N_A / M_n,$$

where h_d is thickness of a dry brush, N_A is Avogadro number, ρ is volume density of a polymer.

In a good solvent, thickness of a grafted polymer in the mushroom regime with low grafting density is $H \sim N\sigma^{1/3}$. Thus, the longer chains, the more diluted a fixing surface should be, so that the grafted chains would remain in the mushroom regime. At the early stages of polymerization, when a number of monomers in each growing chain is small, a surface is bound to isolated polymer mushrooms. But once chains become longer, each mushroom grows until they fall on each other finally forming polymer brushes.

The physical picture of Alexander-de-Gennes model is based on «blobs», as is shown in Fig. 2.17b, their size is determined by grafting distance D. The blobs works as rigid impenetrable spheres, which fill space.

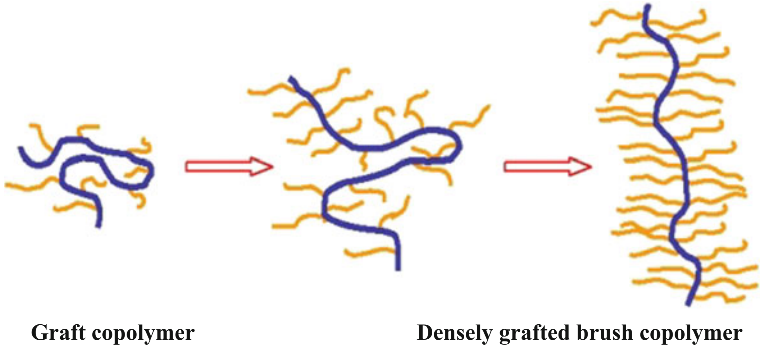
Height or thickness of a brush L is equal to a number of monomers in a chain contained in a column with $(D/\alpha)^2$ area and height L/α and is estimated as:

$$\phi \sim \frac{N\alpha^3}{D^2L} \tag{2.3}$$

Therefore, at high grafting density chains are effectively modeled by hard-core blobes, which generally spread in normal to the grafting plane direction. The Alexander-de-Gennes model determines how a blob size changes as grafting density changes. Introduction of the blob model occurs useful and simplified theoretical tool, which deals with the physical sense of the problem.

Transition from «grafted» copolymers to «brushed» happens only when density of the grafted side chains begins to affect a matrix ability to accept random coil configuration.

Macromolecular brushes belong to the general class of grafted copolymers [21, 302, 397–406]. However, in this case the grafting density can be very high, at least, in some segments of a copolymer. Really, polymers with one chain grafted on a repeated unit of a polymer matrix were obtained. This results in very tense situation along the polymer matrix, which makes a macromolecule take unusual conformations due to steric repulsion stipulated by densely packed side chains [407]. Densely grafted side chains reinforce the polymer matrix, but it retains some conformation freedoms. Dynamics of the side chains and the matrix changes as compared with respective homopolymers, and dynamics of the matrix shows that it is plastified by side chains, and the molecule becomes dynamically more uniform.



Overloaded structure of polymer brushes appears due to limited mobility of side chains. Linear brushes, also called bottle-brush copolymers, as molecular architecture are well known in biology, where they are responsible for different functions, including mucociliary clearance of breathing ways and mechanical performance of articular cartilage.

In turn, polymer brushes are subdivided into a range of classes, among which star brush copolymers, brush block-copolymers, heterografted brush copolymers, gradient brush copolymers and molecules with double grafted side chains (brushes of brushes) are most important [385].

Thus, if a tetra-functional initiator is used for polymerization of poly(2-hydroxy ethyl methacrylate) with 2-(trimethylsilyloxy) ethyl methacrylate groups, the obtained polymer can be functionalized with formation of 4-arms macroinitiator. This product, in turn, can be used for production of 4-arms star macromolecular brushes [408].

SP-containing polymer brushes used as photoswitchable, reversible optical sensors that show selectivity for different metal ions and drastic changes in surface wettability present a special interest [409, 410].

It should be noted bifunctional polymer brushes orthogonally derivatized with oxotitanium and nitrilotriacetate-Fe(III) groups for enriching both mono- and multi-phosphorylated peptides for mass spectrometry analysis (Fig. 2.18) [411].

Topologically different materials, for example, brush macromolecules with block-copolymers of grafted side chains and «standard block-copolymers», in which one or more segments along a polymer chain are brush copolymers of different compositions, can be related to brush copolymers. The first type of grafted polymers is formed when macromolecular brushes are used as macroinitiators for polymerization of the second monomer [412].

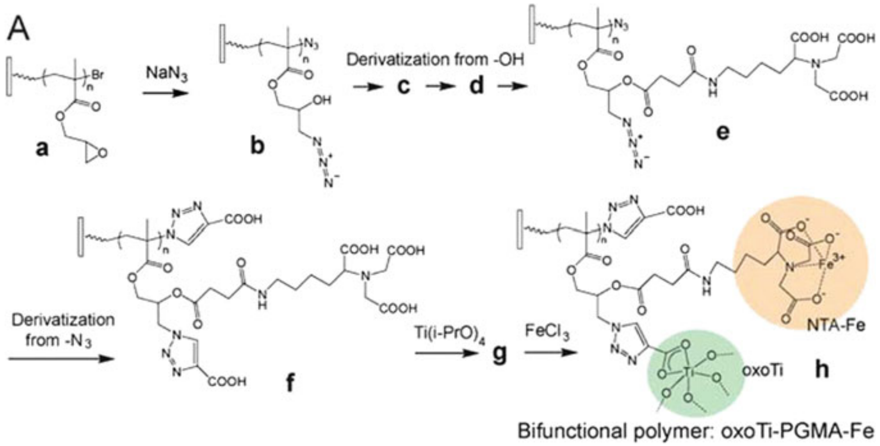
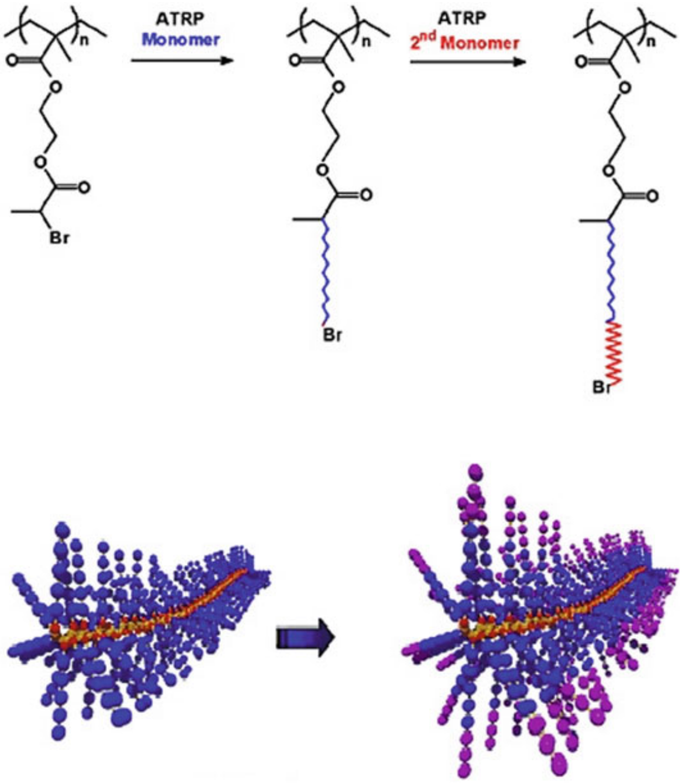


Fig. 2.18 Scheme of synthesis of bifunctional polymer brushes



Homopolymer side chains **Block side chains**

The resulting nanostructured macromolecules can form soft/hard core/shell systems, macromolecular channels, stable worm-like micelles or inverse micelles, and other complicated architectures. It is important that these materials served as templates for production of gold nanowires [413].

Interesting approach to synthesis of a material, which can also be related to brush block copolymers, is formation of a precursor of macroinitiator with the following elongation of a chain by another monomer. This brings to «standard» for block-copolymers architecture along a brush matrix. Another block can be used for formation of a segment with separated phases for physical linking of brush-copolymer macromolecules, for example, shown in the following schematic drawing (Fig. 2.19).

To study self-assembly in large domain ordered nanostructures [414], PS-*b*-polylactide brush copolymers are synthesized by combination of three controlled methods of polymerization. A block-copolymer matrix for double grafted polymerization was prepared for RAFT polymerization of solketal MMA followed by polymerization of 2-(bromoisobutyryl) ethyl methacrylate. Branches of polylactide

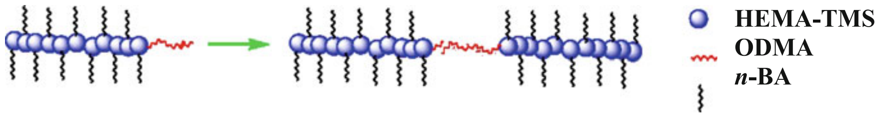


Fig. 2.19 Schematic image of brush copolymer with linear architecture of block-copolymer along matrix, where *n*-BA is *n*-butyl acrylate, ODMA is octadecyl methacrylate, HEMA-TMS is 2-(trimethylsilyloxy) ethyl methacrylate

were «grafted-from» from the first block after removal of a ketal groups, and PS branches were grafted by ATRP from the second block. A similar structure was obtained by consequent copolymerization of matrix precursor of a monomer-initiator and a macromonomer [415]. This results in formation of a block-copolymer brush synthesized by the «grafting-from» and «grafting-through» combination.

One more interesting topology of brush, which is important for PMC problems, is shown by synthesis of materials called hetero-grafted copolymer brushes. For example, brush copolymer with grafted PEO and poly(butyl acrylate) is obtained by the following scheme. First, precursor is prepared for CRP initiator by preliminary «grafting-through» polymerization of a macromonomer with low molecular weight co-monomer [416, 417]. Then, protecting groups on the precursor monomer units are transformed with formation of fragments capable of initiation of ATRP, and the final product is synthesized using «grafting-from» polymerization of a second monomer with initiated groups distributed along a brush copolymer chain.

Combination of copolymerization gradient and synthesis of macroinitiator provides access to brushes with controlled gradient of grafting density along the initial matrix [418, 419]. Gradient macroinitiators are prepared by spontaneous copolymerization of monomers with different reactivity or by controlled addition of one monomer to copolymerization of monomers with relatively similar copolymerization constants [420]. If macroinitiator with gradient of initiating centers along a matrix is used in grafting from copolymerization, the resulting molecule has higher density of side chains on one end of the matrix than on the other. Upon compression the rod-globule transition goes on the end where a brush is densely grafted, leaving a molecule with ball-like «head» and broadened «tail», so called «tadpole conformation» (Fig. 2.20) [419].

First, tadpole shape is formed of the block-grafted copolymers of bromide PS and methacryloyl-end poly(*tert*-butyl acrylates) and then hydrolysis of poly(*tert*-butyl acrylate) side chains to PAA side chains, which form pH-sensitive micelles in water [421].

Another combination of «grafting-from» and «grafting-through» methods can result in formation of such type of polymers, which are called «double grafted» brush copolymers. This topology appears when macromonomers are polymerized by «grafting-from» method of linear macroinitiator.

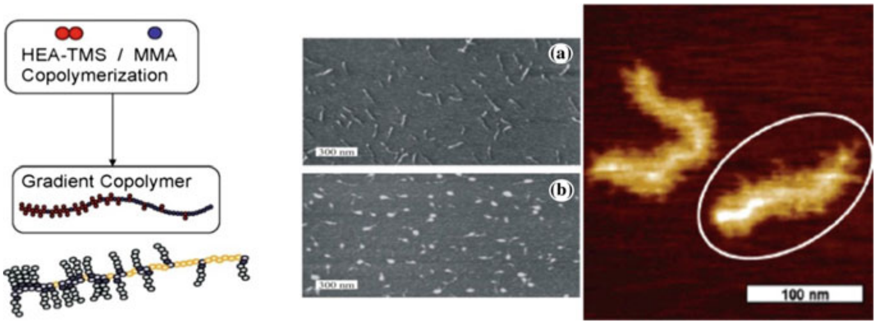
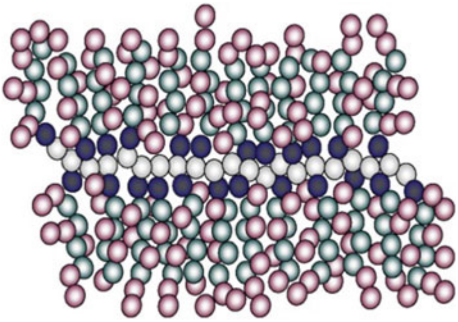


Fig. 2.20 Formation of a «tadpole» from block-grafted amphiphilic copolymers



In many cases, this can be considered as a brush copolymer in which each grafting is a brush copolymer [380].

Binary polymer brushes containing homopolymer and di-block copolymer brushes, which is the attractive class of ecologically sensitive nanostructured materials, should also be noted [422].

It is important that grafted polymerization is a convenient method for production of «tailored» polymers playing important role in PMC chemistry. For these purposes, for example, PEI was grafted to «tailored» polyurethane using the second 4,4′-diphenylmethane diisocyanate linked to carbamate half of polyurethane [423].

As is seen from this brief review, grafting polymerization methods are continuously improved, which advances fine control not over a polymer structure, but also over its chelating junction. At the same time, in many cases in these processes no proper attention is paid to the problems of formation of homopolymers and methods of their removal from products.

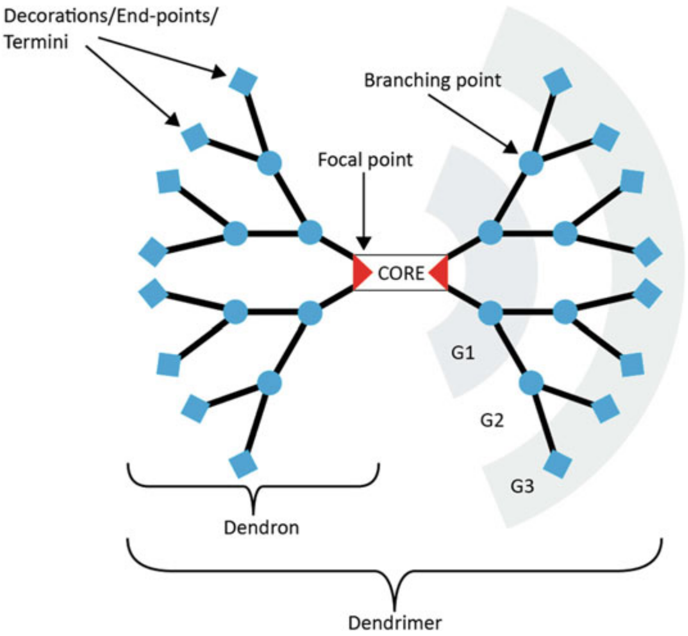


Fig. 2.21 Anatomy of a dendrimer. This example is the AB_2 type, where each branch is made from a monomer A which is divided into two monomers B

2.3 Dendrimers as Polymer Chelating Ligands

Dendrimers (originated from Greek «dendron», tree) relate to the class of polymer compounds, which have numerous branches [424–444]. Other proposed synonyms to these compounds were arbolors and cascade molecules; however, they occurred less commonly used. Dendrimers are multiply branched approximately spherical big molecules and have distinct chemical structures (Fig. 2.21) [445].

2.3.1 General Characteristics of Dendrimers

Considering chemistry of polymers, dendrimers are almost ideal monodisperse macromolecules with regular, highly branched 3D structure; they are even called polymers of the 21st century [446]. They consist of three architectural components, such as core, branches and end groups, and they are built from an initial atom, nitrogen, to which carbon and other elements are linked via repeated series of chemical reactions, forming spherical branched structure. A number of branches increase during their formation at each elementary act of monomer addition. As a result, while molecular weight of the dendrimers increases, shape and hardness of molecules change, which is, as a rule, accompanied by change in physico-chemical properties of the dendrimers, such as intrinsic viscosity, solubility, density, etc. Reactions used till now in synthesis of polymers and dendrimer-like polymers are not, as a rule, chain reactions. Usually, these are well known reactions of condensation, substitution, and linking by multiple bonds.

As a result of the first stage of polymerization in the ends of branches free groups are formed, each of which can react with two additional monomers, thus forming first generation (G1) dendrimer. There can be a finite number of these consequent stages, since at some moment a close-packed structure of monomers is formed, which prevents further polymerization. For example, a layer of G9 dendrimer already contains 3069 monomers, and diameter of this molecule is ~ 10 nm. In other words, dendrimers are highly branched nanostructures with controlled composition and architecture, having functional groups incorporated in a regular «branched upon branched» structure. Such high density of functional groups confined in the limits of nanometer containers makes dendrimers especially attractive as chelating agents of high capacity for metal ions [447, 448].

The existing synthetic approaches provide production of regular dendrimers, whose macromolecules have strictly definite molecular weight. Besides, it should be noted that many properties of dendrimers, such as glass-transition temperature (T_g), depend strongly on chemical origin of terminal groups placed on the surface of the spherical molecules. All aforementioned facts attract interest of researchers-chemists to synthesis of dendritic macromolecules. Thus, by now dendrimers have been synthesized basing on polyethers and polyesters, polyamides, polyphenylenes, polysiloxanes, polycarbosilanes, etc.

Utmost sizes, configuration and molecular-weight characteristics of regular dendrimers can be predicted theoretically. Since growth of macromolecule branches in all directions is equally probable, they become almost spherical already after 3–4 generations. Then, hence molecular weight of all macromolecules at each stage of controlled synthesis increases by the same value, the formed polymers are almost monodispersing, i.e. they contain macromolecules of equal molecular weight and size. Thus, for PAMAM dendrimer the ratio of average-weight and average-number molecular weights is very close to unit (PDI = 1.001–1.005), which is a sign of monodisperse polymer.

The key parameters, which determine structure and size of dendrimer macromolecules, are: N_c, functionality of a core (index of core branching), i.e. a number of dendrons grown from the core of a macromolecule: N_b, index of unit branching, a number of branches formed by each repeated unit; G, generation number. Ideal dendritic structures can be described by exact mathematic expressions using terminology of polymer chemistry. Thus, the number of terminal groups z is increased in accordance with the

$$z = N_c {N_b}^G,$$

which means that in the simplest case of trifunctional core and difunctional branching center ($N_c = 3$, $N_b = 2$) number of terminal groups increases from 2 to 48 in the core in the fourth generation.

The number of repeating units N_r greatly increases with the generation number even for the simplest case:

$$N_r = N_c \frac{N_b^{G+1} - 1}{N_b - 1} \tag{2.4}$$

and the molecular weight of M, respectively, increases exponentially with each generation:

$$M = M_c + N_c \left(N_r \frac{N_b^{G+1} - 1}{N_b - 1} + M_t N_b^{G+1} \right) \tag{2.5}$$

where M_c is weight of the core and M_t is weight of terminal units.

Using the aforementioned parameters, the following can be calculated theoretically: DP or a number of repeated units, a number of terminal groups, molecular weights of the core, repeated units, and end groups. In Table 2.4 calculated and experimentally found characteristics of macromolecules of a PAMAM dendrimer are compared. It is seen that the calculated and experimentally measured values of molecular weight for the samples with predetermined number of generations almost coincide.

Experimental data on sizes of macromolecules are in the range of the calculated data determined by two extreme conformations respecting to extended and corrugated dendrons.

The best results were obtained by now for PAMAM dendrimer, whose efficiency of branching reaches 95%. The cascade polymers produced by one-stage method display efficiency of branching of terminal groups no better than 70%. Probably, their most noticeable difference from polymers produced by controlled synthesis is higher polydispersity.

Table 2.4 Calculated and experimentally found values of molecular weight and diameter of macromolecules of PAMAM dendrimer

G	DP	$M_{theor.}$	M_{ex}	$d_{theor.}$	$d_{ex.}$
0	3	360		9.6–19.2	11
1	9	1044		12.8–28.8	16
2	21	2411		17.6–41.6	24
3	45	5154	5200	24.1–51.2	32
4	93	10,633	10,700	30.6–65.6	40
5	189	21,563	21,600	38.5–81.6	56
6	381	43,451	44,000	47.5–91.2	66
7	765	87,341	88,000	61.8–104.0	75
8	1533	174,779	174,000	78.0–117	90
9	3069	349,883		98.0–130.0	105
10	6141	700,091		123.0–143.0	124

2.3.2 The Main Types of Chelating Dendrimers

Among most widespread types of dendrimers with the highest value for CPL synthesis, we should mention the following.

1. PAMAM dendrimers are synthesized by divergent method taking ammonia or en as basic reagents. They are built using repeated consequent reactions consisting of (a) double Michael addition of methacrylate to primary amino group with the following (b) amidation of the forming carbomethoxy intermediate with great excess of en (Fig. 2.22).
2. Polypropylene imine (PPI) dendrimers are synthesized by the divergent method beginning from 1,4-diaminobutane (DAB). As an alternative name of PPI dendrimer the name POPAM dendrimers is sometimes used to describe of this class of dendrimers. POPAM denotes Poly(Propylene AMine), much like the acronym PPI. They grow by multiple repeated consequent reactions consisting (a) double Michael addition of AN to the primary amino group with the following (b) hydrogenation under pressure in presence of Raney-cobalt (Scheme 2.21).

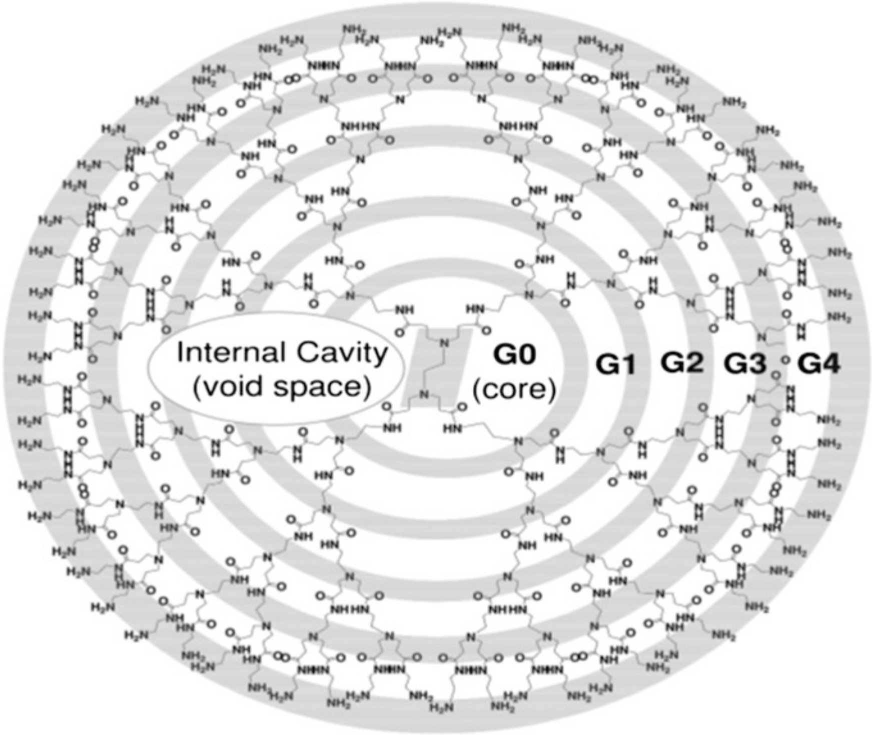
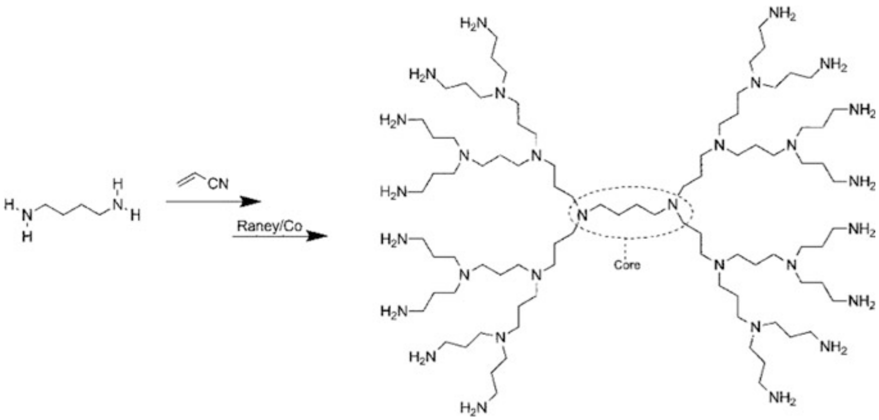


Fig. 2.22 Schematic representation of the G4 dendrimer with 64 amino groups at the periphery. This dendrimer begins from the en core; branches or arms have been attached by Michael addition to methacrylate followed by complete aminolysis of the methyl ester obtained using en [449]



Scheme 2.21 PPI dendrimer synthesis scheme

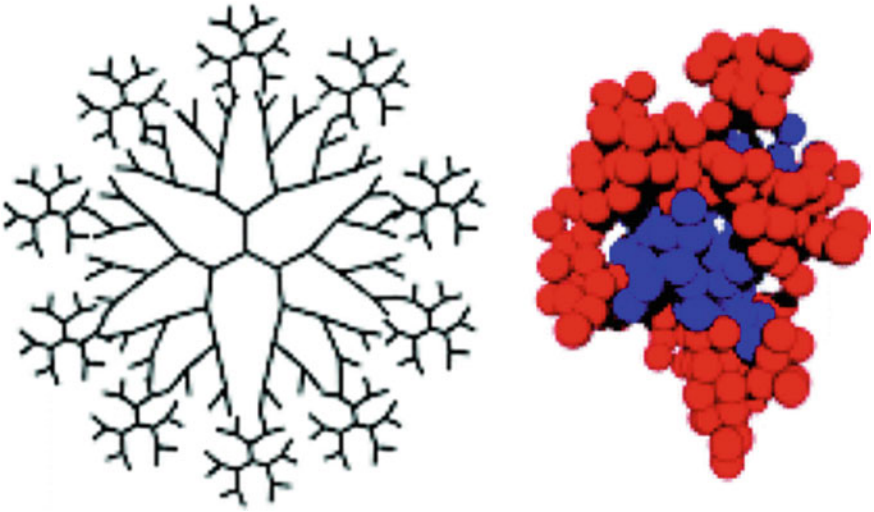


Fig. 2.23 Structure of tecto-dendrimers

3. Tecto-dendrimers. They consist of a dendrimer core surrounded by dendrimers of several generations (for each type of construction) designed for performing functions required for smart-therapeutic nanodevices [450–452]. Different compounds perform different functions, beginning from recognition of the diseased cells, diagnostics of illness, delivery of drugs, and ending by therapy results. It is important that dendrimer core of tecto-dendrimers may or may not contain a therapeutic agent surrounded by dendrimers (Fig. 2.23).

4. In multilingual dendrimers the surface contains several copies of certain functional groups [453].
5. Chiral dendrimers, in which chirality is based on design of constitutionally different but chemically similar branches of chiral cores (Fig. 2.24) [454–456]. As a practical matter, chiral dendrimers are especially interesting, because a combination of well-defined structure with chiral groups brings to a possibility of control over sizes and shapes of interior caverns in dendrimers. They provide development of different application fields, related to chirality, for example, molecular recognition, sensors, catalysts, enantioselective separation, etc. It is important that controlled 3D structure in these polymers resembles natural polymer systems and, consequently, offers new directions for biological and medical applications. Chiral dendritic molecules can be classified by four categories [457]: (a) dendrimer with chiral core; (b) dendrimer with chiral end units; (c) dendrimer with chiral building blocks, and (d) dendrimer with different branches linked to a nonplanar core.
6. Hybrid dendrimers include block or grafted polymers of dendritic and linear polymers (Fig. 2.25) [458]. Hybrid linear-dendritic (a copolymer formed with one or more dendritic fragments associated with one or more linear analogues) and dendronized polymer (a special type of a linear-dendritic hybrid, wherein the linear polymer contains dendrons attached to each repeating unit) are distinguished. To obtain this class of compounds two main approaches are used:

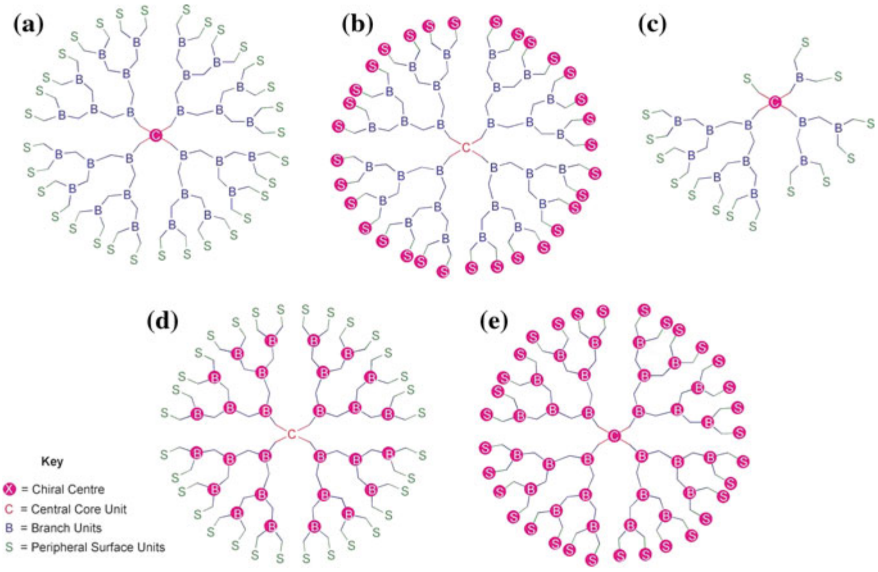


Fig. 2.24 A cartoon representation of the variety of possible formats for chiral dendrimers that feature: **a** a chiral central core, **b** chiral units at the peripheral surface, **c** achiral core coupled to constitutionally different branches, **d** chiral branching units and **e** chiral units at the core, branches and peripheral surface

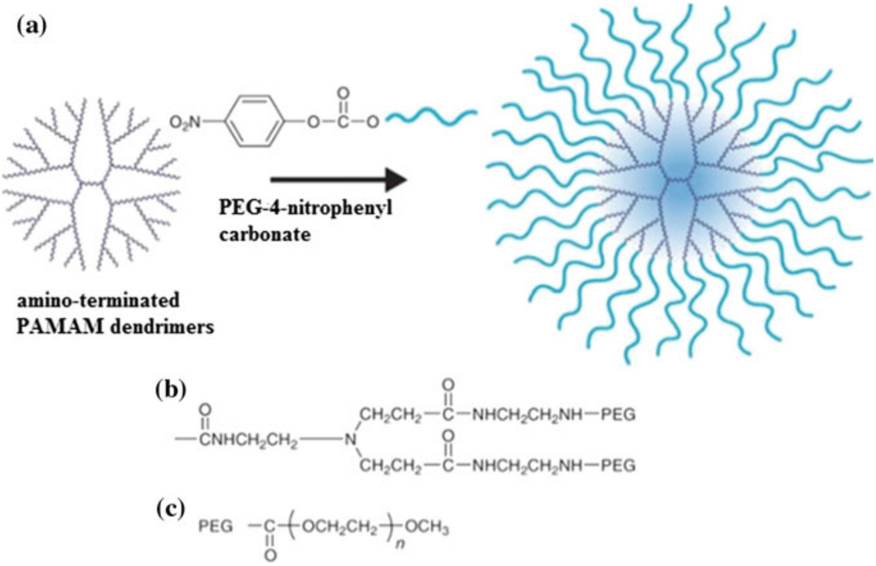


Fig. 2.25 Synthesis of PEG-modified PAMAM dendrimers (**a**). The chemical structures of the terminal units (**b**) and the PEG chain (**c**)

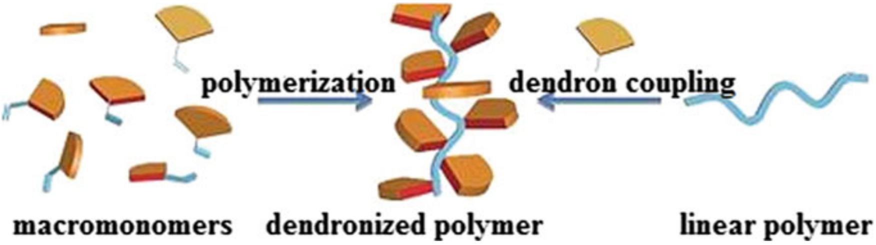


Fig. 2.26 Hybrids of dendritic and linear polymers

> macromonomer and attach-to routes (Fig. 2.26). In the first case, a monomer is polymerized, which already carriers a dendrimer of a certain size, in the second case module synthesis is used according to traditional chemistry of dendrimers based on divergent or convergent methods, with linear polymers or macromonomers used as building blocks [459].

For example, a series of photosensitive hybrid dendrimers G1–G3 is synthesized by the addition of amidoamines dendrons with end groups of *o*-nitrobenzyl alcohol to an alternating copolymer of St and maleic anhydride. It is found that the degrees of attachment of dendrons comprise 74, 42 and 26%, respectively, indicating that the number of attached dendrons decreases from G1 to G3 because of steric hindrance at the higher generation dendrons with large branches [460]. Hybrid dendrimers with PAMAM units and surface groups of *N*-hexylamide type or poly (*N*-methylglycine) blocks are obtained by the ring-opening copolymerization of sarcosine-*N*-carboxyanhydride with the dendrimer. Aqueous solutions of copolymers with poly(2-methyl-2-oxazoline) and PAMAM blocks are synthesized by reaction of polyoxazoline with ω-terminal functional groups [461]. Such dendrimers have 3D hybrid architecture of nano-organized systems containing cavities inside and outside of the dendrimer, and interconnected, which gives them a controlled permeability. Self-assembled block copolymers such as «head to tail» are produced from PAMAM as head and blocks of poly(L-lysine) (PLL) as tail. At that, PL tail blocks undergo «helix-coil» transition as a result of changing the solvent from water to methanol, resulting in a 3D structure similar to the protein molecules [462]. Dendronized alternating copolymers containing crown ether units are synthesized by copolymerization of St having side chains of the polyether dendron (two generations) and maleimide having side units of dibenzo-24-crown-8 [463]. Hybrid dendrimers from PPI (core) and PAMAM (shell) are also described [464].

Design of biocompatible environment-sensitive dendrimers is carried out based on PEG and PAMAM G4 dendrimers with *N*-*tert*-butoxycarbonyl-*S*-acetamidomethylcysteine moiety [465]. PAMAM G4 dendrimers, whose end groups modified by L-phenylalanine or γ-benzyl-L-glutamate and PEO chains are attached to the amino acids units, are obtained for use as nanocapsules [466].

A synthetic route to thermosensitive molecules using alkylamide side groups is proposed. It was shown that the thus obtained PAMAM dendrimers have a lower critical solution temperature (LCST), and the accumulation of *N*-alkylamide groups on dendrimers periphery provides thermosensitivity initially thermo-insensitive dendrimers. It is noted the attempt to extend the application of the technique to lipids based on PAMAM dendrimers with two octadecyl chains as a head group and a hydrophobic tail [467].

An interesting class of hybrid dendritic molecules is dendrigraft polymers [468]. Size of dendrigraft polymers is usually by 1–2 orders of magnitude more than of their dendritic analogues and is from about 10 nm to several hundred nanometers. Another distinctive feature of these polymers is synthesis based on the reaction with grafting polymer side chains serving as building blocks. To obtain these compounds three different synthetic methodologies were used: (1) divergent «grafting-to» methods based on consequent reactions of coupling polymer chains with functionalized polymer-substrate; (2) divergent «grafting-from» methods using cyclopolymerization initiated from functional centers placed on a polymer-substrate; and (3) convergent «grafting-through» methods including coupling preliminary formed polymer chains in one-pot synthesis.

It should be also noted different structural classes of dendritic copolymers such as hyperbranched copolymers, linear-dendritic block copolymers, dendrimer-like star-branched block copolymer, multiarm dendritic initiators, dendritic focal point chain transfer agents etc. [469].

7. Amphiphilic (Janus) dendrimers consist of two insulated parts of a chain end, half of which are donors, and another half acceptors (Fig. 2.27). PAMAM dendrimers also

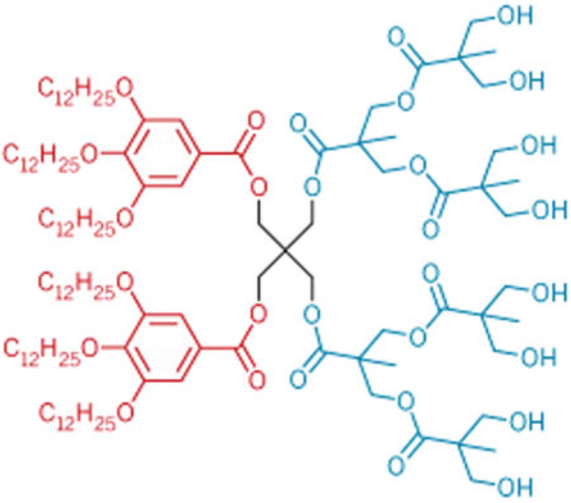


Fig. 2.27 Diagram of the structure of amphiphilic dendrimers

relate to amphiphilic dendrimers consisting of a hydrophilic core of a dendrimer and hydrophobic shells of stearyl acrylate type [470] or aromatic dansyl (1-dimethyl amino-1-naphthalene-5-sulfonyl) and 1-(naphthalenyl)-2-phenyldiazene [471]. Or, on the contrary, amphiphilic dendrimers consist of hydrophobic PEO core and hydrophilic carboxyl groups [472], and the latter can be used as polymer reagents in green technology of chemoremediation in liquid homogeneous phases [473].

8. Micellar dendrimer consists of unimolecular micells of water-soluble hyperbranched polyphenylenes [474].
9. Highly branched oligomers or polymers consisting of dendritic structures containing mesogen group, which can display meso-phase behavior, relate to liquid crystal dendrimers. They consist of mesogen monomers forming liquid crystal dendrimers in lamellar, columnar, and nematic phases (Fig. 2.28) [475].

It is noted co-dendrimers of Janus type G1 or G2, which combine the promesogenic bent-core and a rod-shaped molecular segments synthesized by universal CuAAC click reaction (Fig. 2.29) [476]. Depending on the ratio between the amount of rod-shaped and bent-core blocks these compounds form meso-phases in the range from nematic to complex polar smectic meso-phase, wherein the two kinds of mesogenic fragments are separated on a nanometer scale. If the ratio bent/rod 1:1, the materials form ferroelectric meso-phases and macroscopic polarization is stable in the absence of an applied electric field.

10. Frechet-type dendrimers designed Frechet based on poly(benzyl ether) hyperbranched skeleton (Scheme 2.22) [477–480]. Such dendrimers typically have surface carboxyl groups acting as a convenient anchor point for further surface functionalization or surface polar groups increasing the solubility of the hydrophobic type dendrimer in polar solvents or aqueous media.

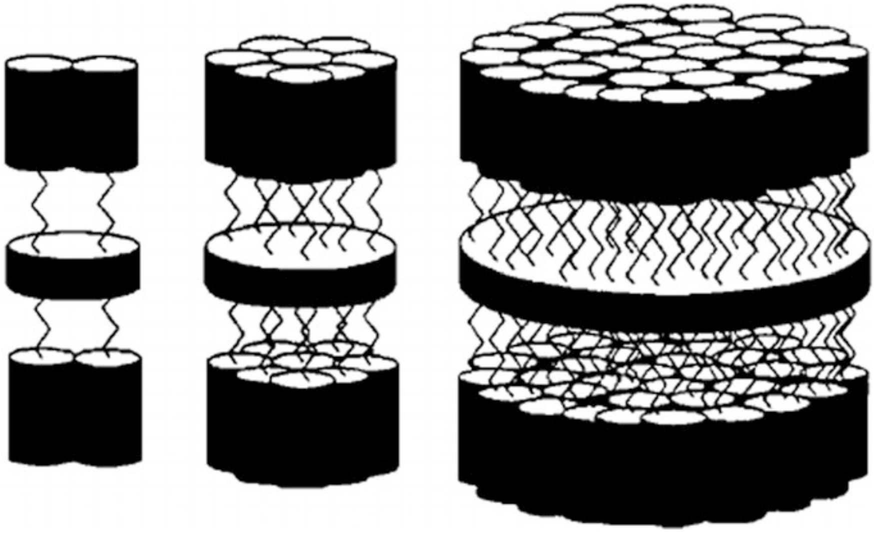
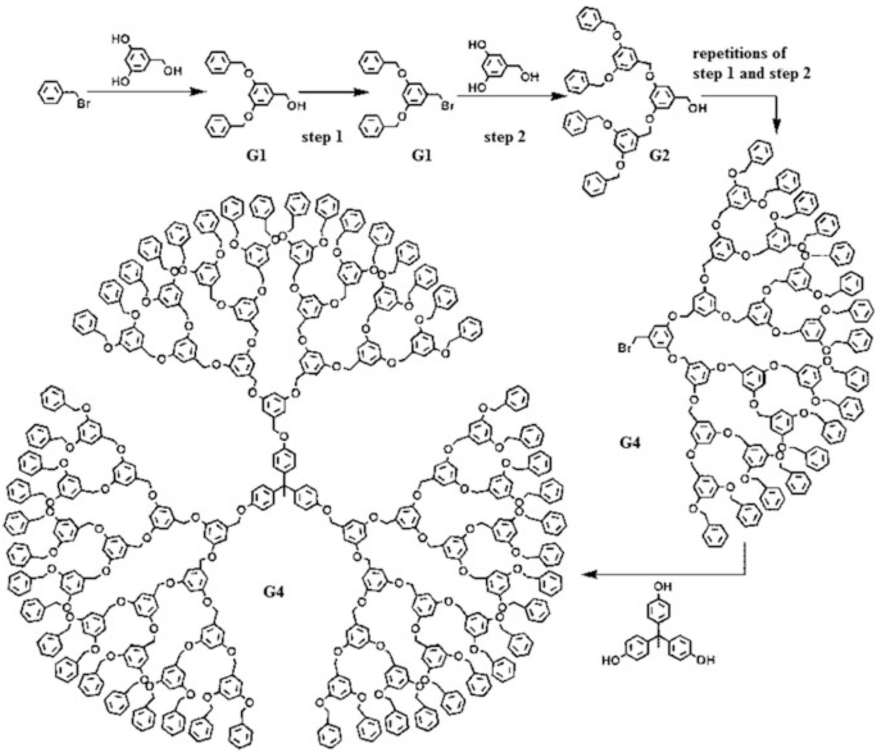


Fig. 2.28 Liquid crystal dendrimers

Fig. 2.29 Preparation of liquid crystal dendrimers via click-synthesis

11. Radially layered poly(amidoamine-organosilicon) (PAMAMOS) dendrimers are inverted unimolecular micelles, which consist of hydrophilic nucleophilic PAMAM interiors and hydrophobic organosilicon (OS) surface groups [481, 482]. Generalized 2D projection of the structure of these nano-sized globular macromolecules is shown in Fig. 2.30. This unique dendrimer family was discovered in 1990, and contains many compositional and functional variants, including dendrimers with terminal alkoxysilyl groups (X = Si–OR).
12. In the polysiloxane dendrimers, the key point in the synthesis of each generation is the alternation of two reactions: the formation of peripheral groups –SiOEt (actually chain growth) followed by substitution at –SiCl (Scheme 2.23) [483–485].



Scheme 2.22 Scheme of synthesis of Frechet-type dendrimers

13. Phosphorus-containing dendrimers represent a broad class of dendrimers containing phosphorus donor atoms in different parts of the dendritic architecture [486–488]. An interesting example is hexachlorocyclotriphosphazene that can be used as branch points for the rapid synthesis of dendrimers with high density of functionality as well as for the synthesis of dendrimers having exactly one function different from all others. These dendrimers are used as the materials providing reusable catalysts, chemical sensors or substrates for cell cultures (Fig. 2.31) [489]. Furthermore, these dendrimers were used for in vivo imaging and in order to clarify the biological mechanisms, particularly for anti-inflammatory dendrimers.

The binding of carbosilane dendrons with phosphine in the focal point with phosphorus-hydrazone dendrons having thiophosphoryl azide in the focal point was successfully carried using the click reactions (Scheme 2.24) [490]. Appropriate

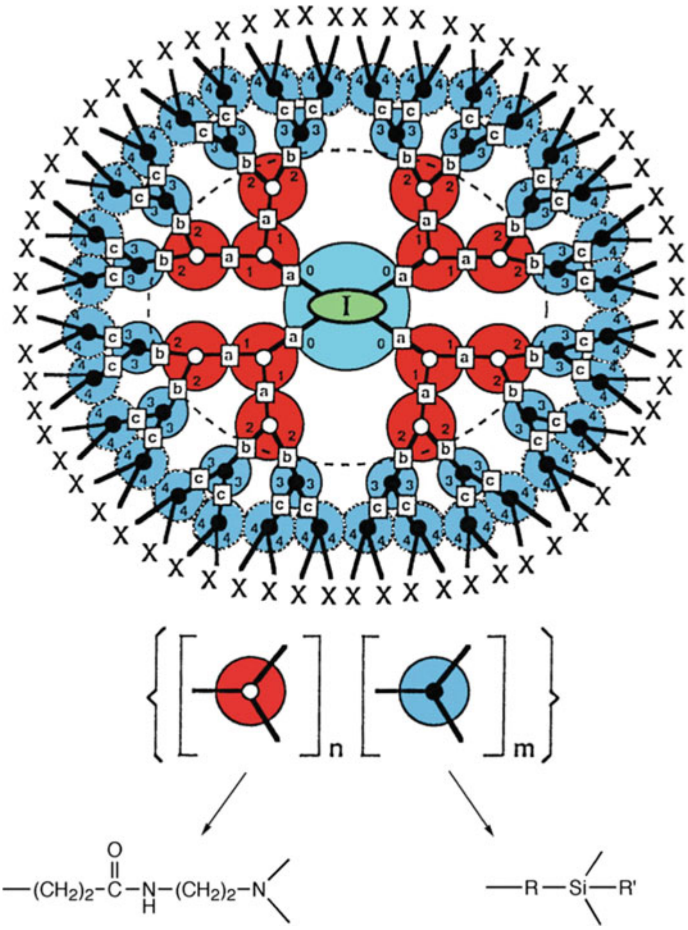
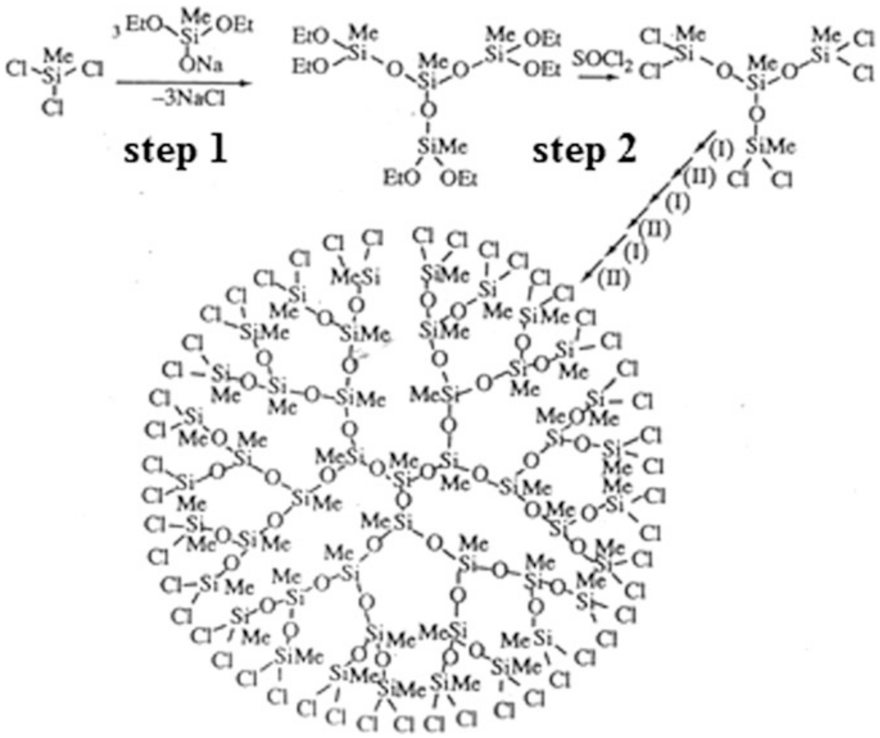


Fig. 2.30 A generalized representation of the structure of PAMAMOS dendrimer. Red: interiors cell s of PAMAM branches; blue: external cells of OS branches. I: Core atom or group of atoms; X: inert or reactive end groups; numbers 1, 2, 3, 4, … denote generation; letters: a, b and c represent PAMAM-PAMAM, PAMAM-OS and OS-OS chemical bonds, respectively

Janus dendrimers have characteristics of both components, thus they are fatty as a carbosilane dendrons and can be easily functionalized with a phosphorus-hydrazone dendrons.

It is noted chiral diphosphine-functionalized Janus dendrimers containing up to sixteen 2,2′-bis(diarylphosphino)-1,1′-binaphthyl (BINAP) units, readily synthesized via the liquid phase organic synthesis with G3 Frechet-type poly(aryl ether) dendron as the soluble substrate [491].



Scheme 2.23 Synthesis scheme of dendrimer based on polymethylsilsesquioxane

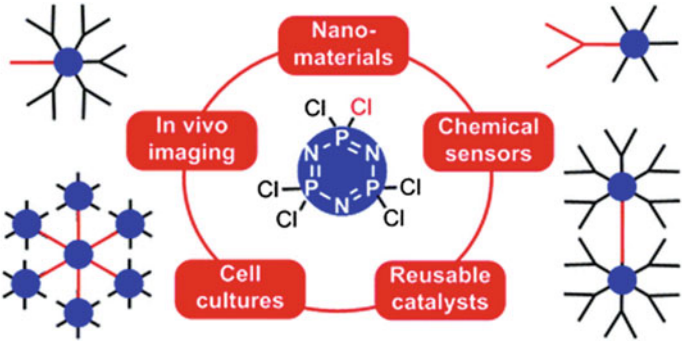
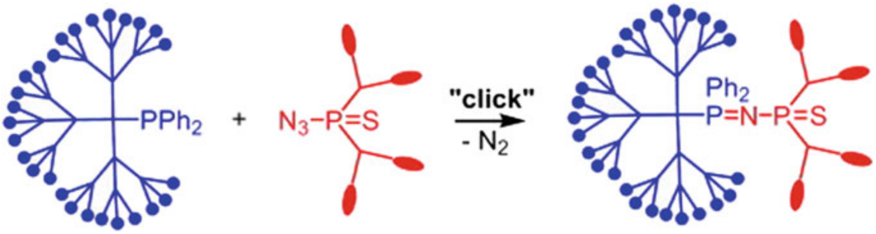


Fig. 2.31 The main directions of use of phosphorus-containing dendrimers based on hexachlorocyclotriphosphazene



Scheme 2.24 The scheme of synthesis of phosphorus-containing Janus dendrimers via click-synthesis

2.3.3 *Divergent and Convergent Synthesis*

Dendrimers are obtained by controlled multi-staged synthesis, in which the main are two strategies of synthesis according to divergent and convergent schemes. The already becoming classical scheme of dendrimer synthesis (Fig. 2.32) beginning from an initial branching center following by repeated reactions of a layer growth and removal of protection is called divergent [492]. A distinctive feature of this scheme is fast increase in a number of reaction centers on the surface of a dendritic molecule associated with increase in a generation number. This, in turn, brings to difficulties of purification of the final compounds from the products of incomplete substitution of surface functional groups, if such are present in the system. The purification problem is caused by very little difference between molecular weights of dendrimers with completely reacted surface groups and products of incomplete substitution.

This difference does not exceed several percent. To overcome this drawback, another approach was proposed called convergent method [477]. If in the case of

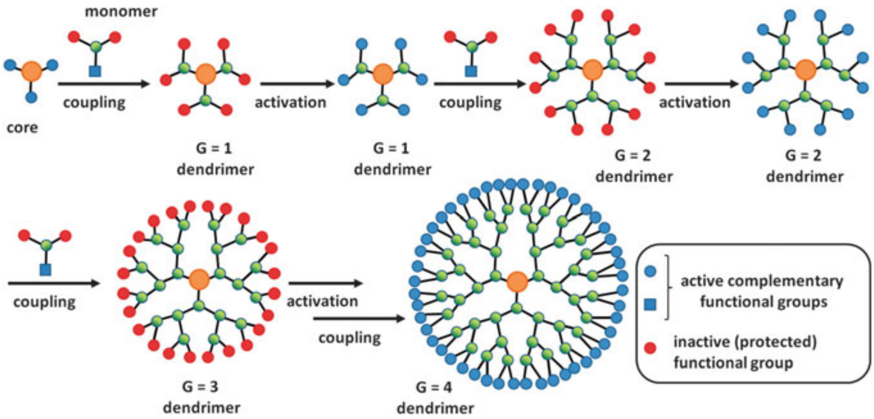


Fig. 2.32 Divergent growth method [492]

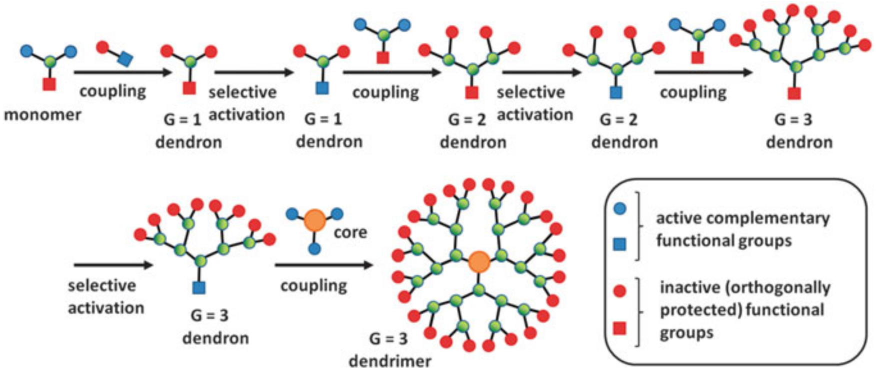


Fig. 2.33 Convergent growth method [492]

divergent synthesis, a dendritic molecule is growing from the center to periphery, in this case, on the contrary, a dendrimer is «collected» beginning from the surface groups. Taking to the notation system introduced before, the convergent growth of a monodendron can be represented by a scheme shown in Fig. 2.33.

An advantage of the convergent approach is a small number of reacting groups at each stage, which, in turn, brings to minimal number of intermediate compounds (products of incomplete substitution). Besides, a difference in molecular weight of initial, intermediate, and final products is so big (1.5–2 times) that it allows easily isolate a target compound in pure form. However, a significant drawback of this method is appearance of steric hindrances emerging at the stage of linking a monodendron to a branching center. There are such a small number of reactive groups (actually one for monodendron—a focal point), which plays a negative role. In the reaction system there is quite low concentration of reacting groups, whose activity is lowered even more due to a great number of «inert» (surface and other) groups, and reaction is impeded.

Most currently known chelating dendrimers are obtained by the two traditional methods and the number of these CPLs sufficiently large. Among the most interesting examples are variety dendrimers with tpy chelating moieties [10, 14]. A series of dendrimer polyallyl- and polyferrocenyl-containing chelating bpy ligands was obtained by the coupling reaction of 4,4′-bis(bromomethyl)-bpy with AB_3 and AB_9-dendrons [493]. Synthesis of G1 and G2 dendrimers with dibenzo-24-crown-8 groups serving as branching blocks is described [494]. A dendrimer with pseudocrown ether, which can chelate Ag(I) and Hg(II) ions, was obtained in the similar way [495].

It is doubtless that the dendrimers themselves are chelating ligands, since for them a considerable probability is typical of multiple-point metal ion coupling by monofunctional ligands due to their high density on the surface [496]. Metal chelates with dendrimers based on PEO and polypropylene oxide can be an example [472]. A consequence from this, in particular, is ability of crown ether groups to migrate over surface (Fig. 2.34), which was called «spacewalk» [497, 498].

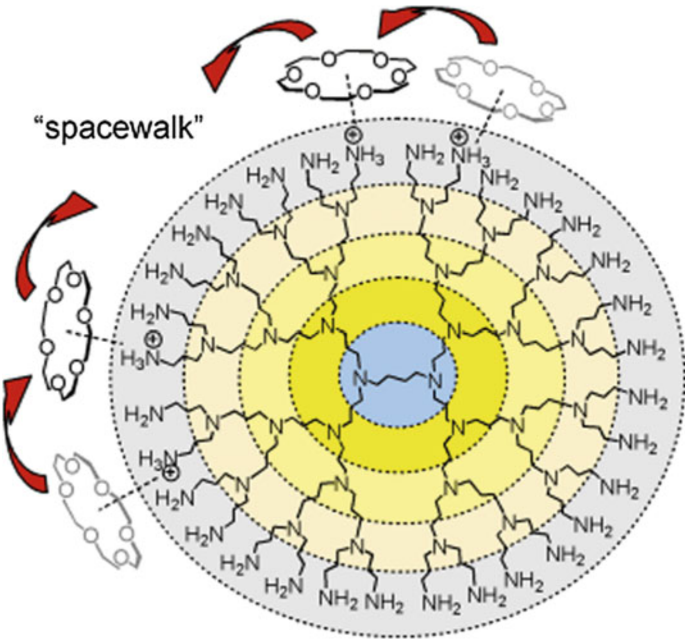


Fig. 2.34 Complex of crown ethers with G4 PAMAM dendrimer

It should be noted numerous examples of dendrimers with porphyrin and phthalocyanine fragments [499]. So, different Pp [500] including 5,10,15,20-tetrakis(4-hydroxyphenyl)-Pp and 5,10,15,20-tetrakis(3,5-dihydroxyphenyl)-Pp can be used as a core of dendrimer [501]. Pp-containing dendritic polymers up to G4 are obtained by Suzuki polycondensation of dendritic dibromide macromonomers and pinacolyl ethers of Pp-diboron acids [502]. Synthesis of the G2 poly(benzyl ether) dendrimers having N_3O Pp in a core (21-oxo-Pp core) is described [503]. Then phenyl-containing compounds (dendrons), from which branching of generations has already begun, can be linked to the Pp cores. At that superstable structure is obtained, which makes it possible to remove a Pp core from a micelle, as a result a cavity is formed, which is appropriate for catalytic and other reactions. Removal of Pp is executed by splitting of ether bonds, and the formed cavity is surrounded from inside by eight carboxyl groups. Something similar happens in depth of protein enzyme globules.

Possibilities of synthesis regarding architecture and chemical composition of produced polymers are broadened considerably at combination of the divergent and convergent schemes used. Taking into account the aforementioned advantages and disadvantages of both approaches, it should be noted that recently a tendency is observed of using a combined approach, which includes linking of monodendrons produced by the convergent method not to a pointed branching center, but to a dendrimer of G2–G3 synthesized beforehand by the divergent scheme.

2.3.4 *Alternative Methods of Synthesis*

For rapid studies of dendrimers, it is highly desirable to develop more efficient synthetic processes to avoid more elaborative and time-consuming stages of activation or protection of monomers in the reaction of condensation and purification using chromatographic separation. To these methods, which make it possible to reduce a number of synthetic stages and obtain a desired dendrimer with high yield, belong: a double-stage convergent growth approach, a hypermonomer approach, and double-exponential dendrimer growth, and orthogonal coupling strategies (Fig. 2.35) [504].

For example, in the double-exponential growth approach [505] first two functional groups of AB_2 monomer are disguised so that it would be possible to selectively take off protection. Then two growing monomers, one of which with protected functional group B, are obtained by removal of protection from the functional group A (divergent type of a monomer), and another one with protected functional group A is obtained by removal of protection from the functional group B (convergent type of a monomer) in individual reactions. The monomer of divergent type is condensed with the monomer of convergent type to produce protected dendritic molecules. Dendrimers of higher generations are synthesized by repetition of selective processes of de-protection and coupling. Therefore, DP depends on a number of generations increasing according to double exponential function from the initial generation (n), as $DP = 2^{2n} - 1$. Double exponential growth was used, in particular, to produce dendritic aliphatic G4 polyethers, beginning from 2,2-bis(hydroxymethyl)propionic acid in six stages with two purifications [506]. If macromolecules having the same generations were prepared by the ordinary divergent scheme, a number of purifications, corresponding to a

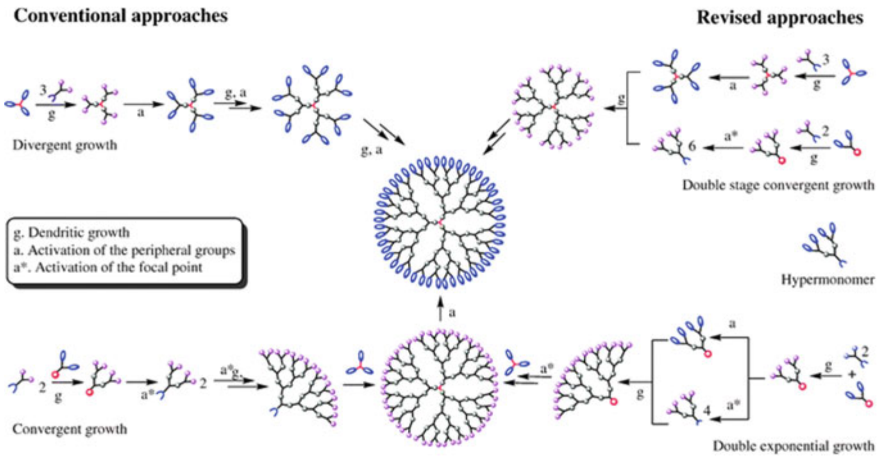


Fig. 2.35 Comparison of conventional and revised approaches

number of generations would be needed. Therefore, this method allows reducing a number of growth stages and simplification of purification of a final dendrimer.

The G6 dendrimer consisting of poly(phenylacetylene) linked with polyether was synthesized in three stages and two chromatographic separations based on orthogonal coupling strategy using Mitsunobu etherification or Sonogashira reaction [507]. Thus also coupling of efficient orthogonal ABC Passerini multicomponent reaction and ABB thiol-yne multicomponent reaction two kinds of dendrimers were synthesized efficiently: dendrimers with two generations in three steps and dendrimers with two generations containing one kind of internal functional group and two kinds of surface functional groups in five steps [508].

The hypercore or the branched monomer approach [509] specifies preliminary assembly of oligomer precursors, which can be linked with organic fragment. Linking of oligomer precursors goes in radial, branch-to-branch direction. A core interacts with two or more moles of a reagent containing, at least, two protected branching centers with the following removal of protective groups. The following release of reactive centers brings to the G1 dendrimers.

Contrary to these methods, the following two methods can exclude time-consuming processes of protection removal or activation. In the two monomer approach two different monomers are used, at that, one of the different functional groups of AB_2 monomer is prescribed for selective interaction with one of two different functional groups of CD_2 monomer, i.e. functional groups A and C react with reactive D and B centers, respectively. A typical example is synthesis of poly(ether-urethane) dendrimer from 3,5-diisocyanatobenzyl chloride and 3,5-dihydroxybenzyl alcohol [510]. Generations can grow in one reactor without intermediate purification stages.

One more approach, which helps to avoid the time-consuming purification process is using PS-PEG resin for synthesis of PAMAM dendrimers. It is a simple and efficient method for preparation of dendrimers up to the G3 [511].

One-pot synthesis of poly(amino carbonate) dendrimer from 2,6-dimethyl-4-heptanol and *tert*-butyl alcohol is performed using high-selective carbonyldiimidazole (CDI) reaction [512].

Introduction of energy using the microwave radiation is a widely used method in synthetic chemistry and is mainly in the organic chemistry [513–515]. Microwave synthesis is a highly effective technique for performing high-speed synthesis and is based on the interaction of electromagnetic waves with the mobile electrical charges, which may be polar solvent molecules or ions in solution. In a solution polar molecules try to align themselves in an electromagnetic and alternating field and so that the molecules are constantly changing their orientations. Thus, by applying the appropriate frequency, the collision between the molecules is achieved, which leads to an increase in the kinetic energy, i.e. system temperature. Therefore, high speeds of heating and uniform heating over the entire sample are possible. Synthesis of dendrimers using microwave radiation at low temperature reduces the reaction time, significantly reducing the occurrence of defects in the dendrimer backbone. For example, using microwave radiation PAMAM G1 dendrimers are synthesized by divergent method in high yields, high purity and in nearly perfect regioselectivity [516].

It is noted the use of microwave amidation method for the synthesis of PAMAM dendrimers with Jeffamine polymer core up to G4 [517]. This method reduces the aminolysis time and minimizes excessive use of reagents and solvents. Quick, easy and one-step microwave synthesis of water-soluble PAMAM dendrimers with the same polymer Jeffamine® T-403 core and the two monomeric, en and dien, cores were achieved with high (90–96%) yields in a short time (110–140 min, from 3.5 to 4 times faster than normal reactions) and under mild conditions using methanol as the solvent [518].

Microwave synthesis allows quick access to the lower generations (one to three) triazine dendrimers with high yields [519]. Using microwave convergent synthetic approach, two reactions of nucleophilic aromatic substitution are performed on cyanuric chloride within 10 min at 60 °C using primary amines (Fig. 2.36). It is important that the substitution with the diamine obtained monochlorotriazine requires 95 °C for 30 min and the purification are performed by an automated chromatography system so G3 dendrimer can be prepared from starting materials in less than one day.

Similarly, starting from commercially available and inexpensive materials, accelerated synthesis of triazine dendrimers of odd generations up to G9 with high yields was performed using microwave radiation (Fig. 2.37) [520].

Unique SAMs, consisting of dendritic viologen-shaped molecules with ω-mercaptodecyl groups (G = 0–3) at the top of the dendritic structure, which can encapsulate a certain amount of metal anionic complexes, determined by dendritic structure, are noteworthy [521]. Such lower generation dendritic molecule is successfully synthesized by microwave heating, thereby providing easy access to the G3 dendrimers without requiring processes of protection/deprotection during generations growth. SAM of dendritic molecules themselves is made by soaking of gold substrates in solutions of molecules in a mixture of ethanol/acetonitrile at room temperature (Fig. 2.38).

A «dumb-bell» shaped molecule can be produced using a reaction of two dendrimers with a cross-linking agent, for example, hexanediol chloride [522]. The

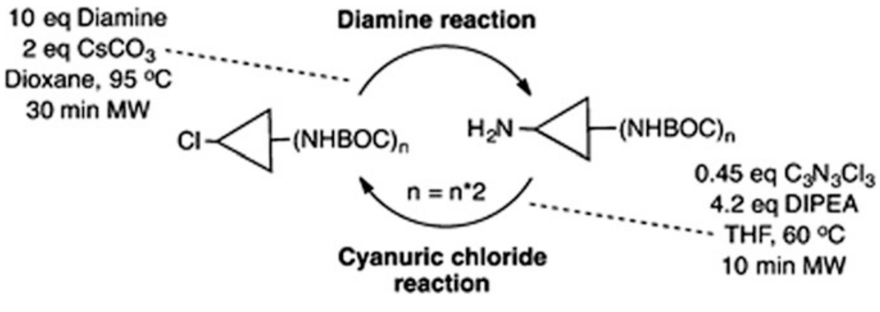


Fig. 2.36 Scheme of microwave synthesis of triazine dendrimers

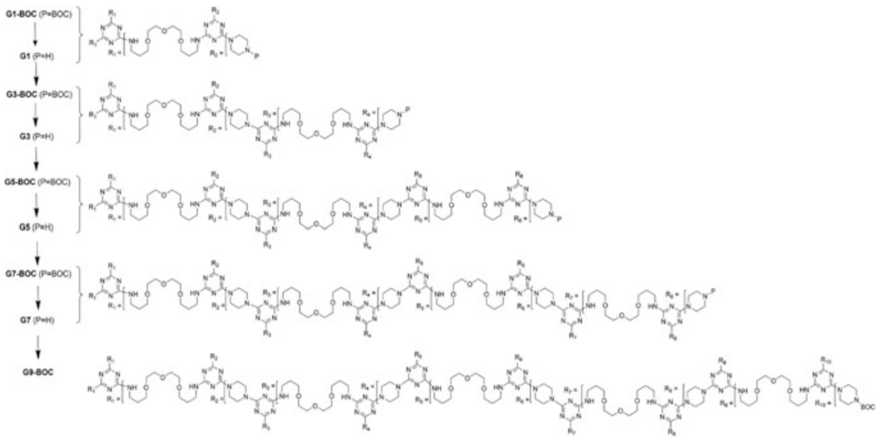


Fig. 2.37 Dendrimers with triazine core

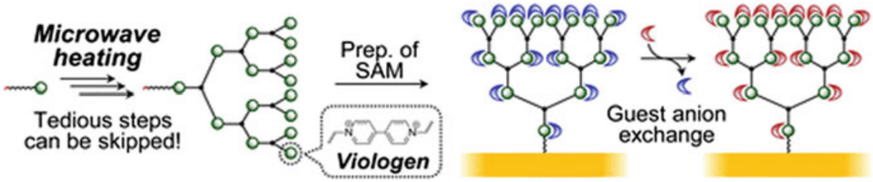


Fig. 2.38 Preparation of dendrimers SAMs using a microwave synthesis

promising way is using 3D polycondensation method for dendrimer synthesis [63, 64, 523]. A solid phase synthesis of inverse PAMAM was developed, and when AB_2 type monomers were used, only one reaction was required for synthesis of each PAMAM generation [524].

2.3.5 Using the Click Chemistry in the Synthesis of Dendrimers

Recently design of dendritic macromolecules has reached a noticeable success, mainly due to extremely advantageous and elegant developed synthetic routes based on click chemistry [445, 525–527]. In particular, very efficient are click chemistry methods used in synthesis of dendrimers via Diels-Alder [528], thiol-yne [529], and azide-alkyne reactions [530–532]. Synthesis of some dendrimer that employs CuAAC and furan-maleimide Diels-Alder click chemistry in layer-by-layer (LbL) fashion can serve as an example shown in Fig. 2.39 [533]. Apparent

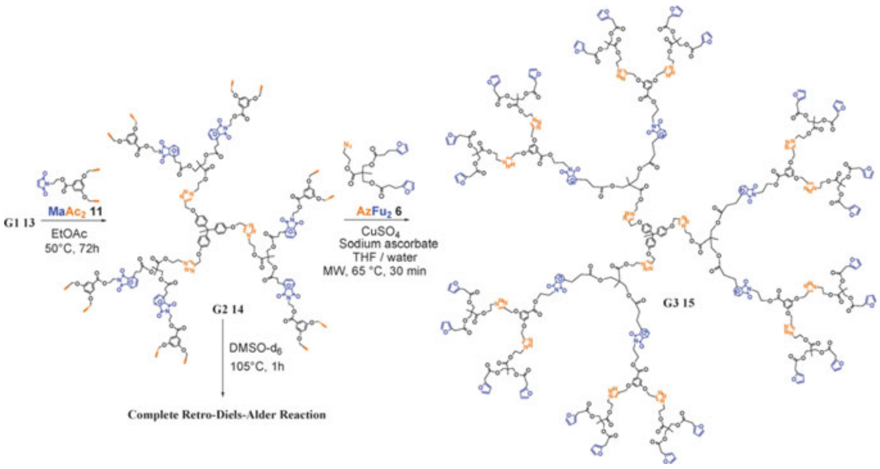


Fig. 2.39 Synthesis of G2 and G3 dendrimers and retro-Diels-Alder reaction

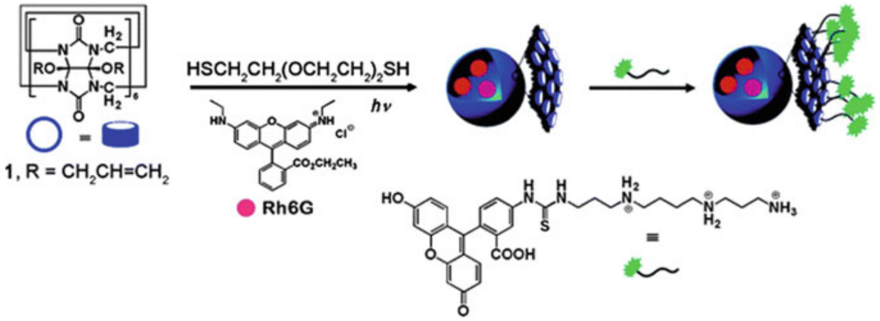


Fig. 2.40 Click-synthesis of *N*,*S*-chelating dendrimers

advantage is potentially «green» character of this methodology of design of macromolecular assembles.

The combination of controlled polymerization methods and click reactions creates an effective platform for the production of polymers with different architectures (Fig. 2.40) [534].

Usually performed CuAAC reaction in the synthesis of dendrimers requires stoichiometric use of the most common click-catalyst $CuSO_4 \cdot 5H_2O$ with sodium ascorbate. An effective, practical and easily accessible catalytic Cu(I) complex with hexabenzyl-tris(2-aminoethyl) amine was proposed to carry out this reaction under milder conditions for the synthesis of relatively large dendrimers. This catalyst can be used to form intradendritic [1,2,3]-triazole heterocycles coordinated with the transition metal ions through their nitrogen atoms (Fig. 2.41) [535].

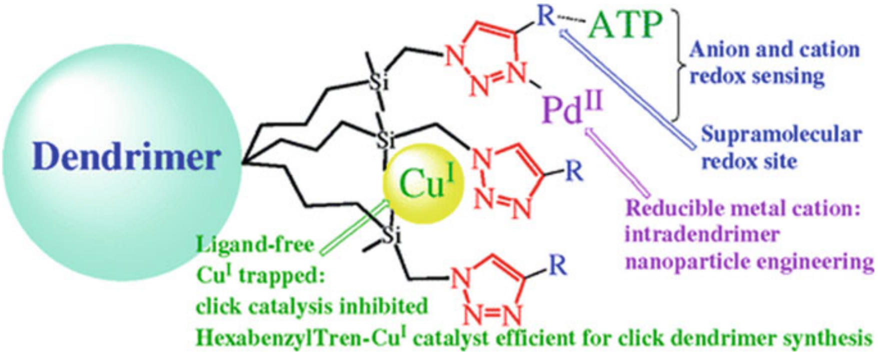


Fig. 2.41 Click-synthesis of dendrimer with [1,2,3]-triazole heterocycles

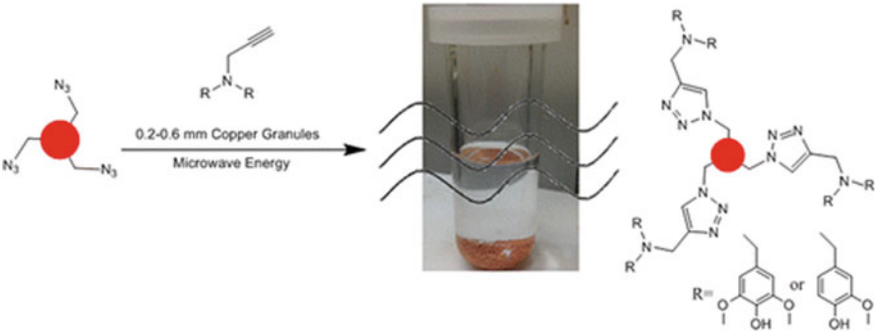


Fig. 2.42 Microwave click-synthesis of polyphenol dendrimers

It is noted the use of copper granules in held by microwave alkyne-azide 1,3-dipolar cycloaddition click-synthesis of antioxidant dendrimers based on lilac aldehyde and vanillin (Fig. 2.42) [536]. Importantly that the copper granules ineffective at both room temperature and at reflux (<5% yield). However, they have shown to be highly effective when synthesis of chelating dendrimer is performed under microwave radiation, giving yields up to 94% for 8 h. Equally important is the fact that the dendrimers obtained by using this method, practically showed no contamination by copper (9 ppm), which was the same as the background level.

2.3.6 The Post-synthetic Modification of Dendrimers

Numerous studies were performed for purposeful synthesis of chelating fragments in a core, inside, and on surface of dendrimers using post-synthetic modification (PSM) (Fig. 2.43) [537].

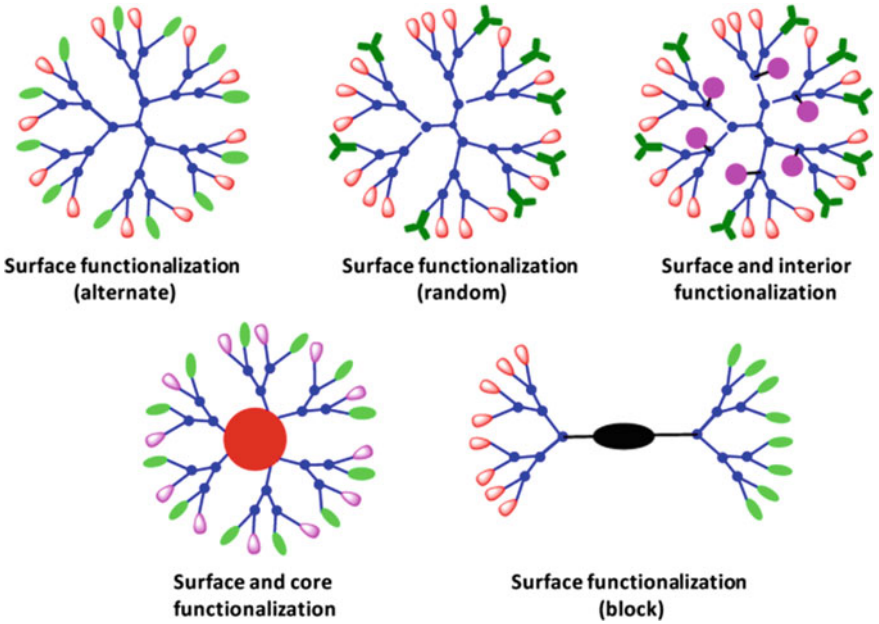


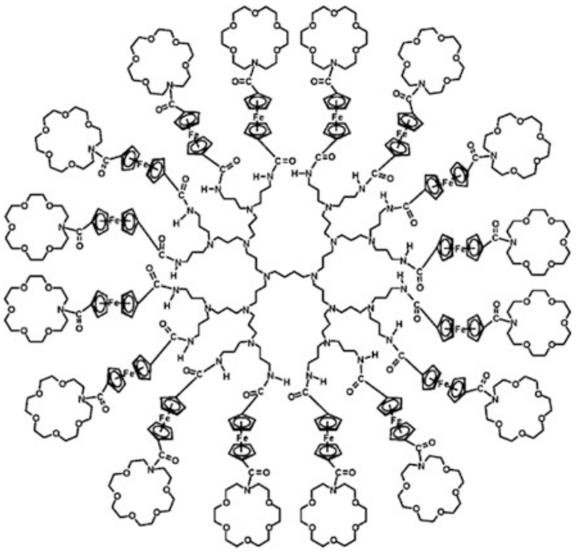
Fig. 2.43 Surface-, interior- and core-functionalized heterofunctional/multifunctional dendrimers

Selective modification of the dendrimer surface by different functional groups is very difficult [538]. However, derivatives of PAMAM dendrimers with acetamide, hydroxyl, and carboxyl terminal groups were successfully synthesized from the G4 PAMAM dendrimers with en core and five primary terminal amino groups [539]. The reaction of acetylation of G5 PAMAM dendrimers, containing reactive amino groups was carried out [540]. Terminal amino groups of G1 PAMAM dendrimer were used as initial material for synthesis of glycidol and acetamide-end-capped dendrimers [541]. Carboxylate-functionalized G5 PPI dendrimers were obtained by double Michael coupling of amine-functionalized PPI dendrimer to methacrylate with the following basic hydrolysis [542]. Modification of PAMAM dendrimers surface by benzoyl thiocarbamide was used to obtain ion-exchanged material having high selectivity to heavy metal ions [543]. Peripheral functionalization of G2 PAMAM dendrimers containing terminal amino groups was performed using 9-anthracenecarboxaldehyde [544]. G1 PPI dendrimer was modified by reaction of terminal amino groups with 2-pyridinecarboxaldehyde [545]. Dendritic chelating oxybatho-phen ligands (up to G3) were obtained by treatment of the respective Fréchet-type dendrons carrying benzyl-bromide groups in the focal point by 4,7-bis(4′-hydroxyphenyl)-phen, where phen is 1,10-phenanthroline [546].

Chemoselective substitution of surface groups in the range of phosphorus-containing dendrimers occurs successful [547, 548]. Reaction of dendrimers carrying $P(X)Cl_2$ (X=O, S) groups on periphery with allylamine and then with a sodium salt of *p*-hydroxybenzaldehyde brings to the aldehyde terminal groups, which can be subjected to further modification, for example by Schiff and Wittig reaction. Thus, terminal functional groups $P(X)Cl_2$ are monosubstituted and then disubstituted not only by amines and aldehydes, but by phosphorus ylids, hydrazine, and chiral compounds. Inner layer of a dendrimer containing eighteen P-N(S) blocks can also be post-modified by allyl and propargyl triates, giving chemoselectively allylated and propargylated dendrimers pointing that accumulation of a certain number of functional groups is possible in well-defined globular macromolecule. These dendrimers with rich surface and internal functionalities can have applicability potential in different fields, especially, in catalysis.

Interaction between phenol, formaldehyde, and G0 and G1 PAMAM dendrimers brings to fabrication of two dendrimers containing benzoxazine side groups [549]. Interesting ion-chelating dendrimers are obtained on the basis of a benzene tricarbonyl core linked to three tripodal branching units, each of which contains a carboxyl, catechol, and 3-hydroxy-6-methyl-pyran-4-one fragments [550]. Surface groups of PAMAM and PPI dendrimers were modified by salicylate-, catecholate-, and hydroxypyridinonate-fragments [551]. A chelating ligand based on xanthate-functionalized PAMAM dendrimer was obtained from polyamidoamine dendrimer with terminal hydroxyl groups [552]. It is also noted surface modification of phosphorus-containing dendrimers for the preparation of (+)-cinchonine fragments [553].

A new family of poly(propylenamine) ferrocenyl dendrimers with azacrown ethers based on DAB was produced by the reaction of functionalized ferrocenyl derivative $\{[\eta^5\text{-}C_5H_4COCl]Fe[\eta^5\text{-}C_5H_4CONCH_2CH_2(OCH_2CH_2)_5]\}$ through amido-ferrocenyl blocks [554].



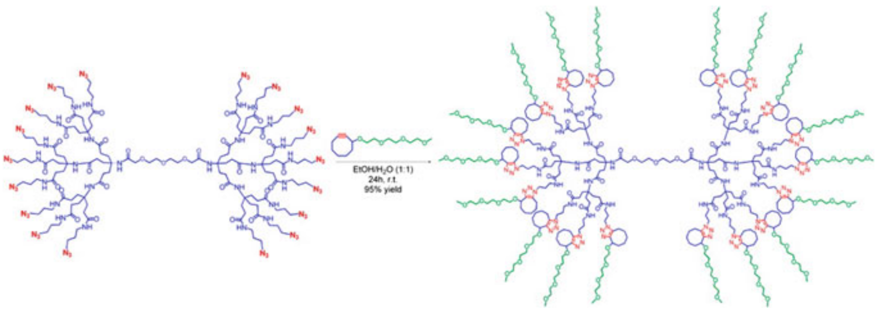


Fig. 2.44 Scheme of functionalization of PAMAM dendron by PEG chains

A copper-free strategy of strain-promoted azide-alkyne cycloaddition, which provides a quantitative functionalization under mild reaction conditions without any metal impurities, is developed for functionalization of poly(amido)-based dendron with PEG chains (Fig. 2.44) [555].

Effective precursors for PSM towards creating chelating fragments were mono-functionalized dendrimers based on polyamide with terminal azide or alkyne moieties derived using microwave 1,3-dipolar cycloaddition [556]. Microwave Huisgen 1,3-dipolar cycloaddition between azide-peptides and dendritic alkynes was used to produce multivalent dendrimeric peptides with yields ranging from 46 to 96% [557].

Strategy of in situ PSM was successfully applied for synthesis of AB$_2$C bifunctional dendrimers with inner acetylene/azide and outer hydroxyl groups [558]. These dendrimers can be easily transformed into dendritic nanoparticles or used as cross-linking agents for preparation of hydrogels.

Highly active surface of dendrimers serves as a basis for their self-assembly to supramolecular structures [559].

An example of modification of dendrimers in a core can be incorporation of resorcinarene [560], anthracene [561], and fluorene [562] cores in PAMAM dendrimer. We shall consider synthesis of two types of dendritic β-diketonate ligands, which contain dbm core and poly(aryl ether) dendron, and range of dendritic 2-(2-pyridyl) benzimidazole ligands [563]. Asymmetrically placed dendrimers with Cz and phenyl azomethine cores were obtained through Ullmann and dehydration reactions in presence of titanium tetrachloride [444]. Derivatives of tetrapyrazinoporphyrazine-containing flexible linear and rigid dendritic groups were synthesized [564].

Crown ethers and tpy ligands were successfully linked to the focal point of light-harvesting phenyl-acetylene monodendrons through Pd-catalyzed coupling reaction [565]. It is also noted dendritic chiral phosphorus ligands, including diphosphines monodentate phosphoramidites and N,P-ligands synthesized by fixing the respective chiral phosphorous units in the core or the focal point of Frechet-type dendrons [566].

It is important to emphasize that the purposeful creation of multi-functional dendrimers, with well-defined structures is necessary not only from the point of view of further chelation of metals, but also for the application of dendrimers in nanomedicine, light-harvesting systems, sensing and catalysis [567]. Furthermore, because of their unique steric structures and rich peripheral functional groups dendrimers are promising for various bioinspiring functions, including artificial proteins, viruses, enzymes, cell structure and light-harvesting antennas [568].

2.3.7 Fixing Dendrimers on Solid Surfaces

Dendrimers occurred to be convenient objects for fixation on different surfaces [569]. The special names dendritic-surface hybrid or dendronized surface were even introduced for such systems. Thus, PAMAM dendrimers with terminal amine groups are fixed on surfaces of carbon nanotubes [570], and PAMAM dendrimers modified by 1,8-naphtalamides are fixed on polyamide-6 used as a matrix for producing fluorescent materials [571, 572]. A detailed study of nanostructured G1–G3 dendrimer, supported on Merrifield resin with hydroxyl-, mesylate- and bromine-end groups showed [573] that particle diameter growth is associated with the end groups of samples and increases nonlinear with the dendrimer, wherein the dendrimer particles after G2 became denser.

Microwave technology is used for grafting PAMAM dendrimers on silica surface [574]. It was found that the amount of amino groups and nitrogen content increase with increasing generation PAMAM. Such dendronized surface links bovine serum albumin through glutaraldehyde, at that the immobilization efficiency increased with the increase in the generation of PAMAM.

Similarly, PAMAM G1–G7 dendrimers are constructed on the surface of ethylenediaminepropyl-functionalized magnesium phyllosilicate lamellas using a modified microwave synthesis [575]. The resulting solid materials showed an increase in their interlamellar space and disorganization of their lamellae packing with dendron growth.

In recent years, numerous studies are conducted with such interesting carrier as graphene oxide. Fixation of PAMAM dendrimers on graphene oxide surface using «grafting to» method can be cited as an example [576]. Obtained dendronized materials proved effective in the adsorption of a number of heavy metals.

2.3.8 Properties of Chelating Dendrimers

The study of the physico-chemical properties and architecture of dendrimers is one of the most promising approaches to solving the problem of designing and directed synthesis of MCD with predetermined properties. However, the dendrimer ligand, unlike low molecular weight analogues is characterized by a number of features that make it difficult study of its physico-chemical characteristics. Oppositely to almost all other macromolecules, including even hyperbranched and star-like polymers, dendrimers do not obey the Mark-Coon-Houwink equation after reaching a certain molecular weight [577–580]. For example, in the case of polyether dendrimers after reaching of molecular weight about 5000, its further increase brings to a decrease in intrinsic viscosity. This phenomenon can be understood taking into account that as a generation number increases, volume of a dendritic macromolecule increases in cubic proportion of a linear size, while its weight increases as an exponent, which does not work for any other polymer. Unusual relations between intrinsic viscosity and molecular weight for the dendrimers correlate with a change in their shape from loose to globular structure with increase in molecular weight.

Dendrimers, like most linear polymers, are (depending on composition and molecular weight) viscous liquids, amorphous powders, or glassy resins, well soluble in most known organic solvents. Viscosity of their solutions is by several orders of magnitude lower than that of linear polymers with similar molecular weight. Unlikely to chain polymers, these ones do not have a crystal state; however, liquid crystal ordering is possible in polymer solutions and melts, containing mesogen groups.

Dendrimers of low generations (0, 1, and 2) have more asymmetric shape and have more open structure as compared with dendrimers of higher generations. As long as chains growing from a core become longer and more branched (in the G4 and higher dendrimer generations), a dendrimer molecule gains a globular shape. When critical branched state is reached, dendrimers cannot grow due to lack of space. This is called «star burst» effect [581]. For PAMAM dendrimer it is observed after G10, which contains 6141 monomer units and has diameter about 124 Å, at that the reaction rate decreases dramatically and no further reactions of terminal groups take place.

Numerous studies of the spectroscopic properties, melt rheology, solution properties of bio- or synthetic dendritic polymers have shown a special behavior of dendritic structures in bulk and in solution [582–586].

Presently there are more than fifty families of dendrimers, each of which have unique properties, surface, branching groups and cores, which can be adapted for different applications. Thus, dendrimers containing photoactive units can be used for probing of metal ions. For example, for these purposes G5 PPI dendrimers are applied, which are functionalized at periphery with strongly luminescent dansyl (1-dimethyl amino-1-naphthalene-5-sulfonyl) units [587].

High local orientation mobility of a dendrimer segments is typical of dendrimers [588]. Therefore, various reactions on a dendrimer surface or «guest-host» assemblies give a way to stoichiometric nanocompounds, such as dendrimer-dendrimer, dendrimer-protein, dendrimer-fullerene, metallodendrimer, etc. These examples convincingly confirm appearance of active dendritic modules based on the platform of synthetic nanochemistry [589].

One of the interesting features of dendrimers is formation of fractal structures, existence of a solid state with extremely low density [590]. Interest shown to chemical compounds with fractal structure is stipulated by, at least, two reasons.

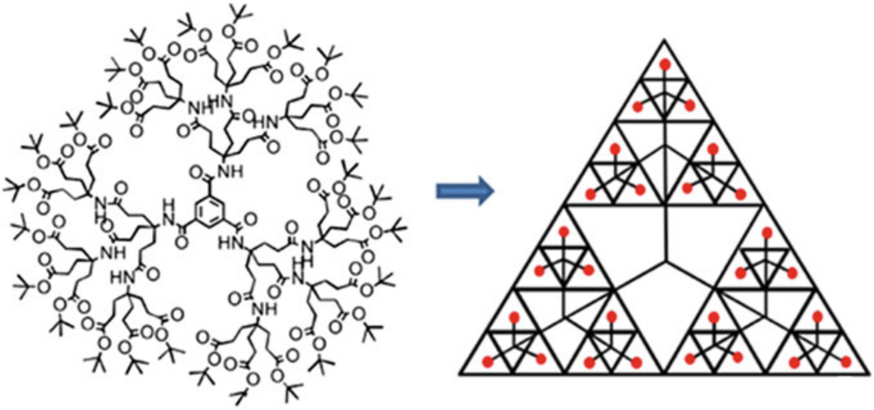


Fig. 2.45 Conceptual progression from branched dendrimer architecture to interrelated, non-tree-like fractal motifs

Firstly, these systems are rather wide spread in nature. Secondly, they are basic structural forming element for a range of macroscopic systems appeared as a result of physico-chemical processes and phenomena similar to fractal structures development. A fractal polymer with all features of Sierpinski triangle can be presented geometrically considering transformation proceeding from a 3-oriented 2D dendrimer to the triangular (1 → 3) branched motif, which can be superimposed on the pattern of Sierpinski triangle predicted as early as in 1916. Dendritic branches divide in two the triangle sides, and these intersection points make a basis for development of Sierpinski triangle (Fig. 2.45) [591].

Dendrimers have specific properties, such as low density, highly developed structure of inner caverns, high specific surface, high sedimentation stability of disperse particles, etc., which characterize them as promising carriers of different substances, including drugs [592–596], and nanoreactors for production of nanometer metal particles [597]. Our interest to these structures is sustained by their high chelating capacity to a wide range of metals.

2.4 Chelating Hyperbranched Polymers

During two last decades a special attention has being attracted to such interesting CPLs as hyperbranched polymers, nanostructured polymers with complicated architecture of macromolecules [20, 53, 63, 64, 598–611]. Nano-dimensionality and polyfunctionality of hyperbranched polymers stipulates apparent attractiveness of these reagents as regards oriented synthesis of polymers with predetermined chelating properties. Possibilities of functioning coordinationally active structured ligands as nanocontainers encapsulating target compounds, or nanoplatforms retaining «host» molecules or functional groups on the surface, will make it possible to obtain and characterize new hetero- and polynuclear metal chelates. The attention to hyperbranched polymers is attracted due to their unique chemical and physical properties, and a possibility of their application in coatings, additions, drug delivery, macromolecular building blocks, nanotechnologies, and supramolecular systems.

Presence of technologically significant methods of hyperbranched polymer synthesis of several types (in particular, aliphatic polyether Boltorn® [52], poly (amidoester) Hybrane® [612] and PEI Lupasol® [613, 614], as well as a number of hyperbranched polyesters [615] and polyurethanes [616–618]) gives a possibility of implementation of their industrial production within the limits sufficient for further application in very different areas.

As well as dendrimers, hyperbranched polymers relate to group of polymers with densely branched structure and a great number of reactive groups (Fig. 2.46). They are alike also because they are obtained by polymerization of monomers with mixed functionalities, usually designated as A_2B or A_3B monomers, thus providing exponential growth of branched structures in two directions and with the same molecular weights. However, there are principal differences between them. Dendrimers are hyperbranched monodisperse polymers, while ordinary hyperbranched polymers are polydisperse. Moreover, absolutely different fundamental synthetic approaches are typical of them: whereas absolute control over all stages of chemical synthesis of dendrimers is required, a simplified approach is needed for production of hyperbranched polymers, similarly to ordinary synthetic polymers technology. Hyperbranched polymers obtained by controlled method in two or three stages, can work as well as dendrimers synthesized in 10 or 12 stages. Dendrimers are polymers with orderly branched structure, while hyperbranched polymers have randomly branched structure.

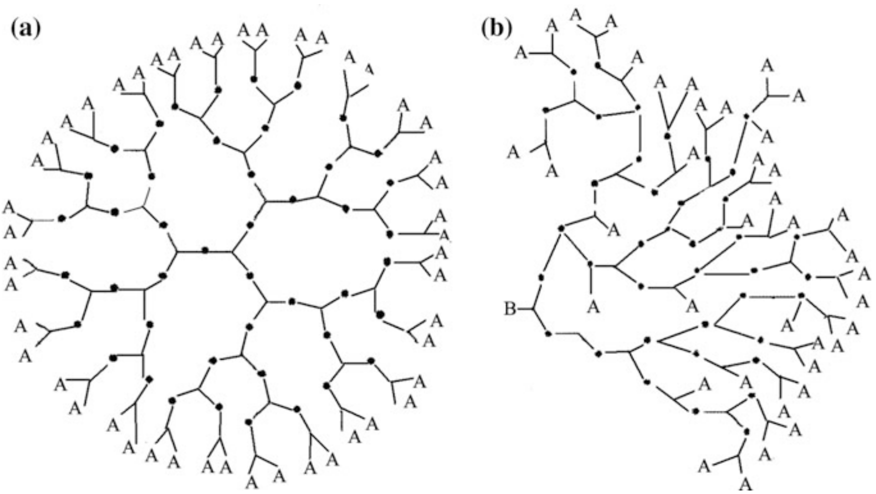
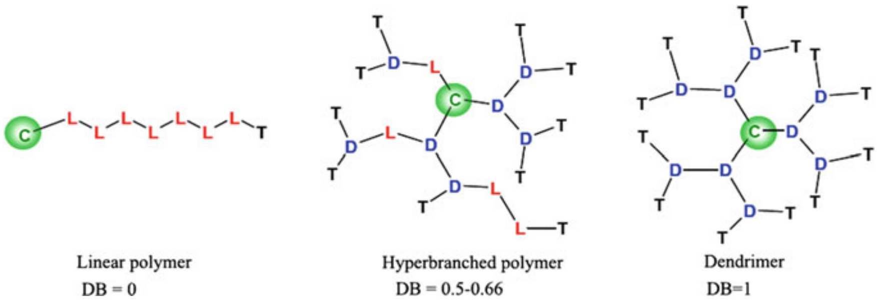


Fig. 2.46 **a** Dendrimer, **b** hyperbranched polymer with B core (functional groups A are on periphery)



Linear polymer DB = 0

Hyperbranched polymer DB = 0.5-0.66

Dendrimer DB=1

Fig. 2.47 Comparison of polymer architectures as a function of degree of branching

There are three main parameters for description of hyperbranched polymers: molecular weight, PDI and a degree of branching (DB). The later can be calculated using the following equation [619]: DB = 2D ÷ (2D + L), where D is a number of dendritic units, L is a number of linear units. This parameter is used for topologic characteristic of hyperbranched polymers and can serve to determine a difference between linear polymers, dendrimers, and hyperbranched polymers (Fig. 2.47).

Dendrimers have no linear units, and in this case a degree of branching is 1. On the other hand, linear polymers have no dendritic units; therefore, DB has zero value. Respectively, hyperbranched polymers should have intermediate value of DB between 0 and 1. Control over branching degree is very complicated and usually non-regular, polydisperse macromolecules with DB = 0.4–0.7 are obtained. This brings to formation of a great number of geometrical isomers, whose number increases with increase in molecular weight and a number of reaction centers of monomers. DB has an extreme value 0.66 at slow addition of monomers and high degree of conversion.

2.4.1 *Star Polymers*

The simplest branched macromolecules are called star polymers, in which several linear polymer chains are fixed only on one fixation point (core) [620]. Based on chemical composition of the arms, star polymers can be divided into two categories: homoarm (or ordinary) star polymers and miktoarm (or heteroarm) star copolymers

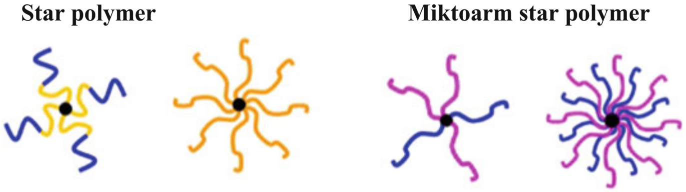


Fig. 2.48 Star and miktoarm polymers

(Fig. 2.48). Homoarm star polymers consist of symmetric structure containing divergent stars with the same chemical composition and similar molecular weight. In contrast, miktoarm star molecule comprises two or more arms with different chemical compositions and/or molecular weight and/or different periphery functionality [621, 622].

To obtain star polymers, methods of controlled polymerization are actively used, which can be separated into three common synthetic approaches: (a) «core-first» approach («from-approach»), in which a polyfunctional initiator is simultaneously used for initiating polymerization of vinyl monomers, thus forming polymer stars (Fig. 2.49a); (b) «arm-first» approach includes reaction of a living macroinitiator (or) macromonomer, an arm, with bifunctional vinyl cross-linker, with formation of

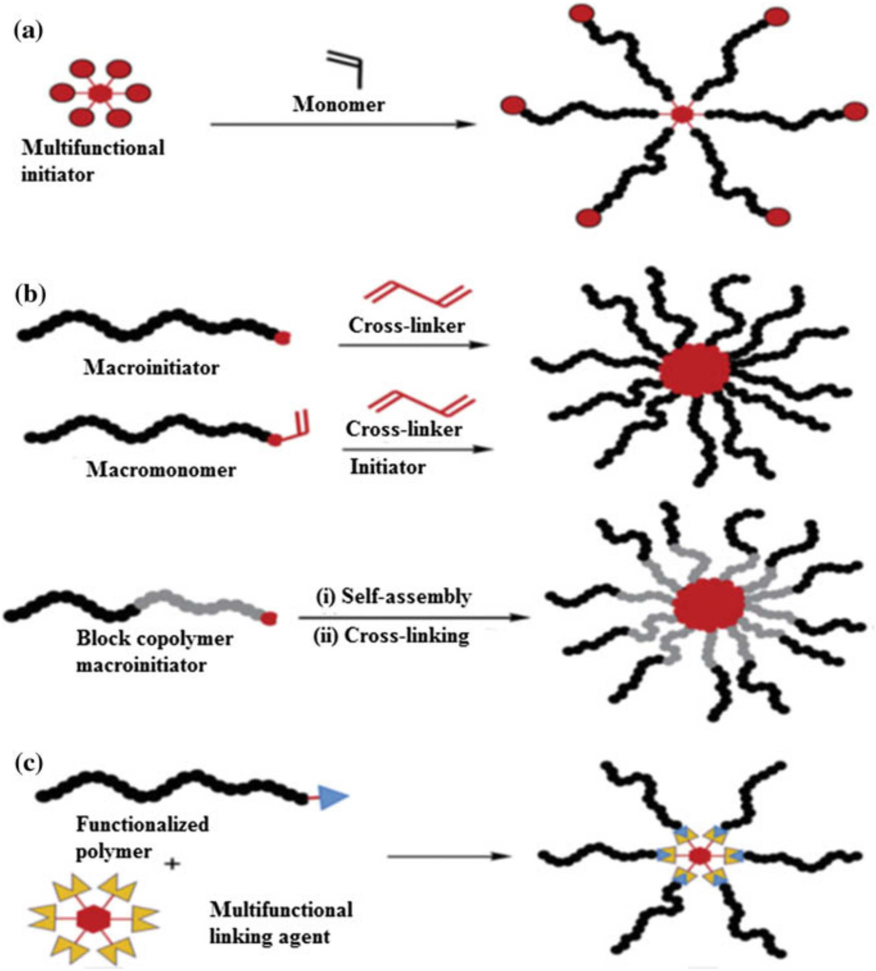
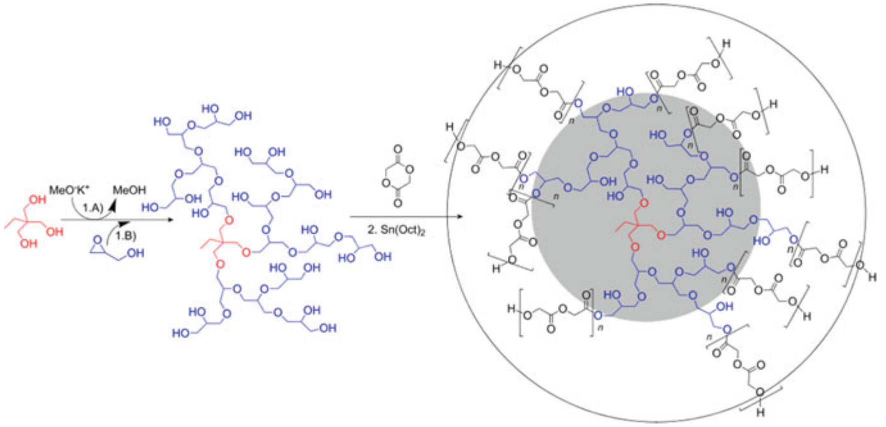


Fig. 2.49 Synthetic approaches to preparation of star polymers via controlled polymerization: **a** the core-first approach, **b** the arm-first approach, **c** grafting to approach



Scheme 2.25 Synthetic route to hyperbranched multi-arm star copolymers by two-stage method

a densely cross-linked core, from which arms are spread (Fig. 2.49b); (c) «grafting-to» approach can be considered as a combination of controlled polymerization and addition reactions, in which a preliminary formed polymer, arm, is prepared through controlled polymerization and introduced into the coupling reaction with polyfunctional cross-linking agent, which works as a core (Fig. 2.49c) [623].

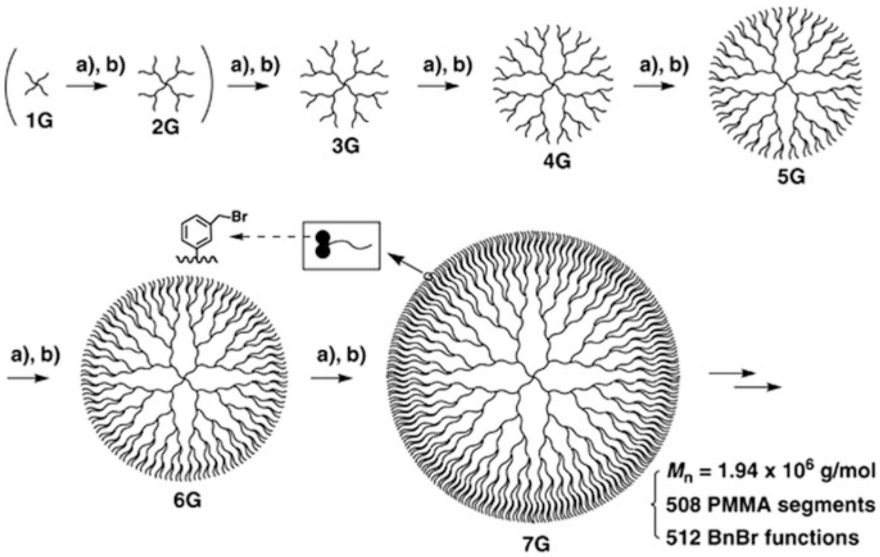
We shall consider as an example a simple two-stage synthesis of multi-arm star poly(glycerols) with several poly(glycolide) arms (Scheme 2.25). At the first stage glycidol is polymerized in anion-type using trimethylolpropane as a tri-functioning initiator, and at the second stage polyethers-polyols are used as macroinitiators for the open-chain polymerization of a glycolide using Sn(Oct)$_2$ as a catalyst [624].

The combination of star-shaped dendrimers and linear chains reveals much more variation of polymer architectures and new molecular properties. Examples are hyperstar that can be obtained by different approaches, but usually «core-first», «grafting-from» or «grafting-onto» approaches used linear polymers for grafting to the dendrimer core [625–627]. For example, the synthesis of a number of dendrimer-like star-branched poly(methyl methacrylate) (PMMA) from G1 to G7 by stepwise iterative methodology based on the «arm-first» divergent approach (Scheme 2.26) [628].

Besides being able to use as chelating ligands, hyperstars actively studied in anion-cured epoxy thermosets [629], and in biomedical areas as the core-multishell nanocarriers [630, 631].

2.4.2 *Methods of Synthesis of Hyperbranched Polymers*

The developed by now methods of synthesis of hyperbranched polymers are divided into three categories [63, 64, 459, 632–635]:



Scheme 2.26 Synthesis of dendrimer-like star-branched polymer by stepwise iterative methodology based on the «arm-first» divergent approach (BnBr—benzyl bromide)

- polymerization by the mechanism of stepwise poly-addition of polycondensation type;
- radical polymerization by the chain poly-addition mechanism;
- other methods (for example, radical polymerization under conditions of living chains, which is a special case of poly-addition, etc.).

The first method is a classical approach to synthesis of hyperbranched polymers, in which AB_x and $AB_x + B_y$ monomers with equal reactivity of B functional groups are used (Fig. 2.50). The reaction includes typical characteristics of a staged reaction of polyfunctional monomers and oligomers formed without linking. In this case growth of a polymer begins from the already existing A and B reaction centers, in other words, new centers do not form during polymerization. As a result of reaction, strongly branched macromolecules are formed, which contain dendritic units (completely reacted B groups), terminal units (non-reacted B groups), linear units (one reacted B group), and one focal point (A group).

Among synthetic approaches bringing to very wide structural variety of hyperbranched products, use of AB_2 monomers is the predominant. This method is used, in particular, for production of Boltorn® industrial polyethers based on commercially available AB_2 monomer 2,2-dimethylol-propionic acid (A = COOH; B = OH) by etherification reaction. In this case terminal hydroxyl groups form a shell of a hyperbranched polymer.

Hyperbranched polymers are synthesized from AB_2 monomer containing bis(*m*-phenylene)-32-crown-10 and two groups set on its opposite ends, linked with a benzene ring. The monomer is easily self-assembled and polymerized in solution,

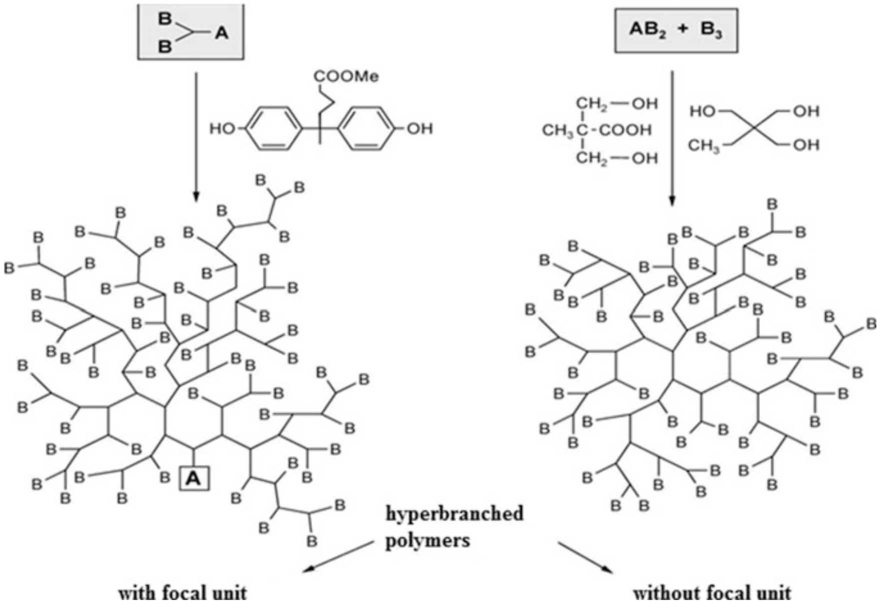


Fig. 2.50 General strategy of synthesis of hyperbranched polymers through AB_x and $AB_x + B_y$ approach ($x \geq 2$; here is 2; $y \geq 3$; here is 3)

at that, to obtain a polymer with high DP, high concentration of a monomer (150 g L^{-1}) is required [636].

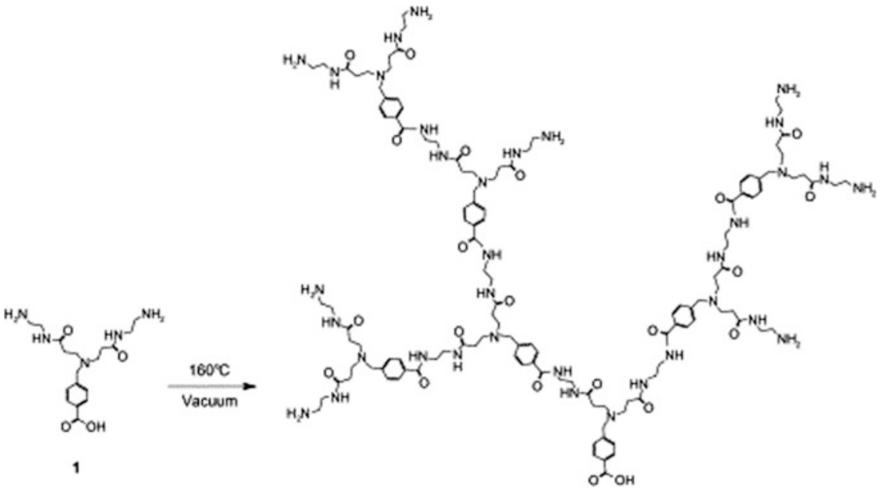
Aromatic AB_2 bis-amino acid monomer **1** was used for production of hyperbranched PAMAM polymers as «dendrimer equivalents» [637]. The analysis showed that purified hyperbranched polymers have $M_n = 2000$ and PDI = 3.2 (Scheme 2.27).

The fraction deposition method with use of another AB_2 monomer, 3,5-bis-(4-aminophenoxy) benzoic acid, permits to prepare hyperbranched polymers with the end NH_2-groups [638]. For them, DB value increased as molecular weight of the formed polymers decreased.

It is noted hyperbranched polymer containing chelating β-ketoester fragments which is synthesized from 2-acetoacetoxyethyl acrylate by the Michael coupling reaction in presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as a catalyst. DB in poly(β-ketoesters) was very high, about 82.9%, and M_n was between 2100 and 12,000 and it increased as temperature of the reaction and a degree of conversion increased [639].

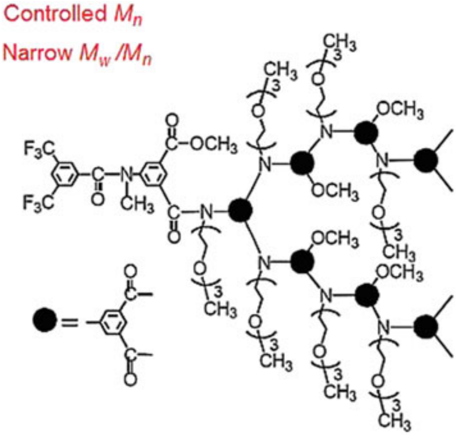
Hyperbranched *N*,*N′*-substituted polycarbamides are obtained using 3,5-diamino benzoic acids containing methyl, benzene, and allyl substituents for AB_2 monomer [640]. This method of synthesis of hyperbranched polycarbamides can be used for creation of libraries of polymers with interior functional groups.

Condensation polymerization of 5-amino-isophthalic acid methyl ether containing chains of *N*-(triethylene glycol) methyl ether is performed [641]. The



Scheme 2.27 Synthesis of PAMAM hyperbranched polymer

formed hyperbranched polymers have $M_n = 3810–18,600$, PDI = 1.11–1.19, are water-solved and are characterized by LCST.



There is an interesting approach in which AB_x type monomer is formed in situ via interaction between primary amino groups of 2-amino-2-ethyl-1,3-propanediol *or* tris(hydroxymethyl)aminomethane with aliphatic carboxylic acid anhydride [642]. It is important to emphasize that the initial substances are commercially available, and the following thermal self-condensation is carried out without catalysts or solvents. DB of the formed polymers is in the range from 0.36 to 0.55. Among the obtained hyperbranched poly (ether-amides) polymer structures with cyclohexyl molecular skeleton have the lowest DB, the highest T_g, and the best thermal stability.

Self-polycondensation of AB_2 monomers using different strategies was successfully applied to achieve DB = 100%, which is a typical property of dendrimers. Besides, due to a change in the reaction rate constants of the first reaction of the group B and the second reaction to the functional group A, hyperbranched polymers with controlled DB from 0 to 100% can be produced [643]. Moreover, molecular weight and molecular-weight distribution of the formed polymers can be controlled.

Also binuclear platinum complexes having one acetylene terminal group and two platinum-chloride groups can be used as AB_2 monomer [644]. Self-polycondensation of such monomer in presence of copper catalyst brings to hyperbranched platinum-polyyne polymers containing platinum-acetylide units and having high solubility in basic organic solvents. It is important to notice that such metal-containing hyperbranched polymers can then serve as precursors for PCMs.

For successful synthesis of classical hyperbranched polymers from AB_x and $AB_x + B_y$ monomers it is necessary to meet the following demands: first, A and B groups should react selectively with each other without side reactions, secondly, intermolecular cyclization should not take place, and thirdly, B groups should have equal reactivity.

This type of polymerization can be performed by slow addition of a monomer in presence of B_f molecule ($f \geq 3$) as a core, which provides structural control over a growing polymer. Thus, hyperbranched polyethers were synthesized from 2,2-bis (hydroxymethyl)propionic acid taken as AB_x monomer and triethanol amine used as a core molecule [645].

Another approach is copolymerization of A_2 monomer with B_n co-monomers ($n \geq 3$). Thus, hyperbranched polyethers with controlled molecular weight are obtained using $A_2 + B_3$ approach by interaction between glycerol and adipic acid without a solvent in presence of a tin catalyst (Fig. 2.51) [616].

The same $A_2 + B_3$ approach was successfully applied for production of hyperbranched polymers containing fragments of ferrocene (Fc) [646]. In this case diols, dithiols, or dichloroarenecomplexes were used as A_2 compounds, and B_3 compounds were preliminary prepared star-like molecules, as well as commercially available triols.

Slow addition of monomer, 2,2-bis(hydroxymethyl)propionic acid, to a trifunctional core gives a product with DB 47% [647].

$A_2 + B_4$ approach was used for production of hyperbranched conjugated poly (azomethines) via interaction between tetramines and dialdehydes [648]. Variation of the ratios between reagents and introduction of dopants, for example, $SnCl_2$ or β-cyclodextrin (CD), makes it possible to change content of terminal amino groups, which brings changes to interaction between the terminal amino groups and imine bonds of the main chain, and provides control over chelating properties of produced hyperbranched polymers.

Fluorescent hyperbranched polymer containing triphenylamine and divinyl-bpy units is obtained by Heck coupling reaction of 5,5′-divinyl-bpy with tris(4-bromophenyl)

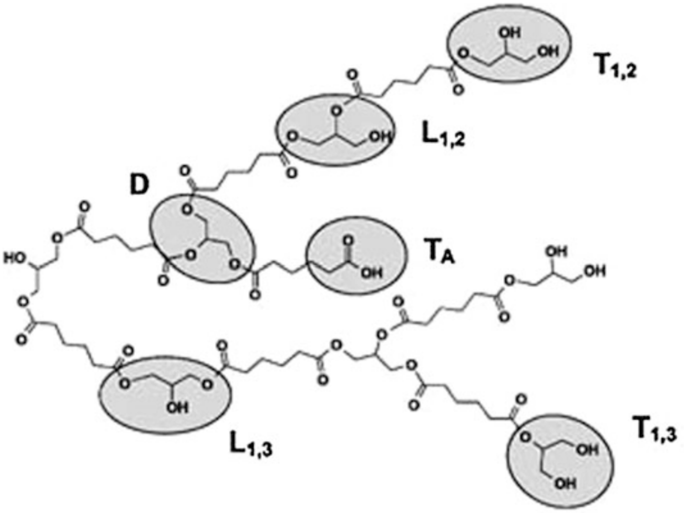


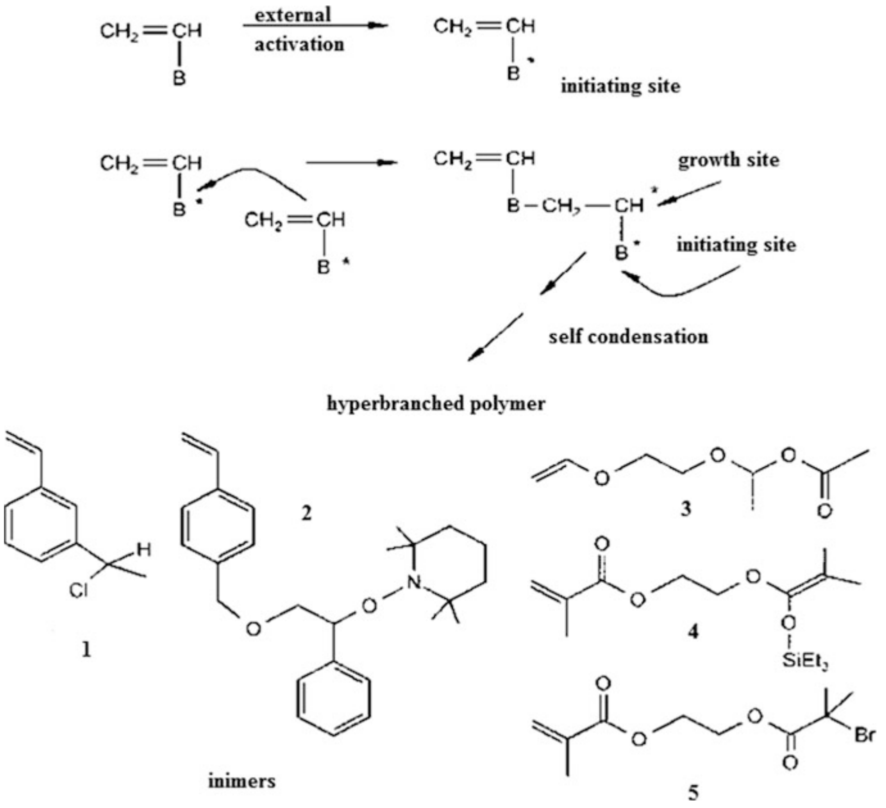
Fig. 2.51 Idealized structure of hyperbranched polyethers synthesized from adipic acid and glycerol in presence of tin catalyst

amine. It has $M_n = 1895$ and $M_w = 2315$, high thermal stability and is well solved in tetrahydrofuran (THF), chloroform, and dimethylsulfoxide (DMSO) [649, 650].

Hyperbranched polyyne with $M_w = 6.55 \times 10^4$ containing triphenylamine as the core, and diketone and pyrrol units is obtained by Glaser-Hay oxidative coupling reaction [651].

A series of water-soluble aliphatic hyperbranched PAMAM with the same or similar chemical structure of a PAMAM dendrimer is successfully synthesized from commercially available AB and C_n types of monomers using one-pot polymerization [652]. Methacrylate was used as AB monomer, and polyamino-compounds, such as en, dien, trien, tetraethylenepentamine and pentaethylenehexamine were used as C_n monomers. Hyperbranched polymers with different end groups and properties can be obtained via regulation of the initial ratio between AB and C_n. However, stoichiometric regulations between pairs of functional comonomers and potential risk of gelation assume serious drawbacks.

The chain growth mechanism for production of hyperbranched polymers has been widely developed after discovery of self-condensing vinyl polymerization (SCVP). Presently used monomer is designated as AB* and it contains an initiating radical in addition to a double bond. The initiating fragment is activated and reacts with the double bond forming a covalent bond and a new active center on the second carbon atom of the double bond (Scheme 2.28). A number of active centers increase in linear proportion to the growth reaction in SCVP, while two functional groups are always used during self-polycondensation of AB_x monomers. If new active centers formed during polymerization have different reactivity as compared



Scheme 2.28 Self-condensing vinyl polymerization (* is a reaction center, which can initiate polymerization) and some examples of AB* inimers (“inimer” = initiator + monomer)

with active centers in the initial monomer, this difference has a considerable effect on structure of obtained polymer. Living free radicals, electrophilic cation fragments and carbanion can serve as active centers.

A Pd-diimine catalytic inimer containing catalytic, initiating and monomer functionalities was used for synthesis of PE of hyperbranched-on-hyperbranched and star architectures by SCVP of ethylene (Fig. 2.52) [653]. It is important that it facilitates synthesis of star-shaped PE using tandem UV-coordination polymerization.

Aromatic polyamides with terminal NH_2-groups containing diphenylquinoxaline units are obtained by free radical polymerization of the 2,3-bis(4-aminophenyl)-quinoxaline-6-carboxylic acid and 2,3-bis[4-(4-aminophenoxy) phenyl] quinoxaline-6-carboxylic acid monomers at room temperature [654].

A variation of SCVP method is reversible addition-fragmentation chain transfer self-condensing vinyl polymerization (RAFT-SCVP), which is used for synthesis of segmented hyperbranched poly(GMA) (Scheme 2.29) [655].

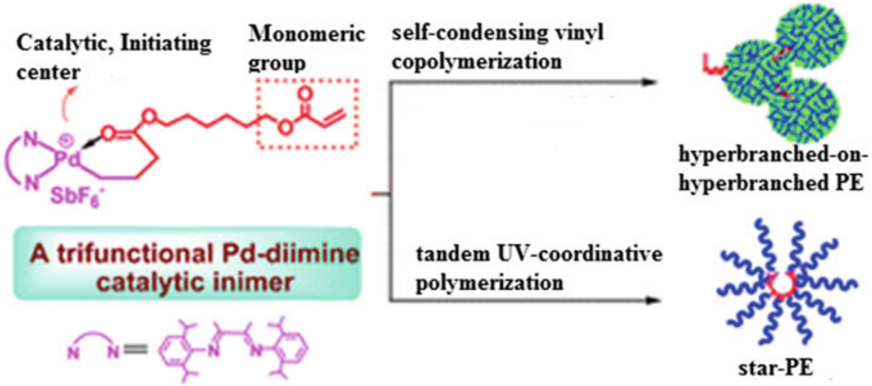
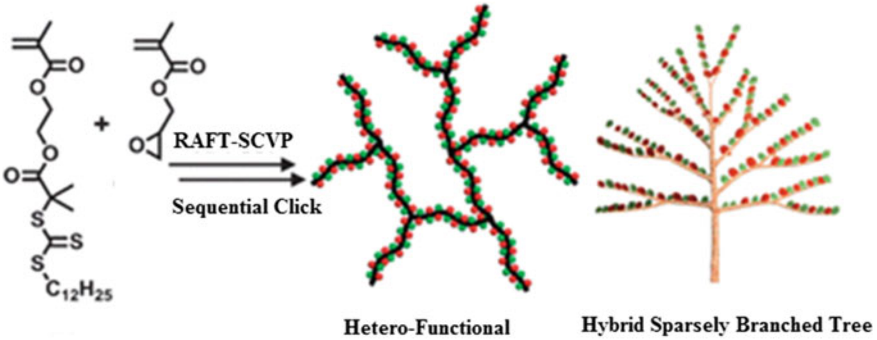


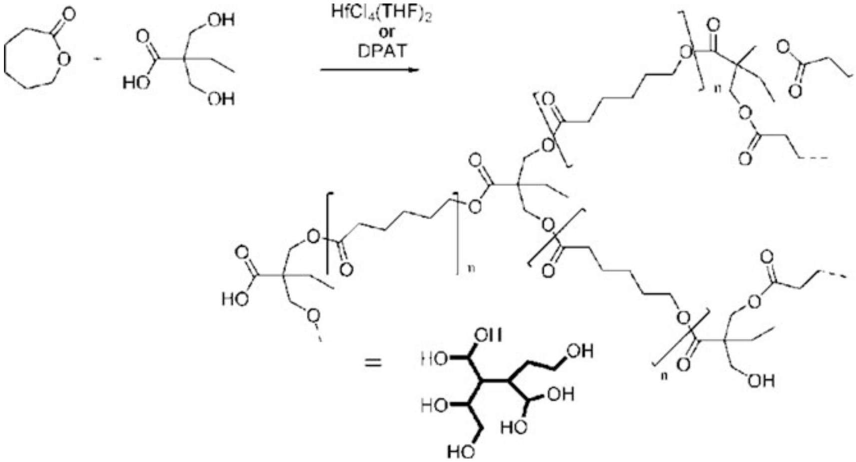
Fig. 2.52 Use of Pd-diimine catalytic inimer for synthesis of PE of hyperbranched-on-hyperbranched and star architectures



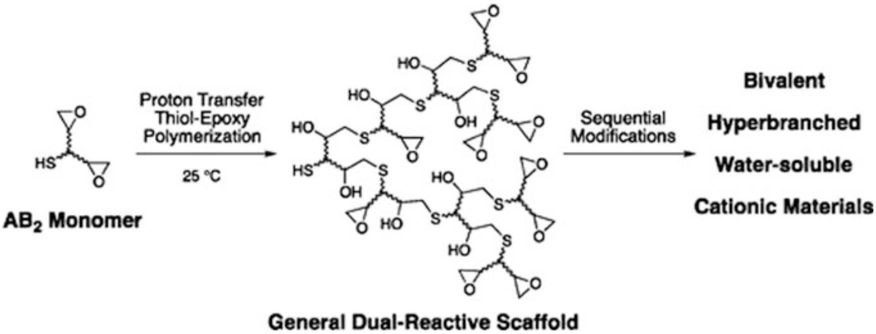
Scheme 2.29 RAFT-SCVP in synthesis of hyperbranched polymers

Apart from SCVP in the chain growth method other approaches are used, such as self-condensing ring-opening polymerization (SCROP), also known as ring-opening multibranching polymerization (ROMBP), proton-transfer polymerization (PTP), etc. For example, in ROMBP method branching units of blocks are generated during the ring-opening reaction, while initial AB monomers do not contain branching points. Polymerization is initiated by addition of respective initiators for generation of active centers, which can provide control over molecular weight and molecular-weight distribution of formed polymers (Scheme 2.30) [656].

PTP of thiol and epoxy groups was, in particular, applied to synthesis of hyperbranched water-soluble cation materials (Scheme 2.31) [657]. For this AB_2 monomer was synthesized, which contains two epoxy and thiol groups. PTP of this monomer catalyzed by bases brings to formation of polythioethers based on hyperbranched polymer with DB = 65–69% containing about 2% structural defects based on disulfide. This polymer contains two reactive centers, hydroxyl group, and



Scheme 2.30 Copolymerization of 2,2-bis(methylol)butyric acid with ε-caprolactone by ROMBP



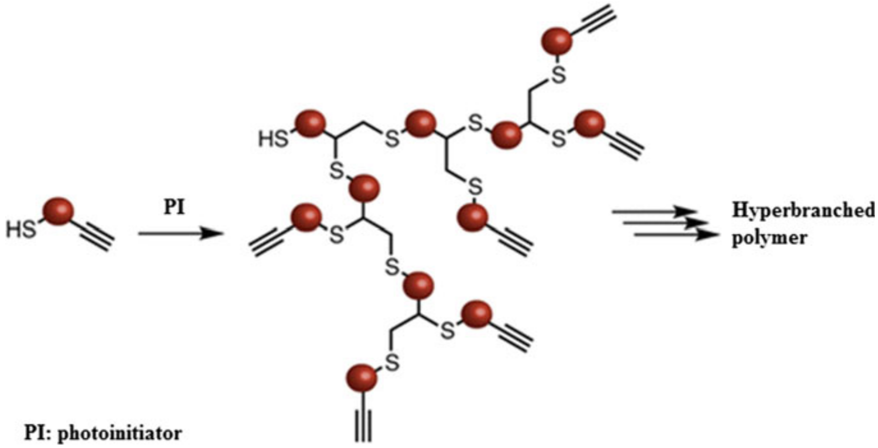
Scheme 2.31 Scheme of synthesis of hyperbranched polymer using PTP method

epoxy block distributed over all branched polymer carrier. Epoxy groups can be used in fixation of alkyl, aryl, and oxyethylene chains via thiol-epoxy reactions, while hydroxyl groups formed during polymerization or following functionalization can be involved in the coupling reactions of positively charged primary ammonium groups to branched polymer carrier.

The abovementioned synthetic approaches cover majority of general methods of preparation of hyperbranched structures. At the same time, in order to broaden structural variety and complexity of designed macromolecular structures, different building blocks are obtained by combination of strongly branched structures, which brings to linear-dendritic block-copolymers, hyperbranched core-star structures, dendrigrafts, and more complicated architectures [658].

Recently new efficient methods of synthesis of hyperbranched polymers have being used for different practical applications. For example, to obtain selective analytic reagents such methods as enzyme-catalyzed polymerization, click chemistry, or slow monomer addition are used [659].

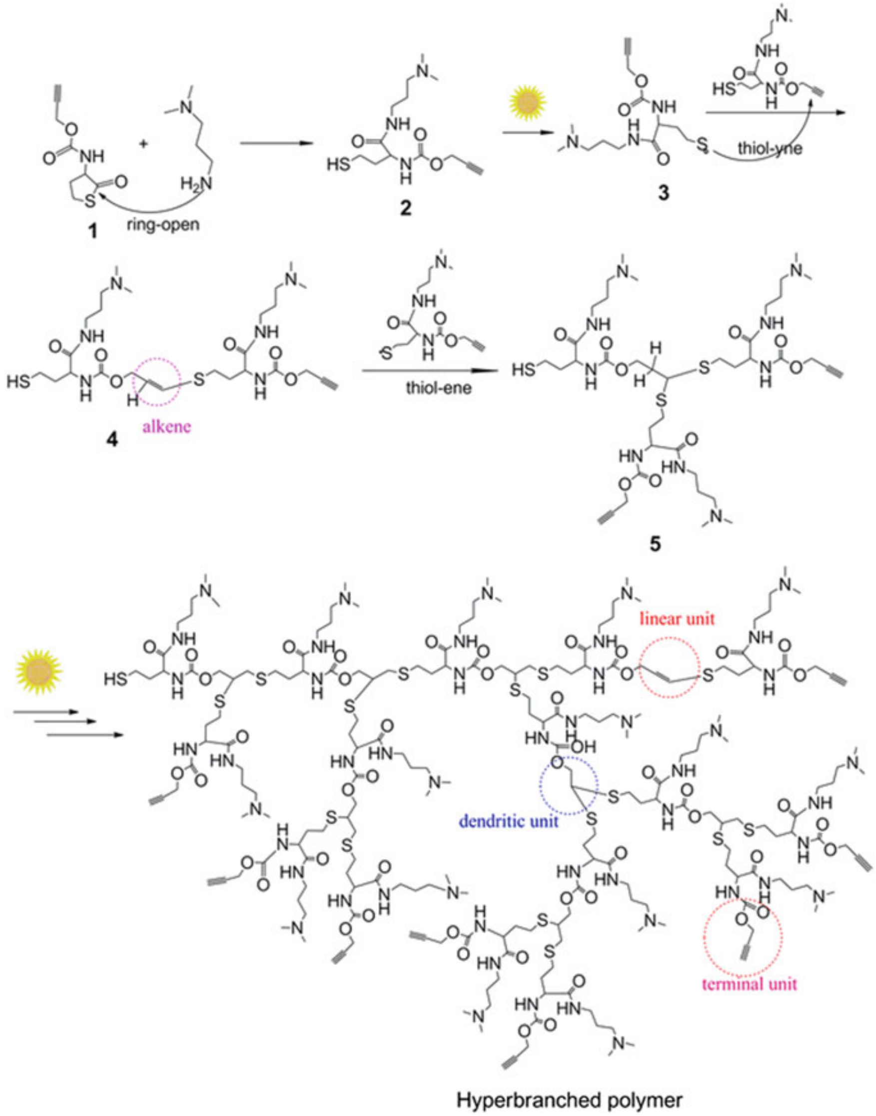
An example of green synthesis of hyperbranched polymers is lipase-catalyzed production of polyfunctional poly(amine-ester)-type of hyperbranched polymers by polycondensation of triethanolamine with polyethers [660]. Another example of green synthesis is synthesis of hyperbranched polymer through thiol-yne photopolymerization of macromolecules carrying thiol group at one end of the chain and alkyne fragment at the other one (Scheme 2.32). These thiol-yne macromonomers were obtained by RAFT polymerization of St initiated by alkyne-containing agent of a chain transfer followed by aminolysis trithiocarbonate groups in thiol fragments. It has been shown that among different parameters of the process (size of used thiol-yne macromonomer, amount of added photoinitiator, or initial concentration of a used macromonomer), the latter is leading, having the effect on final size of hyperbranched structures [661]. However, structure of hyperbranched polymers can be controlled as in the case of dendrimers, and functional groups are not localized in a definite position. This is stipulated by statistic character of coupling stages, steric difficulties of growing chains, and reactivity of functional groups, i.e. growth takes place only from two centers among all branching units, which gives irregular and linear segments. At the same time, low cost of synthesis of hyperbranched polymers makes it possible to produce them in large quantities, giving them advantage against dendrimers in applications. Hyperbranched polymers are thus considered as alternative to dendrimers for different applications in researches and for practical using.



Scheme 2.32 Scheme of synthesis of hyperbranched polymer by thiol-yne photopolymerization method

It should be noted hyperbranched polymers with high DB and low dispersity values produced of slow monomer addition of a thiol/yne monomer to multifunctional core molecules in the presence of photoinitiator and under UV irradiation [662].

New strategy is developed [663], in frameworks of which small monomers can directly grow into big hyperbranched macromolecules under action of sunlight without any catalyst (Scheme 2.33).



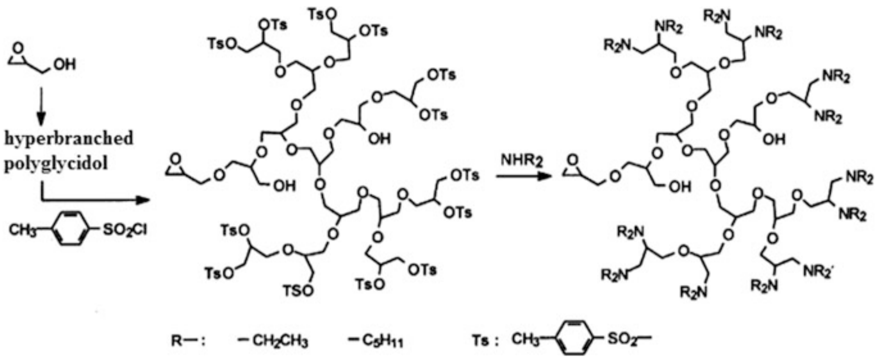
Scheme 2.33 Schematic image of growth of hyperbranched polymer under sunlight irradiation of the mixture of alkyne-containing thiolactone and primary amine

2.4.3 Post-synthetic Modification of Hyperbranched Polymers

Directed chemical modification of hyperbranched polymers makes it possible to perform architectural design of these compounds, determining size, shape, a ratio between length and density, and functionality of their surface. Besides, PSM is also an efficient method, which provides control of amphiphilic balance of polyfunctional macromolecules. High local specific weight of active groups bringing to existence of a number of identical ligands in a molecule is provided increased binding of a specific substrate. All this determines exactly hyperbranched polymers as a unique reagent for development of new composite materials of structural functions and a system for molecules transporting (chromophores, phototropes, catalysts, drugs) with a possibility of choice of delivery of specific compounds.

Four ways of PSM of hyperbranched polymers are based on highly branched architecture and a great number of terminal functional groups of these macromolecules: (1) end capping by short chains or organic molecules, (2) end grafting through living polymerization, (3) growth of hyperbranched polymers on a surface or grafting from/on a surface, and (4) hypergrafting for production of hyperbranched polymers with linear macromolecular core. End capping with small organic molecules can be used to obtain a great number of end chelating groups linked to linear and end units of hyperbranched polymers. Thus, hyperbranched polyamino-end glycidols were synthesized [664] using end modification of terminal hydroxyl groups with toluenesulfonyl chloride with the following nucleophilic substitution of the toluenesulfonyl groups with secondary aliphatic amines (Scheme 2.34).

The greatest number of studies considering the end modification is carried out using a hyperbranched commercial polymer Boltorn 2, 3, and 4 generations, H20, H30, and H40, respectively. Thus, Boltorn polymers are modified by incorporation of tertiary amino groups via interaction with diethylaminopropylamine using CDI



Scheme 2.34 Scheme of the end capping process

chemistry for development of non-toxic and biodegrading gene carriers [665]. Toxicity of modified hyperbranched polymers is lower than that of PEI. Boltorn H40 was subjected to interaction with hexamethylene or isophorone diisocyanates to obtain polyurethane containing soft hyperbranched polyether segments [666].

Interesting end capping modified amphiphilic hyperbranched polymers are synthesized on the basis of aliphatic polymer Boltorn H40, interior part and exterior shell of which contain hydrophobic PCL and hydrophilic PEG segments, respectively [667]. End capping of the surface of amphiphilic polymers using coupling reactions between hydroxyl group of the PEG segment and carboxylic group of folic acid provides carriers for cancer cells transport (Fig. 2.53).

Reaction of hyperbranched aliphatic polyester polyols of three generations with toluylene diisocyanate was used to synthesize respective hyperbranched poly(ester-urethanes) with end isocyanate groups [668].

Aliphatic hyperbranched polyethers synthesized from 2,2-bis(methylol)propionic acid and tris(methylol)propane are modified by end capping method using phthalic anhydride and trimellitic anhydride [587]. Oppositely to the initial, modified polymers can form globular aggregates in the *N*,*N*-dimethylformamide (DMF)/H_2O mixture due to their amphiphilic structure [669].

The end capping method was used for integration of reactive methacryloyl radicals to periphery of hyperbranched polymers produced from pentaerythritol as a «central core» and 1,2,4-benzenetricarboxylic anhydride and epichlorohydrin. The obtained hyperbranched polyethers have good solubility in alkalis and ability to photocuring.

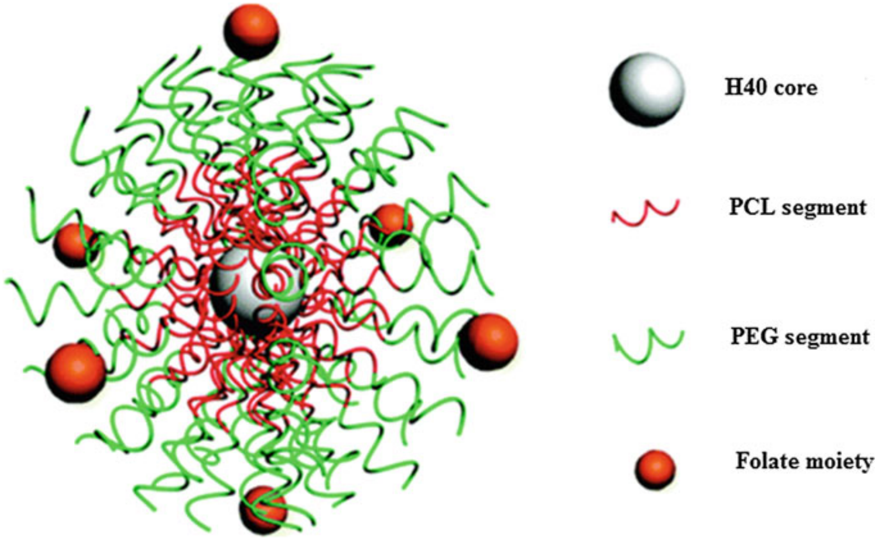


Fig. 2.53 End capping modified hyperbranched polymers

Hyperbranched poly(GMA) was efficiently functionalized along all polymer carrier by click chemistry methods such as azidation of oxiranes, thiol-epoxy, thiol-en, CuAAC and Menschutkin reaction (Fig. 2.54) [670]. This reactions bring to hyperbranched polymers containing chelating heterofunctional groups, including hydroxyl + azid, bi-hydroxyl, tri-hydroxyl, hydroxyl + tertiary amine, hydroxyl + alkene, hydroxyl + carboxyl, alkene + azid, alkyne + azid, hydroxyl + alkyne, bi-hydroxyl + alken, hydroxyl + carboxyl, alkene + azid, alkyne + azid, hydroxyl + alkyne, bi-hydroxyl + alkene, etc., and all of them with ~100% conversion. Also double «thiol-epoxy + thiol-en» and triple «thiol-epoxy + Menschutkin reaction + CuAAC» click-sequences are possible, which makes modification of functional groups even more easily available.

The end capping method is also used for integration of chelating groups in arms of star polymers. Thus, DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) fragments were fixed on a polymer arms with a poly(dimethyl acrylamide-*co*-DVB) core with the following introduction of radioactive labels for biomedical purposes (Fig. 2.55) [671].

Terminal grafting relates to the «grafting-from» type of reactions. Grafted polymers from macromolecular initiators obtained by modifying functional groups of hyperbranched polymers give a core-shell poly-armed star polymers or hyperstars.

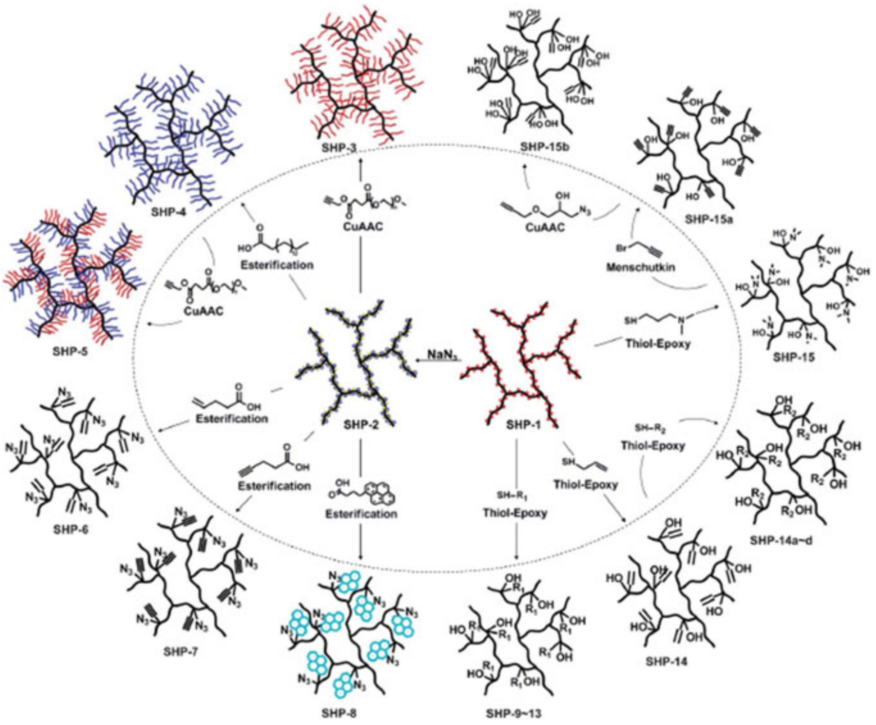


Fig. 2.54 Click-sequences of functional groups of hyperbranched polymers

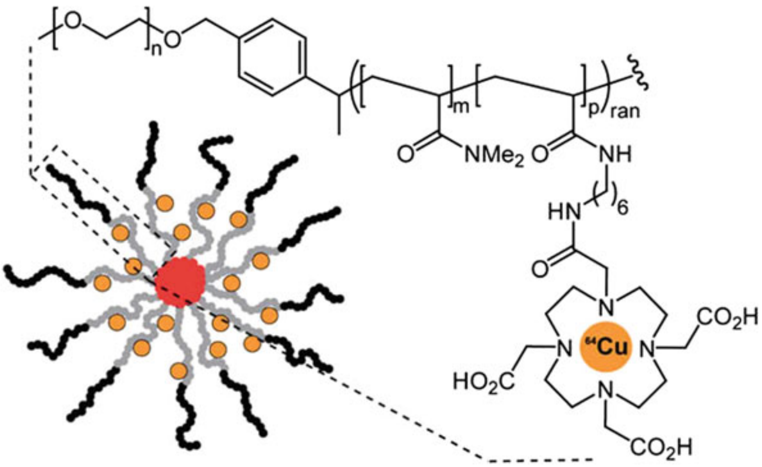


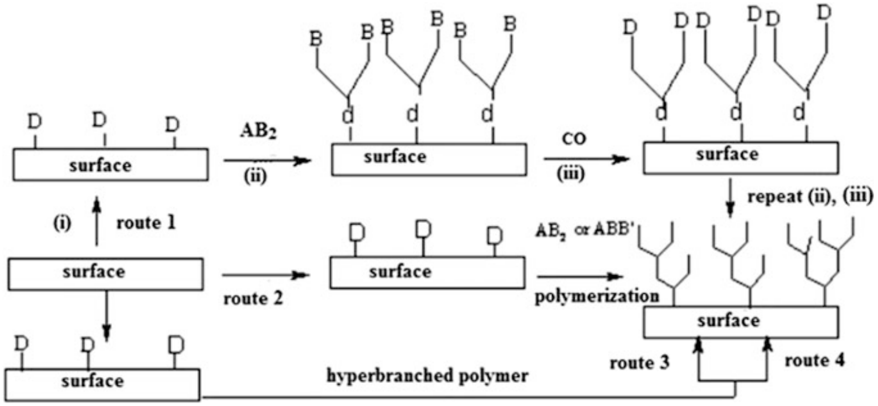
Fig. 2.55 Structure of DOTA-containing star polymers labeled with radioactive medium lived positron emitter ^{64}Cu

Some properties, such as polarity, solubility, and flexibility of the hyperbranched matrices can be controlled by modification using terminal grafting [672]. Three methods of polymerization (for example, anion, cation, and living/CRP) are applied to obtain hyperstars through reaction processes including macromolecular initiator and in situ grafting.

For example, series of liquid crystal copolymers with multi-armed star azobenzene side chains and hyperbranched core is synthesized by ATRP method via multifunctional hyperbranched polyether as initiator and chlorobenzene as a solvent [673]. Multifunctional hyperbranched polyether initiator is prepared based on poly(3-ethyl-3-(hydroxymethyl) oxetane) and 2-bromo-2-methylpropionyl bromide. Azobenzene side arms had liquid crystal conformation of poly [6-(4-methoxy-4′-oxy-azobenzene) hexyl methacrylate] with different molecular weights.

Method of modifying specific or interface surfaces with hyperbranched macromolecules or grafting hyperbranched polymers is called «surface growing» (Scheme 2.35). Hyperbranched grafted polymers can be considered as polymer brushes, which are usually linked to the surface with one end of a polymer chain, so that the polymer can spread from the surface. Surface grafting is efficient strategy for preparation of inorganic/organic hyperbranched polymer hybrid materials and functional devices for improvement of properties of surface objects.

Hypergrafting is a grafting of hyperbranched macromolecules to a multifunctional polymer core, and the obtained hybrid material is called hypergrafted polymer. If a linear polymer is used as a core, a new type of a comb-like polymer cylinder is formed. Hypergrafting method is used, for example, to obtain linear polyglycerol-*gr*-hyperbranched polyglycerol (M_n = 1000–4000) using AB_m monomers, from multifunctional, polydisperse macroinitiator cores by slow monomer addition [674].



Scheme 2.35 Schematic representation of surface grafting

Hyperbranched polymers can be grafted also on other very different substrates. Thus, hyperbranched PAMAM is grafted on particles of resin powder from tire disposal, and the obtained product is well dispersed in water and can be used for curing and increase in impact resistance of epoxy resins [675]. It is noted grafting hyperbranched PEI of different molecular weight on the graphene oxide, which leads to promising adsorbents for potential use in the removal of Pb(II) ions from wastewater [676].

Design of biodegradable hyperbranched polymers are promising area of research, especially for biomedical applications. As an example, hyperbranched CPL synthesized using hybrid copolymerization of ε-caprolactone with GMA as the branching agent and (1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranilideneamino]-2Λ^5,Λ^5-catenadi(phosphazene) as a catalyst in one step can be a typical example [677].

It can be concluded that though there is not yet complete clearness in many aspects of hyperbranched polymers formation, intensity of studies in this field guarantees that successful development of this task is beyond the question.

2.5 Polymeric Films as Chelating Macroligands

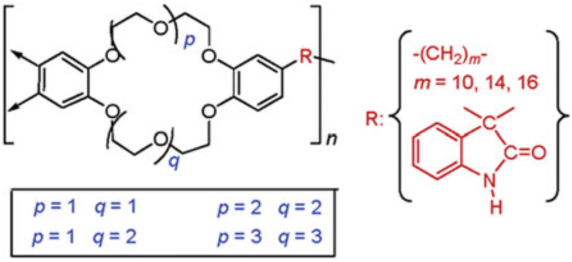
Recently a great attention has been given to such an interesting class of CPLs as polymer films [21, 678–685]. Apart from profoundly studied areas of practical applications of polymer films (semi-transparent membranes, electrode materials in chemical current sources, preserving and packing materials, including anticorrosive ones, etc.) incorporation of a rigidly bound metal in their structure opens more possibilities for practical usage. No less important is the fact that some conjugated polymer films, polyaniline in particular, are commercially produced in large quantities, because, as compared with inorganic materials, they are less expensive to be applied in many electronic and optoelectronic devices such as semiconductor, transport, electroluminescent and photocell elements. It should be noted that many polymer films are related to nanometer materials; therefore, different nanometer effects can be used to produce films with considerably optimized or improved properties [686].

A wide range of practical tasks solved using polymer films or polymer coatings deposited on different substrates requires different fabrication methods, which can be divided into three groups. The first one supposes using of preliminary formed polymer having chelating functionalities for production of films. The second group includes different methods of assembling of polymer films from low molecular weight substances with chelating fragments. And, the last, third group includes different methods of PSM of preliminary produced inert or monofunctional films for development of chelating units.

2.5.1 Polymeric Films Based on Pre-formed Chelating Macroligands

The first group of these methods relates to multistage processes, because it includes stages of production of a CPL, its purification, and processing into a film or deposition on a substrate [21, 582, 684, 685, 687]. The main used approaches are: submerging method, «drop evaporation» method, oxidation or reduction deposition, spin-coating, etc.

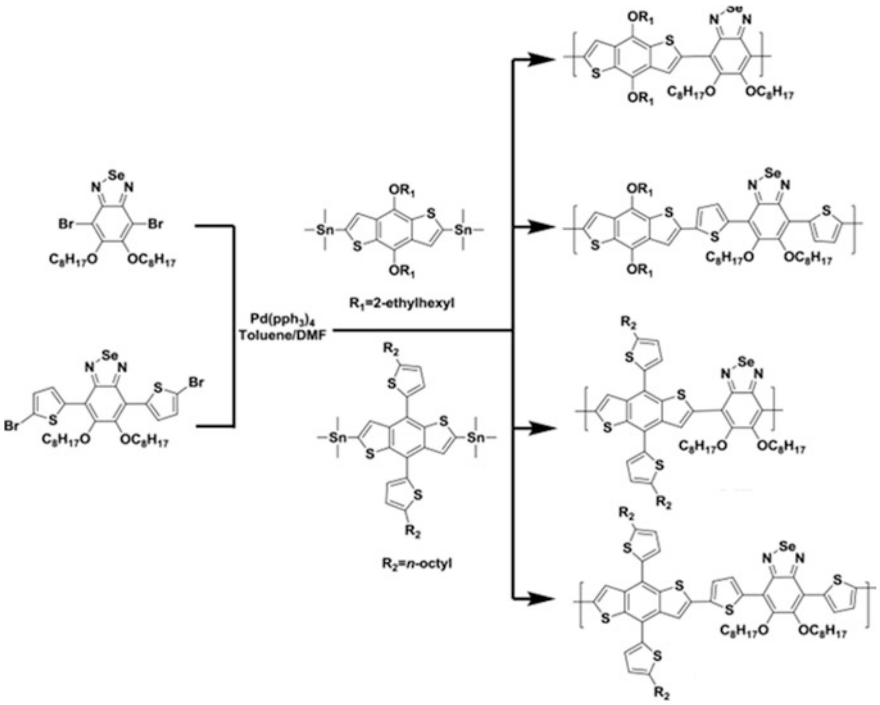
The submerging method is based on holding of a substrate in a polymer solution for some time, during which molecules are adsorbed and a film is formed on a surface. Thus obtained films are stuck to the surface due to chemisorption and low solubility of the formed coatings in a solution applied. This method was used, for example, to obtain thin highly transparent homogeneous films based on copolymers containing alternating ion-conducting segments of 24-crown-8 conjugated with light-emitting fragments of 1,5-distyryl naphthalene [688]. Flexible transparent films are also prepared on the basis of polymers containing dibenzocrown ethers in the main chain, having aliphatic ($C_{10\text{-}16}$), aliphatic-aromatic, or oxyindole spacers. It should be noted that in these polymers supramolecular structures are formed [689].



When forming polymer chelating films from solutions using the submerging method, one starts from very simple approaches for thick film fabrication to more sophisticated methods of thin film production, even to multilayered, and then to monolayers. However, when using this method, often films with non-uniform thickness are formed depending on viscosity of liquid, evaporation rate of a solvent, etc. Films with good processability caused by high solubility of polymers in polar aprotic solvents can be obtained by evaporation of a solvent from CPL solutions. Thus, for example, polyamide films were obtained from monomers based on isophthalic diacids, containing a benzo-12-crown-4 unit as a side group or benzodipodand subunit in the side structure, which represented an opposite part of alicyclic crown ether with an open chain [690]. To form films, solutions with 10% concentration of a polymer are needed, and a solvent is removed by heating at 100 °C for 4 h in air-circulating oven and then at 120 °C for 4 h in vacuum.

The drop evaporation method is used for modification of electrodes with small surface areas. Drop deposition of several micro-liters of a polymer solution of a certain concentration with the following evaporation of a solvent makes it possible to obtain a film, which is well reproducible by amount of the polymer and its composition. Structural homogeneity of a film depends to a great extent on the evaporation procedure: the latter should be rather slow. Composition of an initial film (including chelating groups) can be changed during its treatment by a respective reagent by the same «drop evaporation» method. Thus, to increase stability of PEI film in acid solutions, it is treated by dibromobutane solution in isopropyl alcohol, which brings to cross-linking of the polymer and decrease in its solubility with low pH [691].

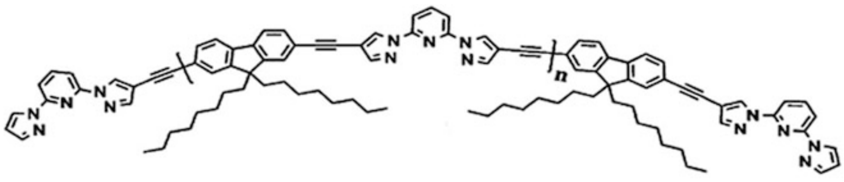
The essence of the spin coating method is that a CPL is solved in appropriate solvent, and the solution is spun. A spin coating is the preferable way for deposition of thin, homogeneous films on plane substrates. It has been applied, in particular, for coating of a quartz glass by polymers containing chelating spun bpy and planar phen fragments. M_n of these polymers are 11,000 and 13,000 (PDI $\approx$ 1.5), respectively [692]. The chelating bpy fragment was incorporated into spin-coated films made of regioregular conjugated polymers including alternating 3-alkylated oligothiophene and bpy [693].



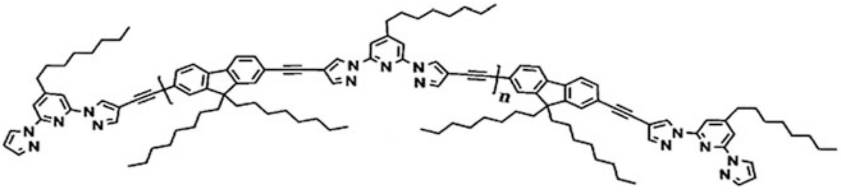
Scheme 2.36 Synthesis of 2,1,3-benzoselenadiazole-based conjugated polymers

Spin-coated thin films **I** and **II** are also obtained on the basis of 4-ethynyl-2,6-bis(pyrazolyl)pyridine (BPP) copolymers with fluorene in the main chain and M_n about 10,000 [694].

2,1,3-Benzoselenadiazole-based conjugated polymers are soluble in ordinary organic solvents and can be spin-cast for formation of smooth homogeneous thin films (Scheme 2.36) [695].



I



II

Thin films (9–70 nm) of a range of polymers, which contain in the main chain a dibenzo-18-crown-6 block linked with aliphatic spacer of different lengths (C_{10} or C_{14}) and origins, are prepared from chloroform solutions by spin coating on a silicon substrate. Geometry pattern of the grazing incidence small angle X-ray scattering (Fig. 2.56) correlates with a size of out-of-plane structure and with the length of repeated unit of the polymer. Heat treatment of the samples improves nanostructures due to increase in number of lamellate consistencies and vertical orientation of molecular columns [696].

Simultaneous copolymerization and film formation are performed in aqueous solution with addition of an oxidant (ammonium persulfate) for obtaining ultra-thin self-doped polyaniline films based on substrate of indium-tin oxide (ITO). The used monomers were aniline and its derivative *o*-aminobenzenesulfonic acid. Rate of the film formation depends on the monomers ratio: the rate is higher at higher concentration of aniline, and the film thickness is determined by duration of assembling and temperature [697].

In order to deposit monomolecular layers, Langmuir-Blodgett (LB) method is used, which gives name to thus obtained films. Phthalocyanines with substituents containing hydrophobic and hydrophilic groups are used for creation of monomolecular layers [698]. Soluble fluorine-containing polyamidoimides are obtained from 2,2-bis [*N*-(4-carboxyphenyl)-phthalimide-1,4-il] hexafluoropropane and different diamines as LB multilayers [699].

One of the methods of synthesis of multilayered films is based on gradual LbL deposition of molecular layers. For example, when designing solid solar cells of the sandwich type from polythiophene-Pp composite films, at the first stage a spin-coated film of poly(3-dodecylthiophene) on a gold electrode is obtained [700]. Then a layer of electrochemically produced bithiophene film is deposited on it, and at last, a tetrathienyl-Pp film is obtained on the top using the same electrochemical polymerization (1 or 10 cycles) in order to fabricate gold electrodes modified by polythiophene-Pp film. An aluminum electrode was deposited on the obtained polythiophene-Pp film by vacuum sputtering forming sandwich-like solid solar cells.

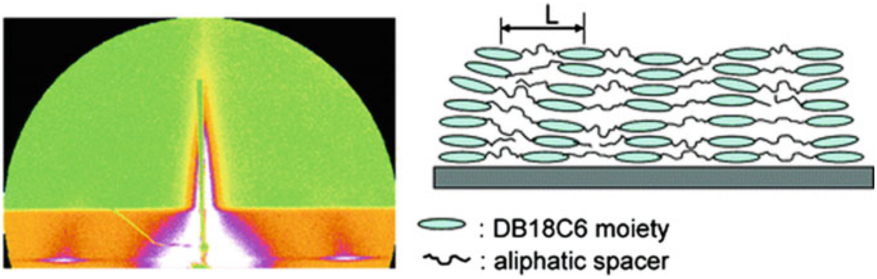


Fig. 2.56 The grazing incidence small-angle X-ray scattering patterns and out-of-plane structure (interference maximum near the horizon) of the polymer repeating unit in the main chain dibenzo-18-crown-6 linked to an aliphatic spacer of different length

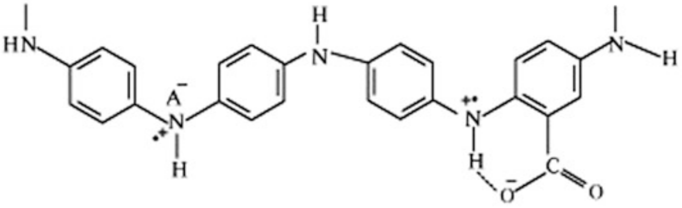
2.5.2 *Assembly of Polymeric Films from Chelating Monomers*

The most widely spread methods of assembling polymeric films from low molecular weight compounds with chelating functionalities are chemical, electrochemical, plasma-chemical, and photopolymerization methods.

Thus, chemical polymerization was used to obtain films of poly(1,8-diaminonaphthalene) on a porous polycarbonate membrane, which can serve as a template for synthesis of nanometer structures [701]. At that, poly(1,8-diaminonaphthalene) obtained using the method of chemical polymerization is closer by its properties to electrically synthesized polymer. Moreover, in aqueous solutions nanowires were formed, as well as two types of structures, nanowires and round shaped structures not fitting to pore size, can be obtained by chemical polymerization in acetonitrile solution.

Resulting in optimal conditions of chemical polymerization (oxidizer—ammonium peroxydisulfate) film of aniline and *o*-aminophenol have good conductivity and high electrochemical activity to pH 11.0 with a wide potential region (from −0.20 to 0.80 V). Among all the factors that affect the properties of the copolymers, the ratio of *o*-aminophenol/aniline concentrations is a major [702].

Chemical co-polymerization of aniline with *o*-anthranilic acid in aqueous solution of hydrochloric acid can be applied for production of copolymer films in situ by submerging an object glass into polymerized medium [703, 704]. It is established that presence of *o*-anthranilic acid has an effect on the yield, the induction period, the time of transformation of monomers and the growth rate of film formation.



Electrochromic copolymers based on *o*-phenylenediamine and aniline are easily formed by chemical oxidized polymerization [705]. Coefficients of reactivity of *o*-phenylenediamine and aniline are 9.70 and 2.74, respectively, showing stronger tendency to homopolymerization than to copolymerization between them. The copolymers have a much greater plasticity and uniformity of the film, as well as higher electroactive and electrochromic best tricolor than homopolymers. Thus, the film of the copolymer containing 50 mol% of *o*-phenylenediamine is red at −0.5 to 0 V, then becomes green in the range of 0 to +0.6 V, and then blue from +0.6 to +1.35 V (Fig. 2.57).

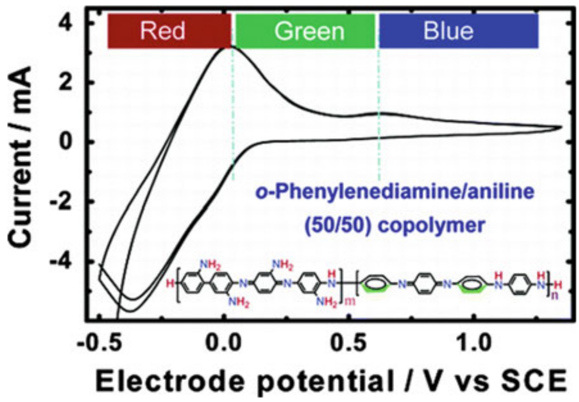


Fig. 2.57 Current versus potential relationship and electrochromism of *o*-phenylenediamine/aniline copolymers

The method of electrochemical polymerization is most widely used for production of CPL films. First, films are formed directly on an electrode surface, and the product of reaction, electroactive film, has high electric conductivity. Secondly, electrosynthesis provides high current yield and strict stoichiometry of the process, therefore a film of a required weight and thickness is obtained. Thirdly, properties of a polymer film can be controlled during its synthesis [691].

Electrochemical polymerization is an elegant, attractive, and easy strategy for immobilizing chelating fragments on electrode surfaces [706]. This principle is based on electrochemical oxidation (or reduction) of preliminary obtained monomers for formation of polymer films containing chelating units. The obtained polymer films should be electron conductors to provide electron transport in matrix (and then following polymer growth). The most often used chelating monomers are derivatives of *o*-aminophenol [680] and *o*-phenylenediamine [184].

Mechanism of electrochemical polymerization of these substituted monomers is not completely explained, despite of a great number of data in this field. However, presently it is generally recognized that the first stage in the electropolymerization process is electro-oxidized formation of a cation-radical from a chosen monomer. The oxidation reaction is continued by dimerization process, and the following reactions of oxidation and coupling. This brings to formation of oligomers and polymers on the electrode surface. It is also clear that morphology and physical properties of CPL films depend, first of all, on conditions of electrochemical polymerization.

Using three methods (cyclic voltammetry, potentiostatic and potentiodynamic methods), electrocatalytic oxidative polymerization of *o*-phenylenediamine at the electrode reduced graphene oxide/glassy carbon, in which reduced graphene oxide acts as a catalyst, was carried [707].

5-Amino-phen can be polymerized electrochemically forming electro-conducting polymer using potentiodynamic or potentiostatic method on different electrode substrates: composite, formed by carbon paste in epoxy matrix, carbon glass, or an electrode made of polycrystalline gold [708]. Poly(aminoanthraquinone) films which were successfully applied as analytical sensors for Ce(III) ions were obtained using the same methods [709].

Electropolymerization of 3-amino-5-mercapto-1,2,4-triazole on a carbon glass electrode in 0.1 M H_2SO_4 solution [710] is used to form nanostructured films, while uniformly conducting polymer films from poly(*N*-(1-naphthyl) ethylenediamine dihydrochloride) are easily and reproducibly prepared by anode oxidation of a monomer in the acid aqueous solution [711], and head-to-tail polymerization of the monomer was observed. One-stage method of potentiodynamic deposition is a convenient way for production of poly(1,5-diaminoanthraquinone)/reduced graphene oxide nanohybrides, in which 1,5-diaminoanthraquinone and graphene oxide are initial materials [712]. Poly(1,5-diaminoanthraquinone) displays a barleycorn-like structure and is covalent grafted to the surface of the reduced graphene oxide (Fig. 2.58).

Poly(*o*-aminophenol) films were potentiostatically produced at different potentials of electrodes in acid aqueous solution [713].

Numerous studies were performed on electrochemical polymerization of monomers containing chelating *o*-phenylenediamine fragment. Thus, electropolymerization of *o*-phenylenediamine on Pt electrode was carried out from deoxygenized water-acid medium by cyclic voltammetry method [714]. The kinetic equation $V = k[\text{monomer}]^{1.19}[\text{acid}]^{1.23}[\text{electrolyte}]^{0.87}$ is obtained from the value of anode current density using cyclic voltammetry measurements. Apparent activation energy is 28.34 kJ mol^{-1}. Electrochemical polymerization of two derivatives of 2,5-di (2-thienyl)-1H-pyrrole, in pyrrol cycle of which of 3-pyridine or phen units are contained [715], was used for preparation of conducting polymer films on a carbon glass electrode, their maximum electric conductivity is (6.5–9.2) × 10^{-2} C cm^{-1} (1.4 V). Color of the pyridyl films changes from brown-yellow to deep blue at transition from the neutral state to the oxidized. Similarly, phen films were green-yellow (λ_{max} = 451 nm) in neutral state and light blue (1.4 V) in entirely oxidized

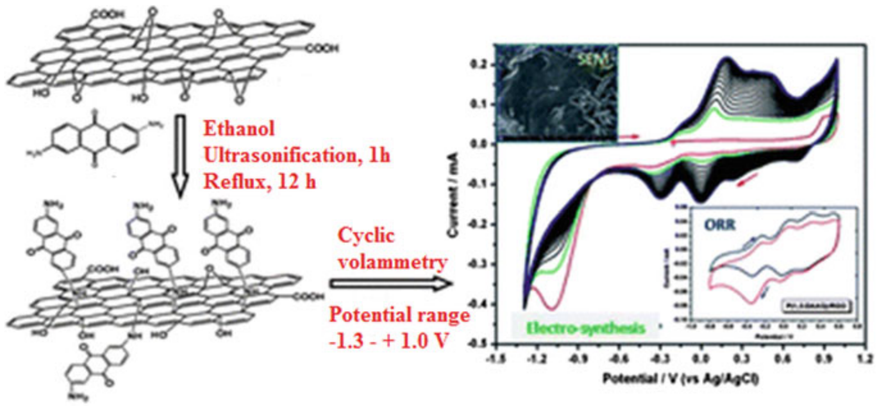


Fig. 2.58 Covalent grafting 1,5-diaminoanthraquinone to the surface of the reduced graphene oxide and current versus potential relationship of grafted polymers

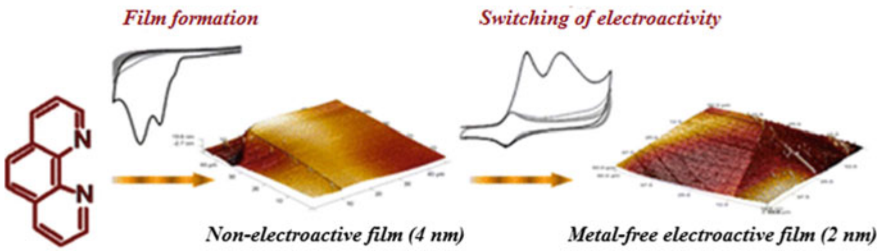


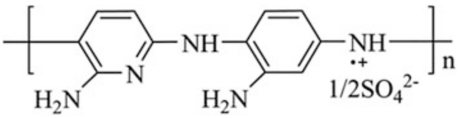
Fig. 2.59 Scheme of electrochemical reduction of phen

state. Electrochemical reduction of phen in water-acid electrolyte on a carbon glass electrode brings to covalent modification of the electrode (Fig. 2.59) [716]. After that, the deposited film can be switched to electroactive form using electrochemical oxidation. Electroactive film can also be generated by alternative reduction and oxidation voltammetry cycles of phen solution in aqueous sulfuric acid.

Electropolymerization of *o*-phenylenediamine in Ils, 1-ethyl-3-methylimidazolium bromide and *N*-methylimidazolium tetrafluoroborate, on a carbon glass electrode performed using cyclic voltammetry is interesting regarding green chemistry principles [717]. An example of biocatalytic electropolymerization can be polymerization of *o*-phenylenediamine on a carbon glass electrode, whose surface has been modified by grafting of L-tyrosine [40]. The obtained modified electrode has high electrocatalytic response to presence of ascorbic acid and is used to find concentration of ascorbic acid in vitamin C pills. It should be noted that a great number of CPL films, in particular, based on derivatives of *o*-phenylenediamine and 3,4-ethylenedioxythiophene are applied as biosensors [718].

Platinum disc microelectrode (50 µm in diameter) [719] and glassy carbon electrode [720], modified by PPD, were used for H_2O_2 sensors, and electrically synthesized PPD was used for support of Prussian blue high-disperse layer [721]. The observed high stability of Prussian blue as a catalyst of H_2O_2 decomposition is due to presence of organic polymer in the microstructured composite film. The results give an idea on design of high sensitive, stable, and free of noise biosensors.

Another interesting chelating monomer is 2,6-diaminopyridine, its electrochemical polymerization was performed using cyclic voltammetry in sodium hydroxide aqueous solution [722]. In the produced films interpenetrating network structure is formed, which is possible on doping of the polymer anions during oxidation, or, on the contrary, during reduction.



Based on this polymer, electrochemical sensor for detection of ascorbic acid is designed. First, a layer of poly(2,6-diaminopyridine) is deposited on the surface of a carbon glass electrode by electropolymerization technique, then negatively charged nano-gold and positively charged 2,6-diaminopyridine were alternately adsorbed on the modified electrode using LbL method. The sensor is characterized by high electrocatalytic activity of ascorbic acid oxidation by bi-layered 2,6-diaminopyridine film, thus providing abundant amino groups and positive charge, which advance electron transfer between the electrode and ascorbic acid, and increase sensitivity of the electrode [723]. Mediator-less ammeter biosensor of H_2O_2 is also prepared by immobilizing horseradish peroxidase enzyme on platinum wire electrodes coated by colloid gold and modified by 2,6-diaminopyridine. The studied biosensors show high selectivity, good stability, and reproducibility in design [724].

An example of electrochemically produced CPL with bpy fragment are stable polypyrrol films containing fragments of 4,4′-dimethoxy-bpy and are obtained using electropolymerization at the anode potential from −0.51 to −0.35 V and cathode wave value −0.77 V [725].

Numerous works are concerned with modification of surface of the electrodes with phen fragments. Thus, carbon glass surfaces are modified by phen derivatives, such as 5-amino-phen and 5,6-diamino-phen, using cyclic voltammetry scanning from +1.2 to +2.7 V [726]. Surfaces having phen chelating ligands with different functional groups are promising for detection of transition metal ions. Carbon glass electrodes are modified electrochemically by poly(5-nitro-phen) and poly(5-amino-6-nitro-phen) layers (Fig. 2.60) for designing sensors for heavy metal ions (new sensor platform) [727]. In particular, this was demonstrated by formation of

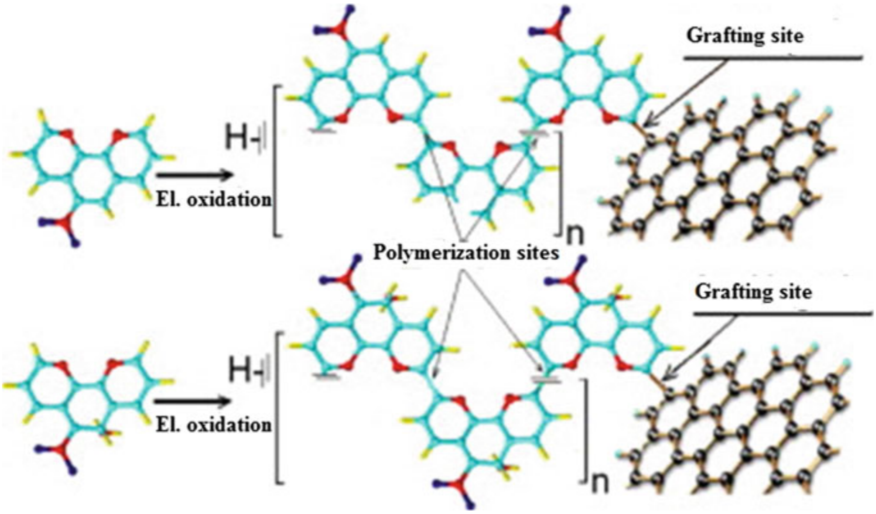


Fig. 2.60 Scheme of electrochemical polymerization of phen on carbon glass

chelates between carbon glassy-grafted poly(5-nitro-phen) and poly(5-amino-6-nitro-phen) layers and Cu(II) ions.

Electrochemical modification of a carbon glass electrode by phen groups is performed in two ways: reduction of respective diazonium ions and reduction of phen (Fig. 2.61) [728]. Initially grafted electrochemically inactive organic film becomes electrically active after it is subjected to electrochemical reduction and oxidation. At that thin homogenous phen films (<2 nm) are deposited on the surface of pyrolysis photoresist film electrode.

Electrochemical synthesis is used for production of a chelating ligand of *N*,*N*-type, poly(3-amino-1,2,4-triazole) on Pt electrode [729] in ammonium oxalate solution.

Poly(1-amino-9,10-anthraquinone) chelating films were prepared by electrochemical oxidation of a monomer in sulfuric acid solution [730] or in acetonitrile using $LiClO_4$ as a background electrolyte [731]. The same ligand also was electrically polymerized on platinum substrates from aqueous solution of hydrochloric acid or nonaqueous electrolytes [732, 733]. Both in water and in nonaqueous solutions the electropolymerization process obeys to the first order kinetics with respect to concentration of a monomer (Fig. 2.62).

Nanowires based on poly(1-amino-9,10-anthraquinone) were directly synthesized on a steel electrode preliminary modified by a thin film from poly(1-amino-9,10-anthraquinone-*co*-*o*-phenylenediamine) through SiO_2 mesoporous template (Fig. 2.63) [734]. It is shown that after removal of the template, nanowires of about 30 nm in diameter and 200 nm in length were fixed to the surface of poly(1-amino-9,10-anthraquinone) with high adhesive strength of polymer nanostructures.

A series of cross-linked poly(2-hydroxyethyl methacrylate) films containing 1,2-diaminoanthraquinone is synthesized for optical biomedical analysis of nitrites (nitrite-monitoring of biological liquids) and ecology (control over nitrite level in drinking water) [735].

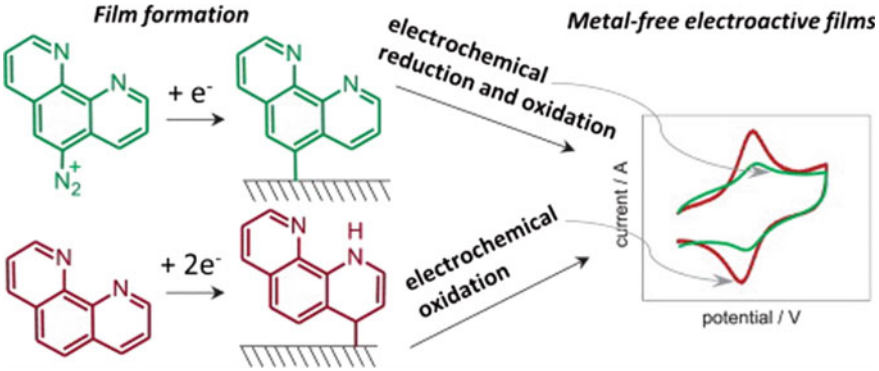


Fig. 2.61 Modification of carbon glass electrode

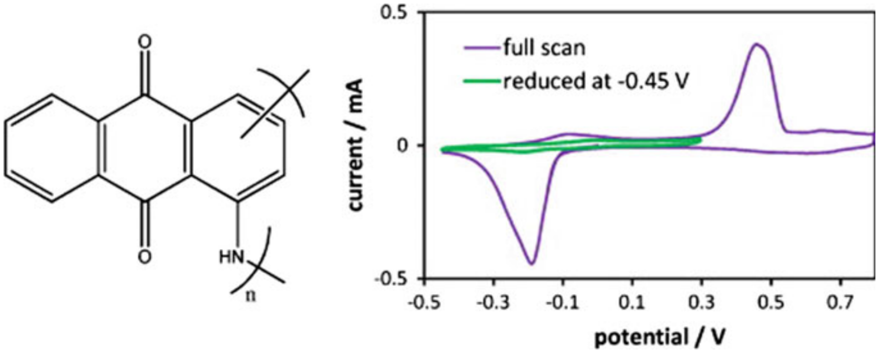


Fig. 2.62 Poly(1-amino-9,10-anthraquinone) synthesized using electropolymerization

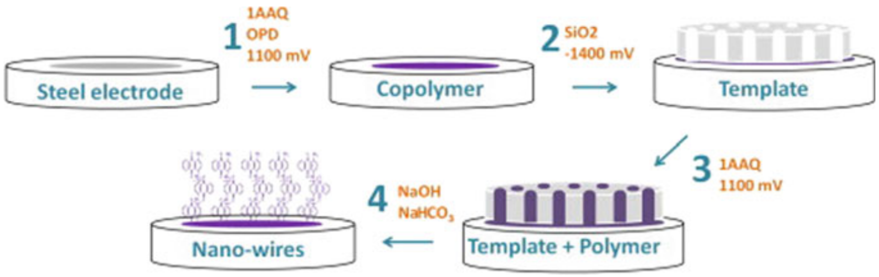
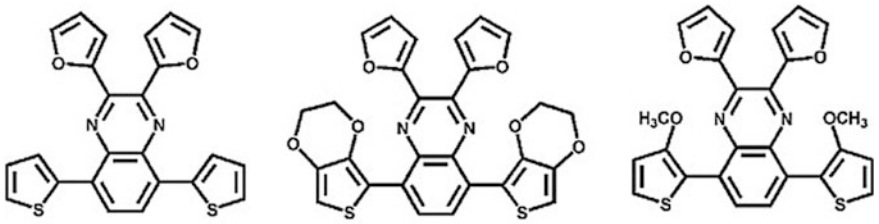


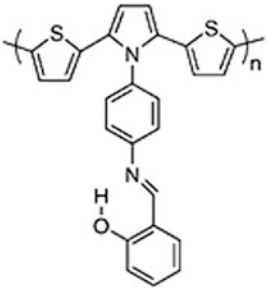
Fig. 2.63 Production of nanowires based on poly(1-amino-9,10-anthraquinone) through SiO_2 mesoporous template

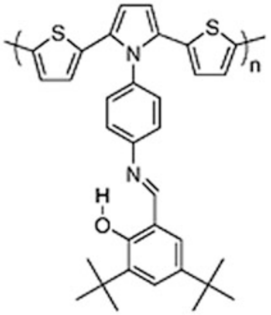
Electrochemical method was used to obtain donor-acceptor π-conjugated polymers with 2,3-di(2-furyl) quinoxaline chelating fragment: poly [2,3-di(2-furyl)-5,8-bis(2-(3,4-ethylenedioxythiophene)) quinoxaline], poly [2,3-di(2-furyl)-5,8-bis (2-thienyl) quinoxaline] and poly[2,3-di(2-furyl)-5,8-bis(2-(3-methoxythiophene)) quinoxaline] [736]. All synthesized polymers contain 2,3-di(2-furyl) quinoxaline unit in the main chain as acceptor block and different derivatives of thiophene as donor aggregates. Colorimetric analysis showed that the first and third polymers were green in the neutral state unlike the second polymer, which has a light blue color.



Poly(*o*-aminophenol) is produced electrochemically in previously deoxygenated acid medium. Initial rate of the reaction of electropolymerization on a platinum electrode is low and obeys to the equation $V = k_2[D]^{0.50}[HCl]^{1.125}[M]^{1.29}$. Apparent activation energy is 68.63 kJ mol^{-1} [737].

Electrochemical oxidation of *N*,*N*′-bis(3-methoxy-salicylidene)-1,3-propylendiamine brings to formation of a conducting CPL on the electrode surface [738, 739]. Similarly, 2,5-di-thienylpyrrole monomers containing salicylidenaniline fragments are electrically polymerized with formation of electrochromic conjugated films [740].





CPL films of N,S-type are deposited in situ on the surface of a carbon glass electrode using electrochemical oxidation of 2-mercapto-4-amino-5-cyano-6-phenylpyrimidine [741]; the polymer film consists of homogenous nanoparticles. Another chelating monomer of N,S-type, 2-aminothiazole is polymerized on Pt electrode using cyclic voltammetry from 0.01 M monomer solution containing 0.3 M ammonium oxalate solution with formation of homogenous and compacted film [742]. Poly(2-aminobenzothiazoles) are obtained by electropolymerization with 2-aminobenzothiazole and 6-ethoxy-2-aminobenzothiazole used as monomers [743].

Chelating 2,3-di(2-thienyl) quinoxaline fragment was included in an electrochemically synthesized conjugated polymer [744]. The similar chelating 2,3-di (2-thienyl) quinoxaline fragment is contained in some other monomers: 10,12-bis (4-hexylthiophen-2-yl)dibenzo[f,h]thieno[3,4-b] quinoxaline and 10,13-bis(4-hexyl thiophen-2-yl)dipyrido[3,2-a:2′,3′-c] phenazine [745]. We shall focus on electrochemical polymerization of sulfur monomers of 8,11-bis(4-octyl-2-thienyl)-acenaphthyl-[1,2-b] quinoxaline and 8,12-bis(4-octyl-2-thienyl)-acenaphthyl- [1,2,5] thiadiazolo[3,4,i]quinoxaline [746], as well as 6-(4-octyloxyphenyl)-4,8-bis(thiophene-2-yl)-3H-[d]imidazole [1,2,5] benzothiadiazole, and 4-(4-octyloxyphenyl)-2,6-bis (thiophene-2-yl)-3H-[d]imidazole-acenaphtho[1,2-b] quinoxaline [747]. The fluorescent polymer having reversible redox behavior, based on terthienyl with quinoxaline group directly linked to the third position of the central thiophene ring, is synthesized by electrochemical polymerization of 4-(2,5-bis(2,3-dihydrothieno[3,4-b] [1,4] dioxin-5-yl)thiophen-3-yl)pyrrolo[1,2-a] quinoxaline [748]. This polymer studied by fluorescence technique is selective with respect to Fe(III) ions (Fig. 2.64).

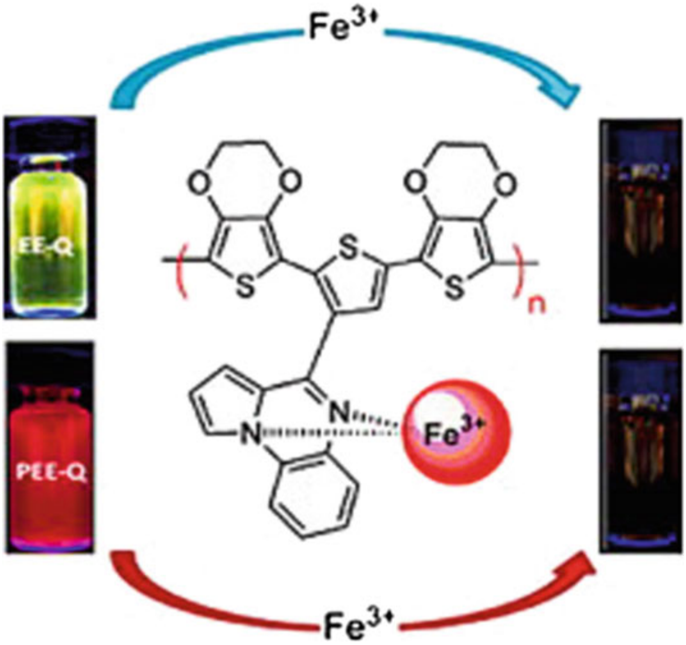


Fig. 2.64 The fluorescent polymer having reversible redox behavior, based on terthienyl with quinoxaline group, as a selective sensor with respect to Fe(III) ions

Electrochemical polymerization of 4-[(2,5-dithiophen-2-yl)thiophen-3-yl] pyrrol chelating monomer leads also to a fluorescent polymer [749].

Study of electropolymerization of protoporphyrin IX on highly oriented pyrolytic graphite (HOPG) showed [750] that Pp are adsorbed on electrode and are spontaneously self-assembled in ordered monolayers. Depending on origin of the substituents on periphery of the Pp ring, reduction of substituted tetraphenyl-Pp takes place in the range of negative potentials as a result of formation of π-anion radical and di-anion, and oxidation of Pp with formation of π-cation-radical and di-cation proceeds in the range of positive potentials [751]. In the case of tetrakis (*p*-aminophenyl)-Pp poly-Pp film is formed on electrode during electrooxidation. Electrochemical polymerization of the asymmetric 5,15-bis[4(-*N*,*N*-diphenylamino) phenyl]-10,20-bis[3-(*N*-ethylcarbazoyl)]-Pp with electrically active functionalities brings to formation of conjugate conductive and stable polymer films on the surface of semi-transparent ITO electrode [752], which makes them promising candidates for application in optoelectronic devices.

Electropolymerization of another Pp monomer, 5-(4′-aminophenylamino)-10,20-diphenyl-Pp, with amino group linking the Pp core and the aniline block makes it possible to obtain a polymer film forming a smooth layer on ITO and growing in normal direction to the electrode surface [753]. ITO electrode coated by electrochemically prepared film of poly(tetrathienyl)-Pp is photoactive electrode in photoelectrochemical cell of Z-scheme type [754].

Electrochemical polymerization of tetra-(4-hydroxyphenyl)-Pp on ITO brings to formation of films with nanostructured morphology [755], the same is attributed to electropolymerization of poly-1,3-bisdithienyl benzene, having a Pp group as a side chain [756] and to electropolymerization of Pp-fullerene monomer [757]. In this polymer the Pp blocks are linked via amino-phenyl group with formation of a linear chain, in which Pp is integral part of the main chain of the polymer. Chelating monomers obtained by interaction between Pp in 5,15-positions with tetra- and bithiophene are electrochemically polymerized on gilt electrodes [168].

A crown ether ring is contained in tetra-methyl-substituted 14-crown-4-3,4-pyrrol chelating monomer, which has been electrochemically polymerized for studying a possibility of its using as a sensor for lithium ion [758].

Highly efficient CPL are formed during electrochemical co-polymerization of chelating monomers with traditional monomers. Thus, copolymers of *o*-phenylenediamine and other aniline derivatives (for example, *o*- and *m*-toluidines [759–764]) were widely studied for improvement of chelating properties of homopolymers. In particular, in the case of *o*-phenylenediamine and *o*-toluidine copolymer obtained in aqueous solution of acid on ITO-coated glass electrode, a band at $\lambda = 497$ nm was assigned to head-to-tail mixed copolymer formed as a result of a cross-reaction between *o*-phenylenediamine and *o*-toluidine cation-radicals.

Poly(1-amino-9,10-anthraquinone-*co*-*o*-phenylenediamine) is synthesized using electrochemical method on stainless steel electrodes [765]. Topographic and morphologic characteristics have shown that incorporation of *o*-phenylenediamine increases homogeneity of a copolymer. Electrochemical copolymerization of aniline with 1-amino-9,10-anthraquinone showed formation of a clear picture of nanometer polymer particles up to 100 nm formed in conducting copolymers [766].

Electroactive copolymers of aniline and *o*-aminophenol were obtained on ITO-coated glass and gold electrodes [767] as well as carbon glass electrode modified by multi-walled carbon nanotubes (MWCNT) [768]. Copolymerization rate and properties of a copolymer depend strongly on the ratio between aniline and *o*-aminophenol [769], as in the case of copolymerization of aniline with anthranilic acid [770, 771] or 2-aminodiphenylamine [772].

There is interesting electrochemical copolymerization proceeding through formation of a cation-radical of diphenylamine with chelating monomers 2,5-diaminobenzenesulfonic acid [773], anthranilic acid [774, 775], and *o*-phenylenediamine [776].

Pyrrol and anthranilic acid copolymers with block structure have been produced by electrochemical method: order of the reaction by electric current density, HCl concentration, and monomer concentration is 1.02, 1.44, and 2.0, respectively. Pyrrol has the coefficient of relative reactivity to copolymerization 1.58, while anthranilic acid has 0.14 [777].

Photoluminescent and electroluminescent spectra of poly(*N*-vinyl-Cz) and 2,9-dimethyl-4,7-diphenyl-phen (1:1) films are studied [778].

Electrochemical copolymerization of Cz and dibenzo-18-crown-6 into pure boron trifluoride diethyl etherate was carried out using direct anode oxidation of monomer mixtures on electrodes made of platinum or stainless steel [779]. The copolymer films showed better electrochemical behavior as compared with homopolymers, they displayed excellent fluorescent properties, and good mechanical properties, and had higher thermal stability and higher electric conductivity.

Tuning of chelating groups of thin films of SP-containing copolymers for color-specific linking of a metal ion is performed using two monomers: SP-methacrylate and SP-methacrylate with methoxy-substitutent in 8′-position of benzopyran ring [780]. MMA and 2,2,2-trifluoroethyl methacrylate were chosen as comonomers. It has been shown that each metal ion generates unique calorimetric reaction for SP-containing copolymers.

A conducting polymer containing MC in the polymer backbone was prepared by electropolymerization of a SP fragment covalently linked between two alkoxythiophene units. Utilizing the known metal coordination capabilities of MCs, introduction of cobalt ions into the electropolymerization led to an enhancement of the morphology, conductivity and optical properties of the PMC films (Fig. 2.65) [781].

The main advantage of electrochemical methods is their one-stage approach, in particular, a possibility of exclusion from the technological scheme stages of preliminary synthesis of polymer material, it's following dissolution or dispersion and fixing on a substrate, uniting all these stages in one process. Another important property is that electropolymerization makes it possible to deposit at high rate uniform polymer coatings on substrates with complicated configuration. The third positive factor is a possibility of automation of these processes.

At the beginning of 1990s, when polymer films produced using chemical and electrochemical methods from aniline, pyrrol, Py, thiophene and their derivatives were already widely studied and produced on the industrial scale, a range of works appeared concerned with their plasma-chemical synthesis [21, 782]. Increased attention in this method is explained by the fact that is provides production of thin uniform in thickness structures with a small number of macroscopic defects on substrates of any form and origin. At that, because solvents, surfactants and oxidants are not used, the problem of polymer purification does not arise. Deposition of CPL using polymerization in low-temperature plasma provides fabrication of thin functional layers of thickness from 0.001 to 10 μm using a relatively simple technique of vacuum deposition. Thus, plasma polymerization of en is studied for modifying surface of quartz particles for optimization of concentration of nitrogen-containing coatings produced through rotating barrel of a plasma reactor [783]. Uniform distribution of chelating groups over all surface of a particle is shown. Plasma polymerization of 1-amino-9,10-anthraquinone in electric discharge to a conducting polymer (1×10^4–1×10^5 Ω cm^{-1}) of highly conjugated structure has been carried out [784].

Fig. 2.65 A MC-based conductive polymer prepared by electropolymerization of a SP moiety covalently linked between two alkoxythiophene units and forming chelates with Co(II) ions

To produce CPL based on polymer films, cationic photopolymerization occurs to be a successful method. Thus, it has been shown that photopolymerization of tetra-alkylepoxy-Pp takes at least 10 min of illumination at 90 °C, while thermal polymerization of the same sample takes 10 min of heating in dark at the temperature 150 °C. Tetra-alkylepoxy-Pp acts as a self-sensitizer for cationic photopolymerization [785]. Cationic photopolymerization of liquid monomers based fullerene and Pc was used to obtain polymer films suitable for using in complex solar cell constructions (Fig. 2.66) [786].

2.5.3 *Chemical Modification of Polymeric Films*

A special place among methods of design of CPL films on solid surfaces has chemical modification (functionalization). Thus, modification method for surfaces of PE films by integration of chelating carboxylic acids, in particular, PAA (using

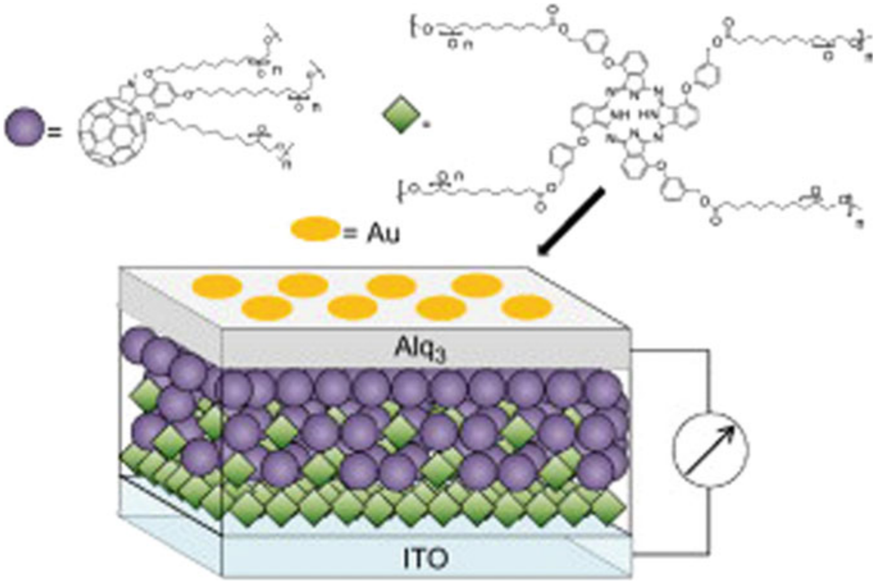


Fig. 2.66 Complex solar cell constructions using polymer films based on fullerene and Pc

PEI or en cross-linking agents) is proposed [787]. The modifying PAA content is 9.12 ± 0.71 mmol of carboxyl groups per 1 cm^2. Modified surface of a PE film has higher affinity to Fe(III) ions than to Fe(II) ions at optimal binding pH 5. These CPLs can be applied in chelatotherapy using heavy metals. Modification of PP films can be performed in a similar way. Chelating ability of films is adapted by changing conditions, for example, grafting density [788]. Even higher chelating activity can be reached by transformation of carboxyl groups grafted to a PP film into polyhydroxamic acids [1]. The obtained modified films show increased chelating capacity with respect to iron ions ($\sim$80 nmol cm^{-2}). This is one of the ways of the biomimetic design of chelating interface surface, which can broaden the application field of PMC in restoring of environment, water purification and active packaging cleaning.

A chelating ligand, IDA was covalently immobilized on poly(MMA-GMA) films prepared using UV-initiated photopolymerization of epoxy groups [789]. Cu(II) ion was chelated by immobilized ligand.

Electrochemical sensor of lead ions was developed by modification of an electrode based on carbon paste using polypyrrol, functionalized by IDA (Fig. 2.67) [790].

The 5-nitroquinoxalines, substituted in 2 and 3 positions by 2-pyrrolyl, 2-furyl, and 2-thienyl groups are used as active components in PVC membranes and electrically polymerized electrodes, which were then tested as possible sensors for different cations [791].

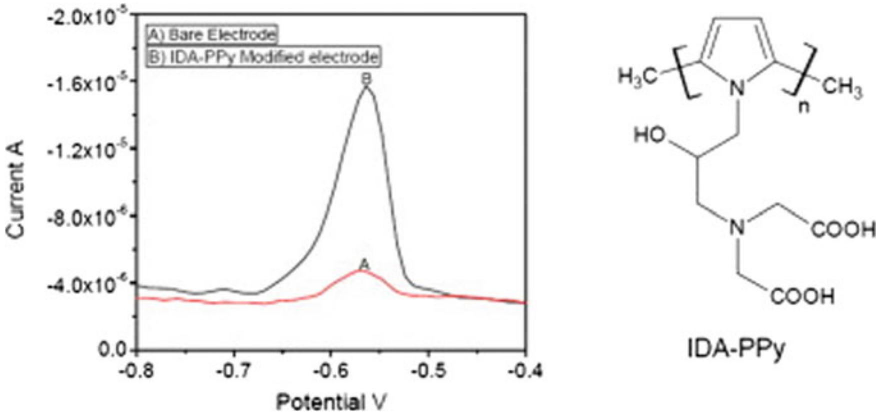


Fig. 2.67 Electrochemical sensing Pb(II) ions using carbon paste electrode modified with polypyrrol modified by IDA

An example of modification of the polymer films using macrocyclic unit can be (2,3,9,10,16,17,23,24-octa-[(4-carboxylate)-phenoxy]-Pc)-St-alkyl(meth)acrylate polymer films [792].

2.6 Liquid Crystal Chelating Polymers

Recently new area of CPLs, liquid crystal polymers (LCP), has being intensely developed. Macromolecular compounds capable of transforming into liquid crystal state under certain conditions (temperature, pressure, concentration in solution) belong to these polymers [793–798]. Since it takes an intermediate place between amorphous and crystal states, it is also often called mesomorphic or meso-phase (from Greek mesos, which means intermediate). Typical features of a meso-phase are presence of orientation ordering in macromolecular arrangement (or their fragments) and anisotropy of physical properties in absence of external actions. The main advantages of the LCP are stipulated by their dual nature, which provides in one material properties of macromolecular substances (with their ability to form films, glasses, fibers, and coatings), and mesomorphic properties of liquid crystals (which, in turn, display dualism of properties).

Similarly, to low molecular weight liquid crystals [799–802], LCP form the same structural types of meso-phases: nematics (N), smectics (S), and cholesterics (Ch) with typical for them arrangement of mesogenic fragments, presence of orientation order in nematics and layer order in smectics. In the cholesteric phase formed by optically active polymers, helical structure is formed, which determines special optical properties of cholesterics (Fig. 2.68).

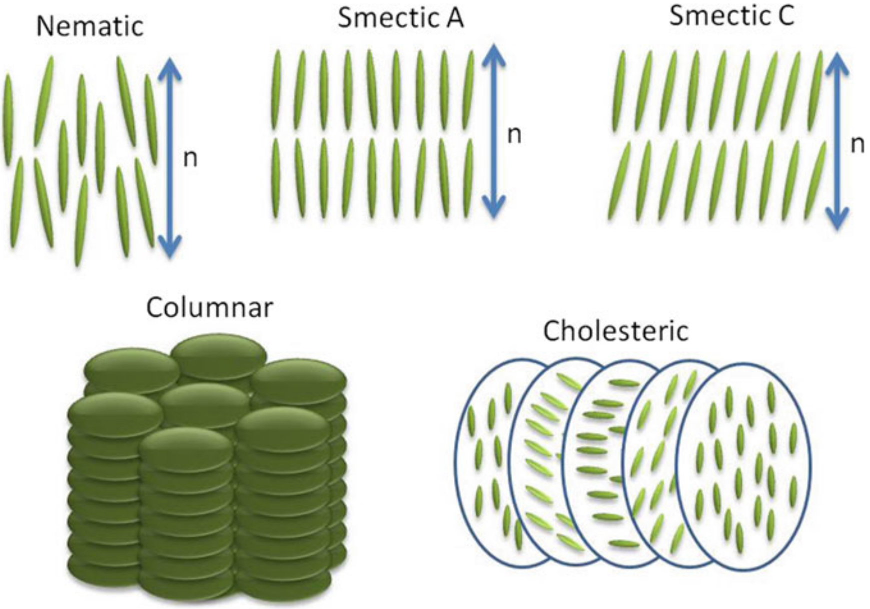


Fig. 2.68 Different phases of liquid crystals

Rod-like structure in a molecule consisting of several aromatic or heterocyclic rings linked directly or through different spacers predetermines behavior of a liquid crystal during heating or in a concentrated solution. If a meso-phase is formed during dissolution of polymers in certain solvents, they are called lyotropic LCP, and if polymers transform in the liquid crystal state or in meso-phase as a result of thermal treatment (heating or cooling), they are called thermotropic LCP. In the case of lyotropic LCP formed in solutions, a certain structural type of meso-phase is realized at exactly determined temperatures and concentrations of a polymer in solution and is displayed on their phase diagrams. Thermotropic LCP transit into the liquid crystal state above the melting point (T_m) or at higher than T_g or at the softening temperature if an initial polymer does not crystallize. These temperatures correspond with the lower boundary of a liquid crystal phase formation, while the upper boundary is so called isotropization temperature (T_i) above which a polymer transit into isotropic melt. Particularly in the temperature range T_g (or T_m)—T_i mesogenic fragments of a LCP organize spontaneously, forming a certain structural type of a meso-phase (N, S or Ch) with respect to molecular structure and molecular weight of a polymer.

Lyotropic liquid crystal state is most typical for rigid-chain polymers capable of very specific phase separation. The liquid crystals of this type are binary or ternary systems, which differ by a structural type as layered, rod-like, and cubic. Lyotropic LCP is characterized by high rigidity of macromolecules, high melting points being near temperatures of chemical decomposition, which excludes a possibility of appearance of a thermotropic meso-phase. However, despite this,

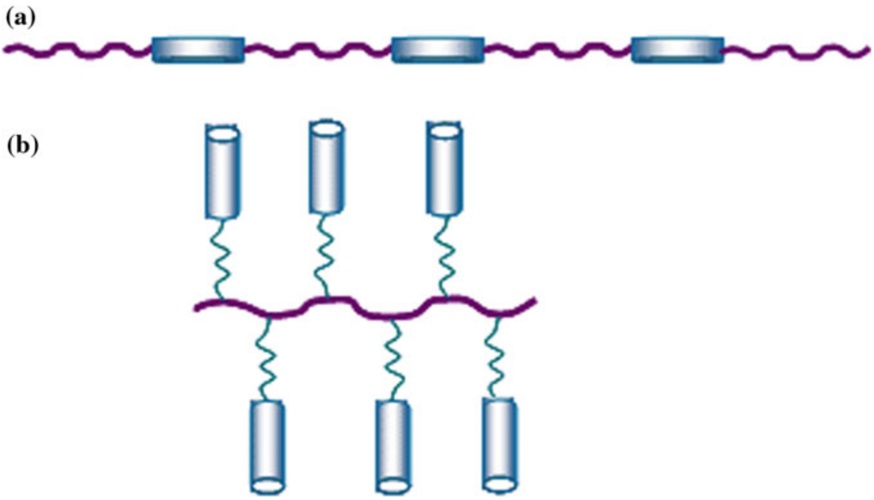


Fig. 2.69 Basic types of LCP: **a** polymers with mesogenic groups in main chain, **b** side-chain or comb liquid crystal polymers

rigid-chain polymers form lyotropic liquid crystal systems in such highly polar solvents, as sulfuric and chlorosulfonic acids, dimethylacetamide with lithium chloride, etc.

Thermotropic LCP is formed by chemical bonding of rigid and flexible fragments into one macromolecule, which can have linear or branched (comb-like) structure (Fig. 2.69). At that, molecules of low molecular weight liquid crystals or their mesogenic groups responsible for formation of a liquid crystal phase are usually used as rigid fragments. In turn, flexible fragments, usually called spacers, lowering rigidity of macromolecules due to their special dilution, decrease T_m of polymers, giving rather high autonomy to rigid mesogenic groups, which is necessary for their cooperative interaction with a meso-phase formation.

Instead of flexible fragments, other chemical groups can be used, which break linear structure of the rigid-chain macromolecules. In particular, a decrease in rigidity can be reached by integration of bulky substituents or chemical groups, which advance appearance of bends in a chain and break in their symmetrical linear structure (for example, due to presence of phenylene or naphthalene cores included in a chain not in *para*- but in *meta*- or *ortho*-positions).

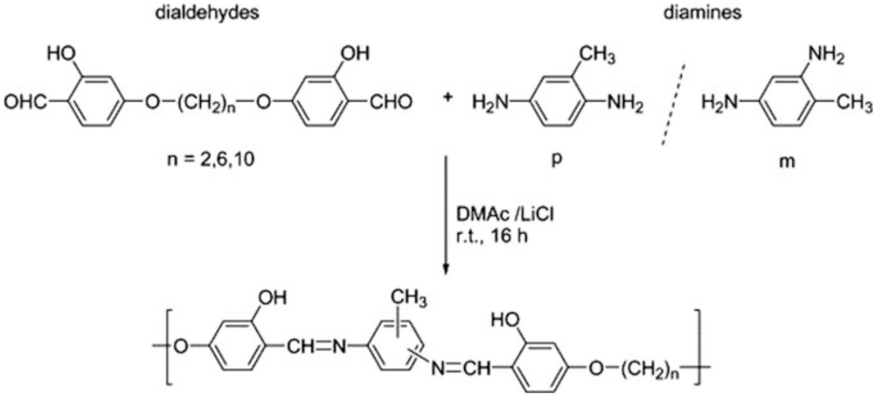
2.6.1 Polycondensation in the Synthesis of Liquid Crystal Polymers

The main structural units of the rigid-chain polymers of linear structure are aromatic or heterocyclic fragments bound collinearly with each other via different spacers. Most often such polymers are produced by polycondensation or co-polycondensation of similar or different bifunctional derivatives [803–814]. Thus, a wide range of polyimines is synthesized by polycondensation of diamines or hydrazines with dialdehydes, diketones or quinones [815–827]. Other known classes of LCP, such as polyimides and polyquinoxalines are produced on the basis of cyclic aliphatic, fluorinated, heterocyclic, Cz, perylene monomers of non-coplanar structure (loop, spiro, and cardo), chiral compounds and compounds with non-linear optical properties and non-symmetric structure [828, 829].

A series of semi-flexible homo- and co-polyazomethines containing imine bond in polymer backbone is synthesized based on hydroxyl-functionalized mesogenic cores with aliphatic spacers (Scheme 2.37) [805].

For polyazomethines containing *p*-substituted diamine, for example, 2-methyl-1,4-phenylenediamine and aliphatic chain with two CH_2-groups (polymer P2), the T_m = 333 °C was measured closely to decomposition, and no meso-phase was detected. However, with an increasing spacer length, the transition temperature decreases, and formation of a meso-phase is more probable. Thus, for P6 polymer two endothermic points are established, at 229 and 259 °C, and the polymer with ten methylene groups (P10) has shown only one T_m, 175 °C, at that, both homopolyazomethines (P6 and P10) have typical nematic textures.

Poly(azomethine ethers), which display thermotropic liquid crystal properties, are formed [807] at polycondensation of different diamines and 4,4′-diformyl-α,ω-(diphenoxy) decane or 4,4′-diformyl-3,3-methoxy-α,ω-(diphenoxy)decane. The mesogenic transition temperatures decrease as a number of methylene groups increases from tetramethylene to hexamethylene; the similar tendency is observed for polymers containing aromatic segments. Nematic meso-phase formed only for the polymer synthesized from 1,4-phenylenediamine and benzidine, and for polymers based on tetramethylenediamine, there was absolutely no meso-phase observed. On the other hand, the polymer with six methylene spacers had a grainy texture.



Scheme 2.37 Synthesis of co-polyazomethines based on hydroxyl-functionalized mesogenic cores and aliphatic spacers

Copolymers of polyazomethine ether obtained by polycondensation in solution with different diamines (for example, 1,4-phenylendiamine, 4,4′-diaminodiphenylmethane, etc.) show nematic liquid crystal thermotropic properties [830].

A study of the effect of length of methylene interchange on molecular mobility and dipole moment of polyazomethine ethers with azomethine-aromatic groups in *o*-position has shown that for them existence of four relaxation processes in solution is typical [831]. Parameters of molecular mobility (relaxation time and activation energy of three local processes) depend nonmonotonically on the methylene interchange length, showing the even-odd effect. In the case of the fourth large-scale process these parameters have high values and increase monotonically as the interchange length increases. This can be due to special features of conformation of the ester part of a macromolecule, which is also confirmed by theoretical analysis of geometric and electronic structure of coplanar conjugated polyazomethines [832].

Another group of polyazomethine ethers has been obtained using polycondensation of diformyl-*o*-diphenoxyalkanes and 2,7-bis-(*m*-aminobenzylidene) cycloheptanone or bis-(*m*-aminobenzylidene) acetone [808].

Mesomorphic properties of these polymers are determined by nature of diphenoxyalkane spacers (length of a spacer is 2, 4, 6, and 8 methylene units in the dialdehyde structure) independently of a diamine structure. At that, polymers synthesized from diamine with a cycloaliphatic core showed high T_m and T_i points as compared with polymers obtained from acetone-derivative diamine and the same dialdehydes [808].

Study of thermal behavior of a LCP including alternating polyazomethine and random poly-ester showed that it has the T_g = 43 °C, which is far lower than the crystallization temperature 97 °C, and two endotherms at 141 and 163 °C. This indicates the transition from half-crystalline nematics to nematic liquid.

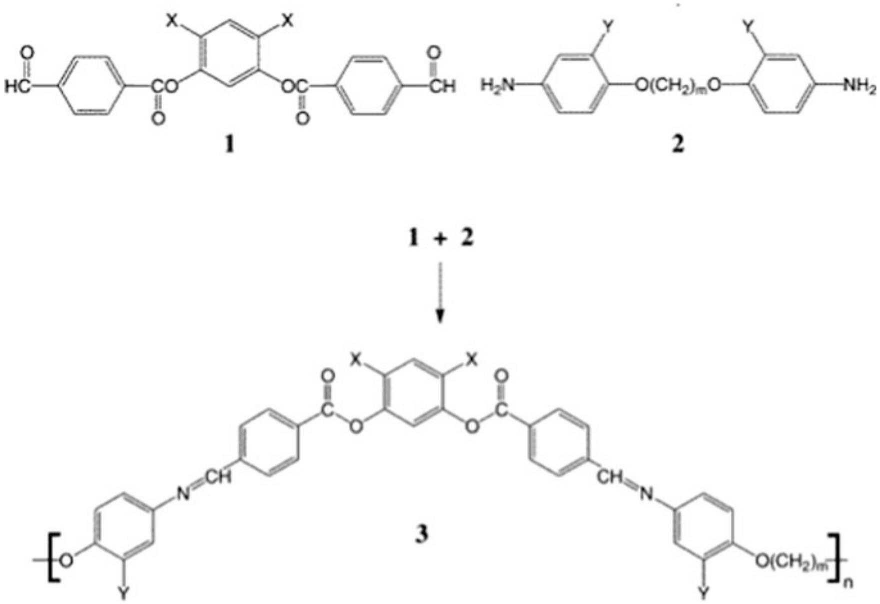
Synthesis of twelve different azomethine polymers with the main chain containing banana-shaped mesogens is described (Scheme 2.38) [809].

Formation of a meso-phase also depends on length of aliphatic spacer and substituents in a mesogen ring. Thus, for polyazomethines with short (m = 6) spacer and carrying two or four halogen atoms, a nematic phase formation was observed, and longer aliphatic spacers (m = 12) governed formation of smectic meso-phase.

Also chiral salicylaldimine compounds including a fluorocarbon chain, with calamic molecular shapes are produced (Fig. 2.70) [833].

Liquid crystal polyazomethine ether with side dimethoxybenzylidene groups has been obtained by polycondensation of a diacid monomer benzalaniline-3′,4′-dimethoxy-terephthalic acid with two diol monomers [834].

Cross-linked LCP are obtained based on the liquid crystal twin epoxy monomers, containing azomethine groups, cured by aromatic diamines [810].



Scheme 2.38 Synthesis of azomethine polymers with the main chain containing banana-shaped mesogens

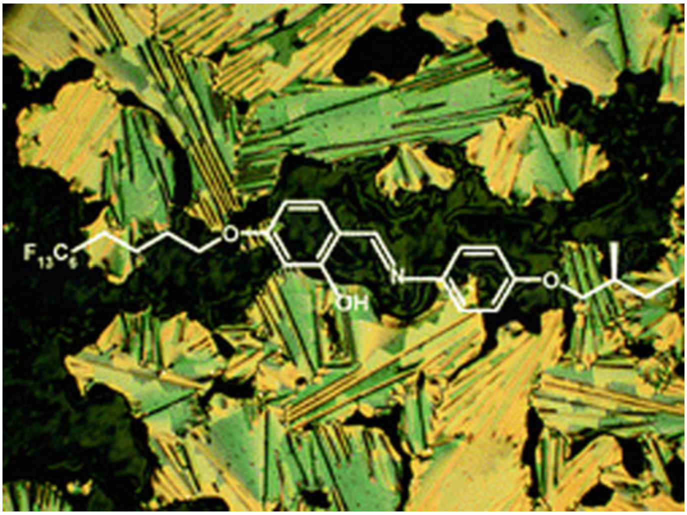
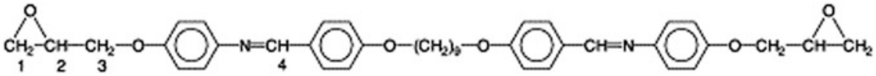
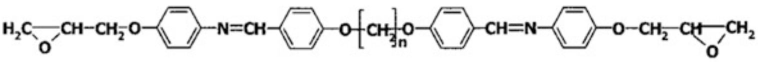


Fig. 2.70 Calamic molecular shapes of chiral salicylaldimine compounds including a fluorocarbon chain

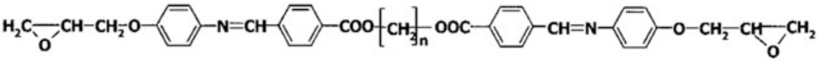


Nematic meso-phase showing schlieren textures was observed for all epoxy monomers after melting with the temperature of the meso-phase formation between 10 and 17 °C.

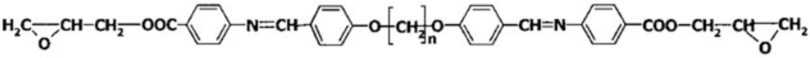
Another series of twin monomers with the end glycidyl group linked to the group of ester or ether and having aliphatic spacers of different lengths was used for producing rod-like aromatic imine structures with ester or ether bonds [811].



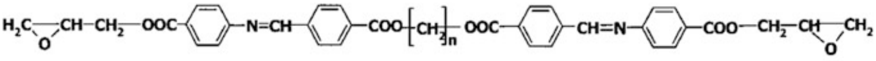
IAn



IBn



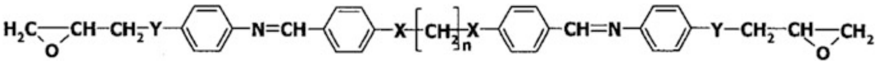
IIAn



IIBn

These monomers show mesogenic behavior, and their architecture influences a type of meso-phase. Thus, monomers of IA, IIA, and IIB series formed nematic meso-phases, and IB monomers formed smectic meso-phases depending on a length of aliphatic spacer. In particular, monomers with odd number of methylene groups formed smectic C meso-phases, while monomers with even number of methylenes formed smectic A meso-phases. After curing of homopolymer epoxy resin by 2,4-diaminotoluene and *p*-amino-acetophenone azine, a cross-linked epoxy resin is formed, which shows nematic meso-phase, excluding monomers of IB series with spacers of 8 and 10 methylene groups, for which smectic C meso-phase is formed. When the tertiary amine, 4-(*N*,*N*-dimethylamino) pyridine was used as a catalytic cross-linking agent, all monomers of IB range formed smectic C phases, whereas monomers of IIA series gave nematic phases [811].

Liquid crystal meso-phases [812] are formed in polyurethanes synthesized from diols containing four phenyl rings linked in *p*-position by azomethine and ether bonds and end spacers from 2 to 10 methylene groups and two isocyanates, hexamethylene diisocyanate and methylene-bis(cyclohexyl isocyanate).



Diols and polyurethanes produced from them showed formation of nematic meso-phase during heating. In both series of polyazomethines the transition temperature decreased as length of a flexible spacer increased, and it was somewhat higher for the polymers synthesized from hexamethylene diisocyanate than in the case of polymers produced from diisocyanates with cyclohexyl fragments [812].

A great number of liquid crystal polymeric crown ethers, as well as azacrown ethers, thiacrown ethers, and crown ethers with different heteroatoms is known [835]. Microcrystallinity in them is conditioned by substituents bound to crown ethers, depending of nature of which, rods, discs or tapers can form bringing to different types of meso-phases.

Thus, LCP of poly-esters containing dibenzo-18-crown-6 units are obtained by polycondensation in solution of 4,4′-(α,ω-alkandiol) dibiphenylyloyldichloride, *cis*-4,4′-bis-(4-hydroxyphenylazo) dibenzo-18-crown-6, *trans*-4,4′-bis(4-hydroxyphenylazo) dibenzo-18-crown-6, and 1,10-decandiol. Copolymers formed nematic meso-phase in melt, which has a texture of twisted fiber, grainy or schlieren-texture, and the T_m and T_i of the copolymer decreased as length of a flexible spacer increased [836].

Polycondensation of 4,4′-(alkylenedioloxy) dibenzaldehyde, *cis*-diaminodibenzo-14-crown-4, and *trans*-*cis*-diaminodibenzo-14-crown-4 in solution was used to produce LCP of Schiff base type and containing cyclic units of crown ether. These polymers have M_n = 13,000–24,000 and transform into liquid crystal state at the temperature above the T_m. Most synthesized polymers had wide meso-phase range, though some of them are liquid crystalline in nematic phase [837]. In the similar way polycondensation of 4,4′-(alkylenedioloxy) dibenzaldehyde and diamine-dibenzo-15-crown ether in solution were used to synthesize Schiff bases of liquid crystal polymeric crown ether. Their M_n = 10,100–13,000 and they transform into liquid crystal state at melting with formation of two types of textures, their T_m, T_g, and T_i depend on a type of flexible spacer [838].

Photochromic LCP, which contains azobenzene and crown ether groups, is synthesized [803]. Positions of the crown ether groups with respect to photochromic fragment have an effect on phase and spectral properties, and on kinetics of photo-orientation of the polymer thin films. These photo-oriented polymer films can be used as sensors of metal ions.

Polymeric liquid crystal crown ethers are formed using polycondensation in the solution consisting of 4,4′-(alkylenedioloxy) dibenzaldehyde, *cis*- and *trans*-4,4′-diaminodibenzo-18-crown-6. All obtained polymers transform in the liquid crystal state upon heating up to the T_m, at that nematic phase has typical schlieren texture, while the smectic phase is focal-conic, and the T_m and T_i depend on a type of flexible spacer [839].

2.6.2 Liquid Crystal Polymers Obtained by (Co) polymerization

Liquid crystal meso-phases can also be formed using polymers with mesogenic fragments linked to the main chain as side groups [809, 814–824, 840]. The principle of production of comb-like LCP with side mesogenic groups is in synthesis of monomers with mesogenic groups and their further homopolymerization or copolymerization with mesogenic or non-mesogenic compounds. Thus, LCP are obtained by free radical polymerization of salicylaldimine monomer 6-[3-hydroxy-4-(4-octadecyloxyphenyliminomethyl) phenoxy] hexyl methacrylate in presence of AIBN [841].

Different meso-phases have been found in methacrylate polymers with liquid crystal fragments in the side chain based on ω-hexyl-, ω-butyl-, and ω-undecyloxy-salicylaldimine with *n*-alkyl or *n*-alkyloxy end substituents [842, 843]. In particular, for decyloxy-, dodecyloxy-, and octyl-derivatives formation of smectic C_2 phase was observed in wide temperature range, while tetradecyl-derivative shows a complicated behavior: first smectic A_d phase appears, which transforms into smectic C_2 phase, and then into smectic C_d phase [842].

Liquid crystal oligomers with side salicylaldimine groups were obtained using free radical polymerization of respective monomers 5-(10-undecenyloxy)-2-[[(4-(hexyloxy) phenyl) imino] methyl] phenol and 5-(10-undecenyloxy)-2-[[(4-(hexyl) phenyl) imino] methyl] phenol [844, 845]. These oligomers form smectic meso-phases similar to those of the initial monomers, and displacement of hexyloxy-chain by hexyl-chain brings to the smectic C meso-phase.

Another way of production of comb-like LCP is linking low molecular weight liquid crystal molecules to a polymer chain. In this case, it is necessary that the polymer and mesogenic molecules involved in the reaction would have functional groups capable of interaction. Thus conducting copolymers of poly [1-(thiophene-3-methoxy)-6-(4-*n*-hexyloxy-2-oxybenzoic acid) hexane] and 3-*n*-hexylthiophene containing side mesogenic groups attached parallel to the backbone are synthesized. In this case transformation of non-mesogenic intermediate polymers to LCP with high temperature-dependent conductivity was observed, which pointed to a decrease in activation energy of the liquid crystal phase [846].

Liquid crystal thermosets epoxy resins with *bis*-azomethine biphenyl mesogenic groups are formed during co-polymerization with non-mesomorphic epoxy compounds. Under action of primary aromatic diamines, *tert*-amines, and during co-polymerization with non-mesomorphic epoxy monomers, a cross-linked network structures are formed [847].

Thermal and photopolymerization of mesogenic azomethine monomers with methacrylic and vinyl ether end groups have been carried out [814].

These monomers showed mesogenic behavior and, in most cases, a variety of smectic meso-phases. Photopolymerization was carried out in presence of a photoinitiator at the temperature, at which monomers formed smectic or nematic meso-phase. It has been established that mono- and di-acrylates have similar textures [814].

Formation of liquid crystal phases is significantly affected by structure of main chain of polymers having mesogenic side groups [815]. Thus, polymer **1** with MMA main chain formed nematic phase upon heating above T_g, and polymer **2** did not form a meso-phase, even if it had the same mesogenic side groups. However, copolymerization of MMA mesogenic monomer with MMA or methacrylic acid brought to polymers **3** and **4** with liquid crystal properties, whereas content of non-mesogenic monomer in copolymer did not exceed 20%.

Formation of symmetric azomethines of smectic A and B meso-phases is shown for the case of thermotropic symmetric azomethines based on poly-1,4-butanediol--bis(4-aminobenzoate) and 1,4-biphenyl carboxaldehyde [848].

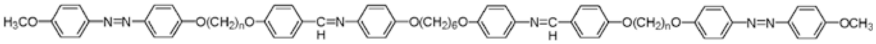
A range of modified polyguanidines was synthesized, which were characterized by their liquid crystal properties (chirality, homogeneity of side chains length, linking mesogens to side chains) [849].

Studies of luminescent thermotropic liquid crystal polyazomethines containing a chromophore mesogen based on fluorene and/or oxadiazole, showed formation of nematic meso-phase containing alternating or statistical oxadiazole units. Mesomorphic state keeps ordering degree of semi-crystalline compounds, which confirms the liquid viscosity. Based on the obtained polymers, it is possible to produce monodomain or multidomain ordered thin films with good mechanical and luminescent properties [850].

The polymer with liquid crystal side chain has been obtained from tolane based on hemi-phasmid benzoic acid and poly-4-vinylpyridine (P4VP) [851]. It forms smectic and hexagonal columnar meso-phases with different compositions, which determine luminescent properties of the polymers.

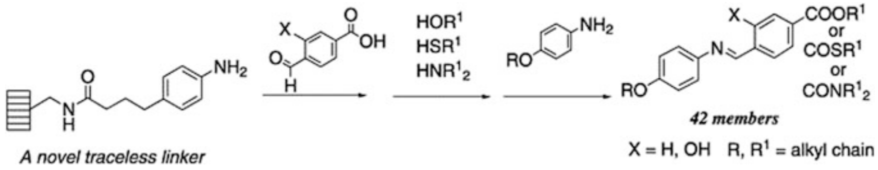
Liquid crystal co-polyesters containing X-shaped 2D mesogenic units and crown ether cycles of *cis*-4,4′-bis(4-hydroxyphenylazo)-dibenzo-14-crown-4 in a side chain were obtained [852].

It should be noted that many studies have been performed with liquid crystal azomethine oligomers in order to incorporate them into a polymer chain [820–826]. For example, a series of semi-flexible liquid crystal tetramers was obtained [820], in which length of the central spacer was six methylene units, and lengths of exterior spacers varied from 3 to 12 methylene units.



All tetramers showed enantiotropic nematic phase, and the transition temperatures depend on length and ratios of external flexible spacers. Properties of this series of polymers were comparable with the respective series containing central pentamethylene spacer, and the transition temperatures showed pronounced odd-even effect with increase in lengths of the external spacers (even spacers gave higher values) [820].

For LCP based on fluorinated carbon chains with end SF_5 groups a transition from nematic to smectic A phase is detected [821].



Recently LCP with very different topology, for example, block-copolymers, graft-copolymers, graft-block-copolymers, etc. (Fig. 2.71) were synthesized [794]. Thus, liquid crystal rod-coil di-block-copolymers (coil-conformation of St segments and rigid-rod conformation of mesogen-jacketed 2,5-bis[(4-methoxyphenyl)-oxy-carbonyl]-St segments) with different molecular weight and low PDI are obtained using ATRP method [853]. Liquid crystal behavior of polymers depends on molecular weight of a rigid segment. Thus, only copolymers with M_n of a rigid block above 9300 can form liquid crystal phases above T_g of the rigid block.

A range of liquid crystal block-copolymers of ABC_2 type with azobenzene fragments in the side chain has been obtained by combination of ATRP and chemical modification reaction (Scheme 2.39) [854].

Photopolymerization of polyfunctional liquid crystal monomers with ester spacers was applied to obtain monolithic ordered LCP nets [855]. Using different strategies of synthesis, it is possible to control molecular orientation of polymers in all three dimensions (Fig. 2.72). A film based on LCP has alternating plane chiral nematic areas near perpendicularly oriented (so called homeotropic) areas, and the

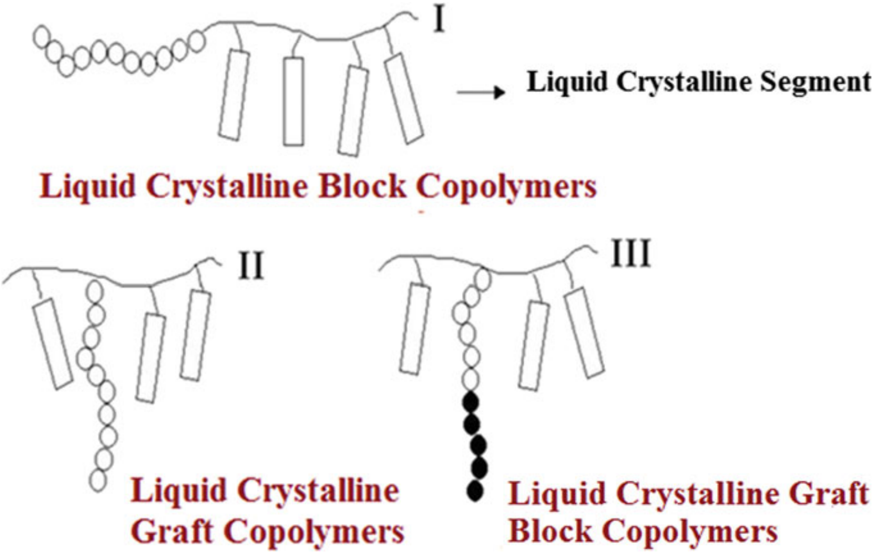
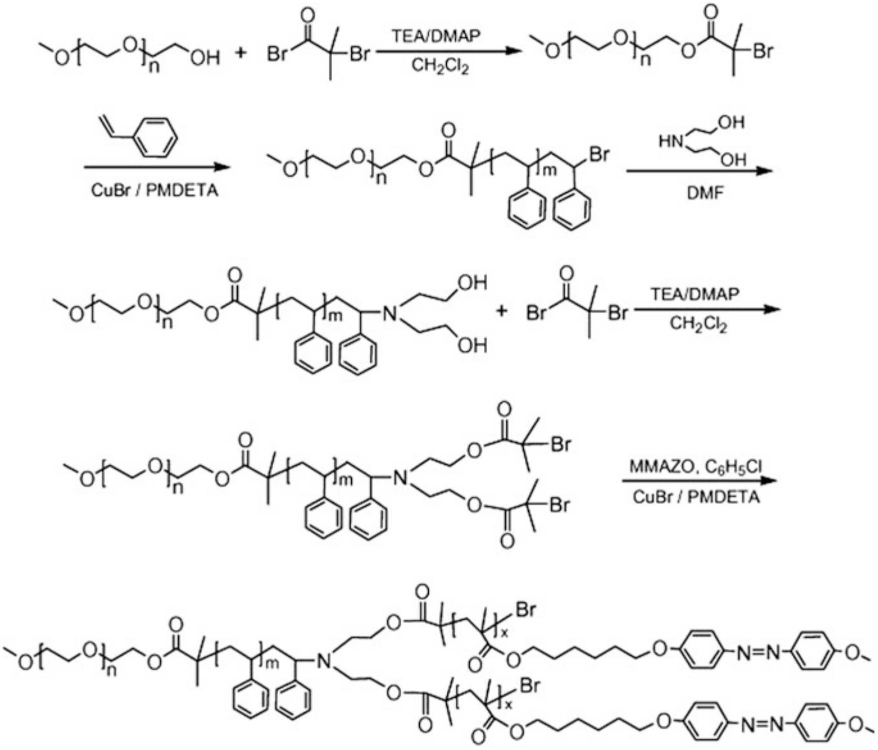


Fig. 2.71 Structures of liquid crystalline block copolymers, liquid crystalline graft copolymers, and liquid crystalline graft-block copolymers



Scheme 2.39 Scheme of production of liquid crystal block-copolymers of ABC_2 type with azobenzene fragments in the side chain by combination of ATRP and chemical modification reaction

film changes its surface texture upon deposition as a coating. It is important to notice that during action of UV light it switches from plane to corrugated state.

Based on interpenetrated liquid crystal-hydrogel polymer nets, stimuli-responsive materials have been obtained [856]. These materials consist of cholesteric liquid crystal nets, which reflect light, and entangled polyacrylate nets, which provide humidity reaction, pH humidity, and pH response.

Numerous studies have been carried out on production of LCP nets of other types [857]. In particular, a cross-linked film based on polyarylamide with fiber morphology occurs photomechanically sensitive [858]. 3D shape of LCP nets prepared with different cross-linking density is determined by the cross-linking density and conditions of preparation, in particular, polymerization temperature [859].

LCP can also be obtained by the photoinduced surface relief grafting, which provides orientation control over meso-phases on surface [860]. In particular, plane, perpendicular and patterned orientation of meso-phases can be easily obtained, using photo-control, with a monomer, 4-propyldiphenylacetylenecarboxylic acid

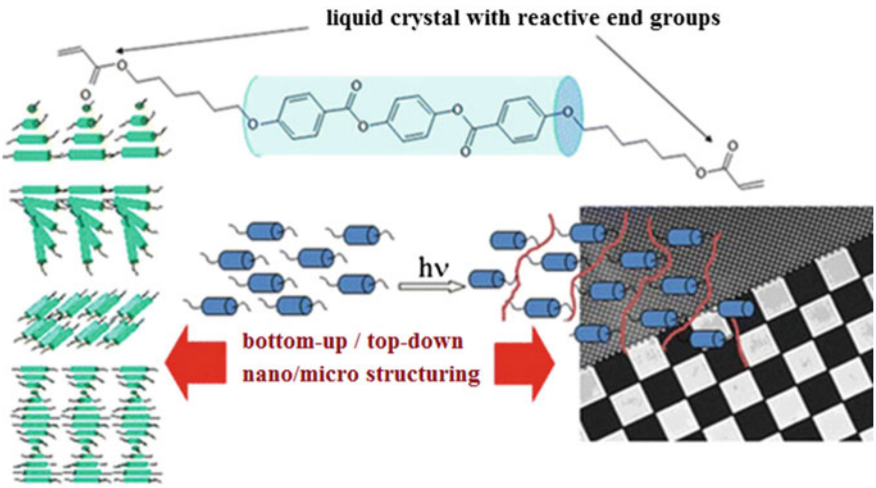


Fig. 2.72 Scheme of photopolymerization of polyfunctional liquid crystal monomers with ester spacers for the production of monolithic ordered LCP nets

cinnamon ester. 3D ordering in LCP is achieved during photopolymerization of the mixture of mesogens sandwiched between two patterned substrates [861].

2.6.3 Liquid Crystal Dendrimers and Hyperbranched Polymers

Recently much attention is focused on liquid crystal dendrimers and hyperbranched polymers [862–868]. Tuning of meso-phase structure of these polymers can be reached using respective molecular design depending on chemical nature of end mesogenic groups, dendritic core, and a number of generations of a dendrimer. Liquid crystal dendrimers can also contain mesogenic groups as a side or main chain, and in the latter case two types of dendrimers are formed: willow-like and octopus dendrimers. A range of other dendritic matrices is obtained: shape-persistent dendrimers, fullerodendrimers, polypedes and rod-coil block *co*-dendrimers [862, 867].

Thus, block *co*-dendrimers consisting of multifunctional mesogenic and Cz-containing 2,2-bis(hydroxymethyl)propionic acid of dendrons are synthesized [868]. Depending on chemical structure of composite dendrons, *co*-dendrimers formed lamellar or columnar meso-phases. Electrodeposition of Cz-containing dendrons afforded globular conformation, in which mesogenic molecular groups play the key role.

Many studies were concerned with dendrimers containing thermotropic liquid crystal fragments, because they can self-assemble in large organized assemblies

[817–819]. For this purpose, PAMAM and PPI dendrimers were functionalized by mesogenic fragments with azomethine groups [816]. Depending on generation of dendrimers, a number of mesogenic blocks varied from 4 to 64. Since mesogenic blocks contain one, two, or three end chains, a vast library of compounds displaying formation of a meso-phase is collected. General mesomorphism observed for all obtained dendrimers is based on chemical incompatibility between their constitutive parts (rigid aromatic parts, dendritic structure and aliphatic chains), and two possible conformations of molecules (parallel or radial) (Fig. 2.73). Presence of one aliphatic chain per mesogenic unit favors parallel arrangement of functionalized dendrimers and formation of smectic A or C meso-phases. Increase in a number of aliphatic chains (two or three) affords radial disposition bringing to formation of columnar structures. At that, temperatures of meso-phase transition depend on a dendritic core origin, a number of generations, and a number of terminal aliphatic chains [816].

Based on dendritic LCP, stimuli-responsive luminescent materials are obtained, which in future can be used as sensors of metal ions (Fig. 2.74) [869].

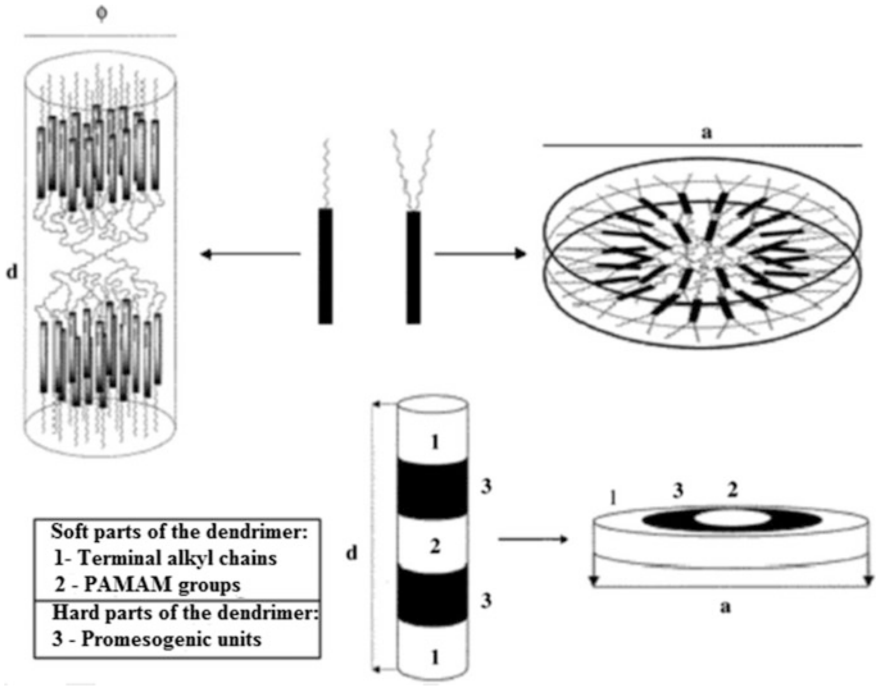


Fig. 2.73 Schematic presentation of two main molecular conformations (parallel and radial) by functioned at the end of liquid crystalline dendrimers and their correlation with a number of grafted terminal alkoxy-chains. Gigantic rods and discs are formed by microsegregation of incompatible segments by analogy with block-copolymers

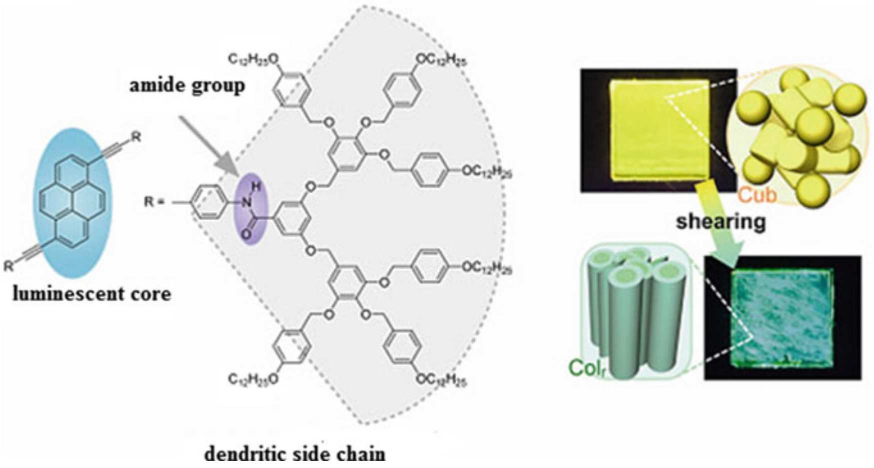


Fig. 2.74 Stimuli-responsible liquid crystals: change of photoluminescent colors triggered by a shear-induced phase transition

Order and frustration in the LCP are studied using the example of the G2 liquid crystal block- and statistic dendrimers with mixed aliphatic and mesogenic terminal groups, as well as homo-dendrimers from several generations containing only mesogenic end groups [870]. It has been established that homo-dendrimers from G1 to G4 show monolayer smectic phase, in G5 they show more ordered columnar phase, G2 block-dendrimer has bilayer smectic phase, while statistic G2 dendrimer does not show any mesogenic phase. The observed phase behavior is most convenient to be considered in terms of frustration due to competition between rigid geometry of the dendritic matrix and close-packing conditions of terminal chains.

Interesting chiral LCP were obtained by coupling methyl-α-d-glucoside (G) and methyl-α-d-mannoside (M) as different chiral structural fragments in a core and in branching centers within dendritic scaffolds surrounded by 12 cyanobiphenyl mesogenes (CB) (Fig. 2.75) [871]. Positional permutation approach of pyranose unit's G and M in the core and branching points was used for studies of mesomorphic properties of chiral homogenous dendrimers GG/MM and respective chiral heterogeneous dendritic homologues GM/MG. It occurs that the temperature profile and structure of the meso-phase of four dendrimers do not depend substantially on the origin of the central chiral core, and the external chirality on periphery predominates considerably over liquid crystal properties.

Liquid crystal co-polymers with multi-arm star azobenzene side chains and hyperbranched core are obtained by ATRP method through multifunctional hyperbranched polyether as initiator and benzene chloride as a solvent [812]. Multifunctional hyperbranched polyether initiator is produced from poly(3-ethyl-3-(hydroxymethyl)

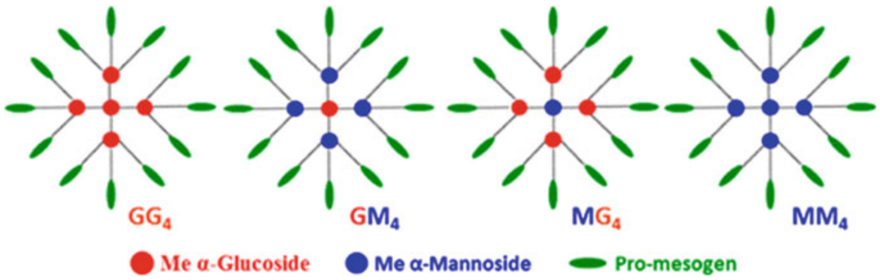


Fig. 2.75 Structures of chiral liquid crystal obtained by coupling methyl-α-d-glucoside (G) and methyl-α-d-mannoside (M) as different chiral structural fragments in a core and in branching centers within dendritic scaffolds surrounded by 12 cyanobiphenyl mesogens (CB)

oxetane) and 2-bromo-2-methylpropionyl bromide. Azobenzene side arms have liquid crystal conformation of poly [6-(4-methoxy-4′-oxy-azobenzene) hexyl methacrylate] with different molecular weights and they form smectic and nematic phases, and the phase transition temperatures from smectic to nematic phase and from the nematic to isotropic phase increase as molecular weight of the copolymers increases from 1.78×10^4 to 9.07×10^4.

Using very different methods of synthesis has brought to building of many thousands of different in structure LCP. Apart from classic linear and comb-like polymers, there is a great number of LCP containing paired mesogens, macromolecules with laterally bound mesogenic groups, disc-shaped and cross-shaped fragments, also alternation of different mesogenic groups is possible in the limits of one and the same polymer chain [872, 873]. The principal possibility of synthesis of LCP consisting of macromolecules of any combination between mesogenic and non-mesogenic fragments opens wide horizons for oriented design of PMC.

Analysis of the considered data points to the fact that by now a considerable experimental material on synthesis of CPL has been collected, which shows intensity of their chemistry development. Currently, the basic principles of design of the chelating polymers are formulated, their structural organization is understood, and development trends in the area are relatively well represented. It should be emphasized that design of CPL is important, and in some cases, a critical task in terms of both subsequent chelation reactions with a metal compound, and for subsequent PMC use.

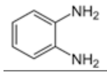
However, until now a convenient classification of chelating polymers is not developed. For subsequent transformations the prehistory of formation of chelating fragments is important, since even the strict observance of all the intricacies of parallel experiments is not always possible to obtain reproducible results. Because very notion of "polymer structure" is a highly-valued and, as a first approximation, is determined by the conditions of its synthesis, CPL are to be classified according to the type of preparation thereof (polymerization, copolymerization of the corresponding monomers, polycondensation or PPM). Moreover, the chelating fragments are crucial in chelation of metal compound, so that the second parameter, reflected in the classification should be the nature, size and spatial arrangement of the chelating fragment, which may consist of both symmetrical and asymmetrical groups. Therefore, CPL classification adopted in this book includes, primarily, the method of preparation and structure of the base polymer and then its functionality. Although this classification is to some extent arbitrary, but two parameters, put in its foundation, more clearly characterize the CPL.

Table 2.5 shows the most typical derivatives of CPLs based on synthetic polymers, and methods of their production. They are classified by type of produced PMC as following the groups: ligands for molecular metal chelate, intracomplex compounds, and macrocyclic complexes. Apparently, this division is very conditional, since in many cases the same chelating fragments can participate in formation of metal chelates of different types, metal chelates with mixed ligands, a variety of bridge structures, and polynuclear metal chelates.

Obviously, presently there are no difficulties in synthesis of polymers with any chelating functionalities. Thus, a technique for producing polymers of chelating type is well developed and continues to improve. At the present stage of experimental studies design of CPL, which are analogues of low molecular weight ligands, for example, acetylacetonates (acac), Schiff bases, etc., does not constitute special synthetic difficulties.

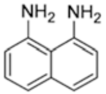
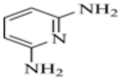
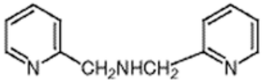
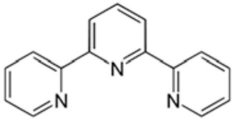
Polymer chelating ligands are often low-tonnage polymers for special purposes; therefore, PPM of industrial polymers such as PE, PP, PTFE, etc. is very perspective. Besides, in the last decade in spite of the well-known, cheap and widely used thermoplastics and elastomers the focus has shifted to more expensive materials.

Table 2.5 Main types of CPL based on synthetic polymers and methods of their preparation

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
Ligands of molecular metal chelates					
$H_2NCH_2CH_2NH_2$	Homopolymer	EP	*N*-(1-naphthyl)ethylenediamine dihydrochloride	Film	[711]
	Homopolymer	Plasma polymerization	en	Film	[783]
	Copolymer	CoP	en + dimethyl amine + epichlorohydrin		[874]
	Polycondensate	PC	en + p-dichloromethylbenzene	Insoluble, 6.51 mmol NH_2 g^{-1}	[875]
	Polycondensate	PC	en + 2-amino-6-nitrobenzothiazole		[876]
	PAAm	PPM	Support + en	[CF] = 0.87–2.78	[877]
	PCD-GMA	PPM	Support + en	2.68 mmol N g^{-1}	[878]
	PCD	PPM	Support + en	[CF] = 3.16, S_{BET} = 36.24, V_{pore} = 0.35, D_{pore} = 43.90	[879]
	Poly[4-vinyl benzyl (2-benzenesulfonate ethyl) sulfide]	PPM	Support + en	[CF] = 3.53	[880]
	2,4-dihydroxyacetophenone formaldehyde resin	PPM	Support + en	Yield = 75%	[881]
$(H_2NCH_2CH_2)_2NH$	PMA	ARGET ATRP	Methyl acrylate (MA) + dien	M_n > 1.5 million, PDI ~ 1.25	[882]
	Polycondensate	PC	Dien + urushiol + formaldehyde		[883]
	PMMA	PPM	Support + dien		[884]
	PAN	PPM	Support + dien		[885]
$(CH_2NHCH_2CH_2NH_2)_2$	Maleic anhydride-*co*-dicyclopentadiene	PPM	Support + trien	Yield = 63–65%, S_{BET} = 3.151	[886]
$NH_2(CH_2CH_2NH)_3CH_2CH_2NH_2$	Polycondensate	PC	Tetraethylenepentamine + 2,2′-biphenol + formaldehyde	Yield = 79%	[887]
$NH_2(CH_2)_6NH_2$	PAN	PPM	Support + hexamethylenediamine	Yield = 30–34%	[888]
	Homopolymer	Oxidative polymerization	*o*-phenylenediamine	Yield = 34–55%	[173]

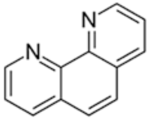
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Homopolymer	Oxidative polymerization	Poly(1,8-diaminonapthalene)	Spherical grains with diameter about 300–500 nm, S_{BET} = 6.73	[178]
	Homopolymer	EP	2,6-pyridinediamine	Film	[722–724, 889]
	Homopolymer	Interface polymerization	2,6-pyridinediamine	Spherical microparticles with an average diameter of 1 μm	[179]
	GL	PPM	Support + *N*,*N*-di(2-pyridylmethyl)amine	[CF] = 1.15	[890]
	Homopolymer	ATRP	tpy monomers		[891]
	Poly(triphenylamine-*alt*-fluorene) or poly (triphenylamine-*alt*-*N*-ethylcarbazole)	Suzuki coupling polymerization	Triphenylamine-based conjugated monomer containing tpy ligands + corresponding diboronate	M_n = 20,950, PDI = 1.25 (M_n = 18,700, PDI = 1.06)	[892]
	Copolymer	CoP	Methacrylic acid 3-(tpy-4′-yloxy)-propyl ester + MMA + hydroxyethyl methacrylate (methacryloyl methacrylate or acryloyl methacrylate)	M_n = 3800, PDI = 3.98 (M_n = 8200, PDI = 1.58 or M_n =10,500, PDI = 1.70)	[132]
	Copolymer	CoP	4- or 4′-vinyl-tpy + tpy-functionalized MMA		[893]
	Copolymer	ROMP	ε-caprolactone + 4′-hydroxypropyloxy-tpy	M_n = 2500, M_w = 3100, PDI = 1.2	[156]
	PVC	PPM	Support + (2-mercaptophenyl)methanol + tpy bearing an isocyanate group		[894]
	PCD	PPM	Support + 4′-(4-hydroxyphenyl)-tpy		[895]
	PEO	PPM	Support + 6-(tpy-4′-yloxy)-hexylamine	M_n = 3400, M_w = 3700, PDI = 1.08, T_m = 57 °C	[896]
	PCS	PPM	Support + 4′-hydroxy-tpy	Yield = 100%, 6.83 mmol N g^{-1}	[229]

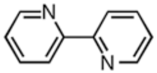
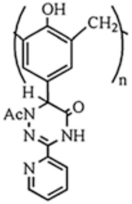
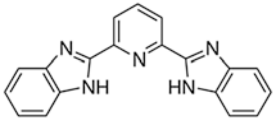
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Homopolymer	Biocatalytic polymerization	4-(phen-5-yl-iminomethyl)-phenol		[263]
	Homopolymer	EP	2,5-di(2-thienyl)-1H-pyrrol, containing phen in pyrrol cycle	Film	[715]
	Copolymer	CoP	5-acrylamido-phen + MMA	$M_n = 4.1 \times 10^4$, PDI = 1.33, T_g = 102.5 °C, [CF] = 2.35 wt%	[897]
	Polycondensate	PC	Poly(phen-3,8-diyl) and their 5,6-dialkoxyderivatives	M_n = 4300–6800	[898]
	Polyarylene ethers	PC	4,7-dichloro-3,8-diphenyl-phen or 4,7-dichloro-2,9-dimethyl-phen + bisphenol A	Soluble, [CF] <=70 mol. %, T_g = 278 °C	[899]
	Polycondensate	PC	5,6-diamino-phen + terephthaldehyde	Yield = 87.2%, [η] = 0.23 dl g^{-1}	[900]
	Polycondensate	PC	4,7-dihydroxy-phen + formaldehyde	Yield = 70%, T_m >300 °C	[901]
	Polycondensate	PC	3,8-dibromo-phen + 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (+ 1,4-dibromobenzene)	Yield = 42%, M_n = 6580, M_w = 21,700, PDI = 3.3, DP = 12.9 (yield = 74%, M_n = 4750, M_w = 26,500, PDI = 5.6, DP = 10.3)	[902]
	PCS	PPM	Support + 5-amino-phen		[903]
	PEG (PIB)	PPM	Support + 5-hydroxy-phen	Yield = 20–40%, M_n = 1550 and 1870 (yield = 20–40%, M_n = 1260 and 2460)	[904]

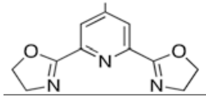
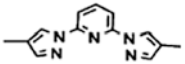
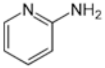
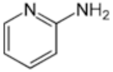
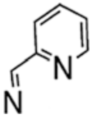
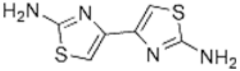
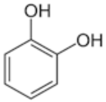
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Polyfluorene and poly(*p*-phenylene ethynylene)	CoP	*p*-arylene ethynylene or 7,7-dihexylfluorene + sterically enshrouded bpy monomer	PDI = M_w/M_n = 14,519/8026 = 1.8 and 24,714/7536 = 3.28 (38,716/9369 = 4.1 and 9757/3471 = 2.81)	[905]
	Polycondensate	PC	5,5′-dibromo-bpy + 9,9-dioctylfluorene-2,7-bis(trimethylene boronate); 5,5′-bis-(diethylphosphinatylmethyl)-bpy + 2,7-diformyl-9,9′-dioctylfluorene; 5,5′-dibromo-bpy + 2,7-diethynyl-9,9′-dioctylfluorene	Yield = 86, 29, 72%; M_n = 35,200 to 59,200; M_w = 55,300–113,500; PDI = 1.57–1.92	[906]
	Polycondensate	PC	5,5′-divinyl-bpy + (R)-5,5′-dibromo-6,6′-di (4-trifluoromethylphenyl)-2,2′-bisoctoxy-1,1′-binaphthyl	Yield = 72.4%; M_n = 3060; M_w = 6170; PDI = 2.02	[907]
	Polycondensate	PC	5,5′-bis(triphenylphosphoniomethyl)-bpy dibromide + 2,5-diformyl-1,4-didecyloxybenzene, 5,5′-bis (diethoxyphosphorylmethyl)-bpy + 2,5-diformyl-1,4-didecyloxybenzene, 5,5′-dibromo-bpy + 2,5-didecyloxy-1,4-phenylene diboronic acid	Yield = 36%; M_n = 1610; PDI = 1.63; yield = 63%; M_n = 6790; yield = 71%; M_n = 1950; PDI = 1.92	[908]
	Wang benzaldehyde resin	PPM	Support + calix[4]arene derivative incorporating two bpy groups	A grafting yield = 3.1%	[909]
	Phenol-formaldehyde and resorcinol-formaldehyde resins	PPM	Support + 3-(pyridin-2′-yl)-1,2,4-triazine-5(2H)-one	Yield = 75%	[910]
	Polycondensate	PC	2,7-bispinacolatoboron ester of 9,9-dihexylfluorene and a 1,4-dibromobenzene derivative carrying two ω-BIP-substituted alkoxy groups in the 2- and 5-position (BIP is 2,6-bis(1′-methyl-benzimidazolyl)-4-hydroxypyridine)	Yield = 88%	[250]

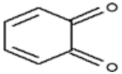
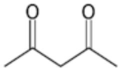
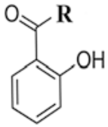
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Copolymer	CoP	Pyridine-bis(oxazoline) (pybox) + norbornene (dicyclopentadiene)		[911]
	Homopolymer (copolymer)	HP (CoP)	4-ethynyl-2,6-bis(pyrazolyl)pyridine (BPP) + (fluorine)	M_n = 10,000	[694]
	PCD	PPM	Support + 3-aminopyridine	[CF] = 0.96–1.04	[912]
	PCD	PPM	Support + 2-aminopyridine, 2-amino-5-methylthio-1,3,4-thiadiazole, 2-amino-5-ethyl-1,3,4-thiadiazole, and 2-mercaptobenzothiazole		[913, 914]
	Polycondensate	PC	4-(pyridinylimine)phenol + formaldehyde	Yield = 75%	[915]
	Polycondensate	PC	2,2′-diamino-4,4′-bithiazole + salicylic acid + paraformaldehyde	Yield = 90%, [η] = 0.231 dL g^{-1}	[916]
$Ph_2P(CH_2)_nPPh_2$	Copolymer	CoP	$CH_2{=}CH_2(C_6H_4)CH_2OCH_2C(CH_3)(CH_2PPh_2)_2$ + DVB + St	Yield = 96%	[917]
Ligands of intramolecular compounds					
	Polycondensate	Enzymatic PC	Catechol + pyrogallol	M_n = 2000, [CF] = 0.0182	[265]
	PAA	PPM	Support + pyrocatechin		[918, 919]

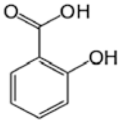
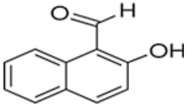
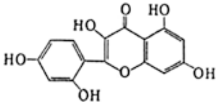
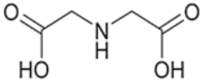
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Homopolymer	HP	*o*-benzoquinonemethacrylate	DP = 22–30 or 110–190	[76]
	Homopolymer	Photopoly-merization	β-methacryloylacetone	$[\eta] = 25.0–37.5$ mL g^{-1}	[65]
	Homopolymer	HP	4-acetylacryloylethylacetate	$T_g = 48.2–61.8$ °C	[95]
	Homopolymer	HP	*p*-vinylbenzoylacetone	$[\eta] = 0.157$ и 1.26 L g^{-1}, yield = 80–98%	[100]
	Polycondensate	Sonogashira coupling reaction	3,7-dibromo-2,8-dimethoxy-5,5-dioctyl-5H-dibenzo[b,d]silole + (Z)-1,3-bis(4-ethynylphenyl)- -hydroxyprop-en-1-one	Yield = 51%, $M_w = 13$ 710, $M_n = 11{,}050$, PDI = 1.24	[920]
	Polycondensate	PC	acacH + terephthalaldehyde	$[\eta] = 0.92$ dL g^{-1}	[921]
	Polybenzimidazole	PPM	Support + 3-Br-acacH	Yield = 72%, $T_m > 30$ °C, $M_n = 6.1 \times 10^4$, $M_w = 1.6 \times 10^5$, PDI = 2.62	[922]
	Homopolymer	HP	Monomers based on (meth)acryloyl chloride and 2,4-dihydroxybenzophenone, 2,4-dihydroxybenzaldehyde, or 2,4-dihydroxyacetophenone	$[\eta] = 0.26–0.41$, $M_w = 20{,}300–31{,}000$, $M_n = 11{,}500–19{,}500$, PDI = 1.41–1.76	[66]
	Homopolymer (copolymer)	CoP	2-hydroxy-4-acryloyloxybenzophenone (+ DVB)		[93, 96]
	Polycondensate	PC	2-hydroxy-4-methoxybenzophenone + ethanediol	$T_m >270$ °C, yield = 60.7%, $M_n = 1156$	[923]
	Polycondensate	PC	2-hydroxy-4-ethoxybenzophenone + 1,2-propylene glycol	$T_m > 270$ °C, yield = 57.85%	[924]
	Polycondensate	PC	2,4-dihydroxyacetophenone + formaldehyde + oxamide (biuret)	$M_n = 10{,}500–14{,}400$, $[\eta] = 1.14–1.22$, yield = 84–88%, DP = 13–19 (soluble, yield = 84%, DP = 3.71, $M_n = 1\,035$)	[241, 925]
	Poly(acryloyl chloride)	PPM	Support + salicylaldehyde		[926]

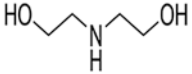
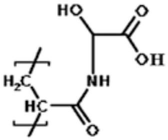
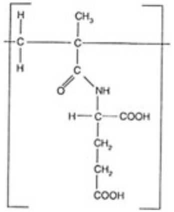
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Copolymer	ATRP	St + 5-chlorosulfonylsalicylic acid	M_n = 3590–11,240, PDI = 1.23–1.5	[927]
	Cyclic poly(salicylic acid)	ROP	Salicylic acid *O*-carboxyanhydride		[102]
	Copolymer	CoP	5,5′-azodisalicylic acid + PEO		[928]
	Polycondensate	Mechanochemical synthesis	Salicylic acid + formaldehyde		[245]
	Polycondensate	PC	Salicylic acid + formaldehyde + melamine (semicarbazide)	Yield = 72%	[929, 930]
	Polycondensate	PC	4-aminosalicylic acid + formaldehyde + urea	Yield = 85%	[931]
	Biodegradable poly (anhydride-ester)	Melt PC	Acetylated disalicylic acid	M_w = 6000, PDI = 1.2, T_g = 23.53 °C	[291]
	PCS	PPM	Support + 5-aminosalicylic acid	[CF] =1.88	[932]
	Chlorosulfonated PS	PPM	Support + 4-aminosalicylic acid	Yield = 98%, [CF] = 2.48, S_{BET} = 99.593, V_{pore} = 0.172, D_{pore} = 6.207 nm	[933]
	Amberlite XAD-4	PPM	Support + 2,3-dihydroxy benzoic acid (salicylic acid)	[CF] = 8.40	[934, 935]
	Polycondensate	Oxidative polycondensation	2-hydroxy-1-naphthaldehyde	M_n = 500, M_w = 1880, PDI = 3.75	[936]
	PCD	PPM	Support + morin	Yield > 95%	[937]
	Homopolymer	HP	GMA-IDA	[η] = 0.688 dL g^{-1}	[938]
	Copolymer	CoP	GMA-IDA + MMA (St or St + DVB)	(water-soluble, D_{pore} = 118 or [CF] = 27.6%)	[104, 939, 940]
	Copolymer	CoP	Vinyl-IDA + NIPAM		[941, 942]
	PCS	PPM	Support + amine + acid	S_{BET} = 34.4–45.4	[943, 944]

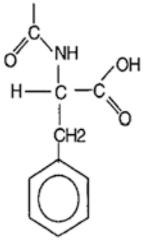
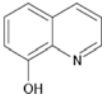
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
EDTA	Polycondensate	PC	Ethylenediaminetetraacetic acid (EDTA) dianhydrides + lactose	M = 132,000	[287]
	Poly(AAm-AA)	γ-induced template polymerization	Support + EDTA disodium salt		[108]
DTPA	Polymer based on the diallyl ester of 1,1-cyclopropane Dicarboxylic acid and of 2-furanmethanethiol	PPM	Support + diethylenetriamine pentacetic acid (DTPA)	Yield = 75–90%, [CF] = 23–53%, PDI = 1.10–1.13	[945]
	Amino polymer-disulfide	PPM	Support + DTPA dianhydride	DP = 67 and 79, PDI = 1.17	[946]
	Poly(2-hydroxyethylmer-captomethyl-St)	PPM	Support + diethanolamine	[CF] = 4.95, yield = 92.8%	[947]
	Homopolymer (copolymer)	HP (CoP)	2-acrylamido glycolic acid (+ 2-acrylamido-2-methyl propane sulfonic acid)	Water-soluble, yield = 96%	[281, 948]
	Copolymer	Suspension CoP	2-methacryloylamidoglutamic acid + 2-hydroxyethyl methacrylate	S_{BET} = 56.7, a swelling ratio of 63%, [CF] = 3.5	[949]

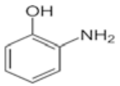
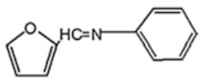
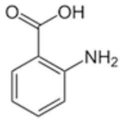
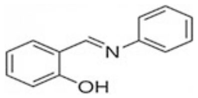
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Copolymer	CoP	Methacryloylamidophenylalanine + 2-hydroxyethyl methacrylate	S_{BET} = 19.1, [CF] = 3.2	[105]
	Homopolymer	HP	8-hydroxy-5-azoquinoline phenyl methacrylate-formaldehyde macromonomer	Yield = 77%, [η] = 0.64 dL g^{-1}, M_n = 1.85 × 10^4, M_w = 3.96 × 10^4, PDI = 2.1	[950]
	Copolymer	CoP	5-(2-methacryloylethyloxymethyl)-8-quinolinol + *N*-vinylcarbazole	M_n = 15,700, PDI = 2.09, T_g = 181, T_d = 383 °C	[951, 952]
	Polycondensate	PC	HQ + formaldehyde + catechol (dithiooxamide, pyrogallol or piperazine)	Yield = 50%, DP = 13.37–18.75, M_n = 4104–14,587, [η] = 0.144–0.158 dL g^{-1}	[953–956]
	Polycondensate	PC	HQ + formaldehyde + salicylic acid	T_m = 379.6 °C, 3850, 1.005	[957]
	Polycondensate	PC	HQ-5-sulphonic acid + formaldehyde + catechol (thiourea)	Yield = 84%, T_m = 391–394 K, DP = 16–23, M_n = 7475–17,188	[958, 959]
	PS	PPM	Support + 5-chloromethyl-HQ	[CF] = 5.88	[960]
	PVC	PPM	Support + HQ-5-sulphonic acid		[961]
	PCD (TosoHaas TSK vinyl polymer resin or GL)	PPM	Support + HQ	[CF] = 2.28, S_{BET} = 2.91 ([CF] = 1.43)	[962–964]
	Poly(*p*-nitro-St) and poly (*p*-amino-St)	PPM	Support + bis- HQ-terminated open-chain crown ether		[965]

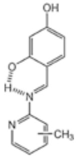
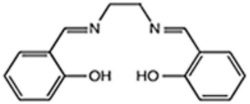
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Homopolymer (copolymer)	EP	*o*-aminophenol (+ aniline)		[680, 737, 769]
	Polycondensate	PC	*o*-aminophenol + formaldehyde + urea	M_n = 5804–13,992, [η] = 0.89–1.27	[966]
	Aminated PS or cross-linked poly(St-*alt*-maleic anhydride)	PPM	Support + *o*-aminophenol		[967, 968]
	4-benzyloxybenzaldehyde, polymer-bound	PPM	Support + *o*-aminophenol (2-amino-4-chlorophenol or 2-amino-4-methylphenol)	791/731, 1.1 (787/870, 0.9 or 664/641, 1.0)	[969, 970]
	Aminated PS	PPM	Support + furfural		[971]
	Copolymer	EP	Anthranilic acid + aniline		[972]
	Block-copolymers	EP	Anthranilic acid + pyrrol		[777]
	Homopolymer (copolymer)	Chemical polymerization	Anthranilic acid (or + aniline)	Yield = 49% (15.0% in acidic medium)	[703, 704]
	Polycondensate	PC	Anthranilic acid + formaldehyde + *o*-toluidine	M_n = 3600, [CF] = 6.18, yield = 80%	[973, 974]
	Poly(THF)	GP	Support + poly(caprolactone)-poly(anthranilic acid)-poly (caprolactone)		[333]
	Homopolymer	HP	Monomer based on 2.4-dihydroxy benzaldehyde, aniline and acryloyl chloride	[η] = 0.417 dL g^{-1}, M_n = 1.89 × 10^4, M_w = 3.26 × 10^4, PDI = 1.72	[68]
	Copolymer	Oxidative PC	2-*p*-tolylazomethinephenol (*o*-phenylazomethinephenol) with air oxygen and sodium hypochloride	M_n = 6780, M_w = 7660, PDI = 1.13, [CF] = 0.5–20% (M_n = 1180, M_w = 1930, PDI = 1.64)	[950, 975]
	Polycondensate	PC	Salicylidene-3-amino-1,2,4-triazole (oligo-2-hydroxy naphthalidene-3-amino-1,2,4-triazole)	M_n = 1980, M_w = 5115, PDI = 2.58, (M_n = 1752, M_w = 4300, PDI = 2.45)	[976]
	Polycondensate	PC	5,5′-((2,5-dioctyloxy-1,4-phenylene)bis-(ethyne-2,1-diyl)bis (2-hydroxy-3-(piperidin-1-ylmethyl)-benzaldehyde + (S)-2,2′-binaphthyldiamine	M_w = 32,590, M_n = 18,180, PDI = 1.79	[977]

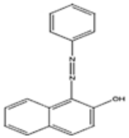
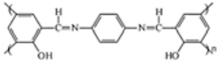
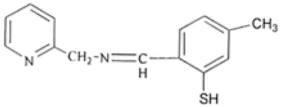
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Polycondensate	PC	Diethyleneglycol bis(2-aminophenyl ether) or triethyleneglycol bis(4-aminophenyl ether) with oligosalicylaldehyde	$M_n = 1100$, $M_w = 5400$, PDI = 4.90 ($M_n = 1100$, $M_w = 5600$, PDI = 5.01)	[978]
	PCS	PPM	Support + 3-formylsalicylic acid and ethanolamine		[979]
	Aminomethylated PS	PPM	Support + 3-ethoxysalicylaldehyde (salicylaldehyde)	[CF] = 0.28–0.75	[980, 981]
	Aminomethylated PS	PPM	Support + 2-hydroxyacetanilide		[982]
	Oligo-2-hydroxy-1-naphthaldehyde	PPM	Support + *p*-aminophenol (triethyleneglycol bis (4-aminophenyl ether) or aniline)	$M_n = 670$, $M_w = 2490$, PDI = 3.71 ($M_n = 390$, $M_w = 1080$, PDI = 2.77 or $M_n = 320$, $M_w = 670$, PDI = 1.85)	[936]
	Polycondensate	Oxidative PC	Schiff bases in an aqueous alkaline medium using NaOCl	M_n = 40,800–60,680, M_w = 43,840–63,500, PDI = 1.039–1.112	[983]
	Homopolymer	PC + oxidative polymerization	2-{[(6-aminopyridin-2-yl)imino]methyl}-phenol	M_n = 33,500, M_w = 78,900, PDI = 2.352	[984]
	Homopolymer	EP	*N,N′*-bis(3-methoxysalicylidene)-1,3-propylenediamine	Film	[738, 739]
	Polycondensate	PC	H−≡−Ar−≡−H (Ar = fluorene or 2,5-dialkoxy-p-phenylene) + dibromo compounds of salphen (*N,N′*-phenylenebis (salicylideneimine))	Soluble, M_n = 9200–14,000, M_w = 27,000–49,700	[985]
	Polycondensate	PC	Salen + hydroquinone, 1,3,5-trihydroxybenzene or 1,1,1-tris (4-hydroxy phenyl)ethane dimeric dialdehyde derivatives with (1S, 2S)-(+)-1,2-diaminocyclohexane (or (1R, 2R)-(−)-1,2-diaminocyclohexane)	$M_n = 6000$	[986]
	Polycondensate	PC	Disalicylaldehyde + (R,R)-1,2-diaminocyclohexane or (R,R)-1,2-diphenylethylenediamine	DP = 27, M_w = 16,771, M_n = 12,261, PDI = 1.37 (DP = 23, M_w = 19,274, M_n = 12,449, PDI = 1.55)	[221]

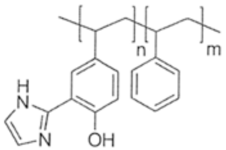
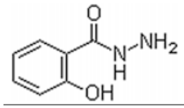
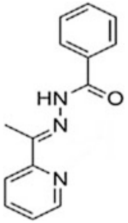
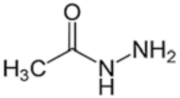
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Polycondensate	PC	A phenolic Schiff base derived from 4,4′-diaminodiphenylmethane and *o*-hydroxyacetophenone + formaldehyde or furfuraldehyde	Yield exceeded 70%	[987]
	Polycondensate	Oxidative PC	1,4-bis[(2-hydroxyphenyl)methylene] pyridinediamine	M_n = 61,000, M_w = 94,200, PDI = 1.54	[988]
	PCS	PPM	Support + 3-formylsalicylic acid, en and acacH		[885]
	PAAm	PPM	Support + 5-chloro-2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde or 5-methyl-2-hydroxybenzaldehyde	Yield = 48–67%. M_n = 4480, 4630 or 4680	[989]
	Polycondensate	PC	1-(4-hydroxyphenylazo)-2-naphthol + formaldehyde	Yield = 70%, [η] = 0.275 dL g^{-1}. M_n = 1.32×10^4, M_w = 2.95×10^4, PDI = 2.23	[990]
	Oligo-1,4-bis [(2-hydroxyphenyl) methylene]phenylenediamine	Oxidative polycondensation	1,4-bis[(2-hydroxyphenyl)methylene]phenylenediamine by air, H_2O_2 and NaOCl oxidants	Yield = 99, 79 or 87%, M_n = 2430, M_w = 2550, PDI = 1.049 (M_n = 1 475, M_w = 1 640, PDI = 1.112 or M_n = 900, M_w = 975, PDI = 1.083)	[991]
	Amberlite IR P69	PPM	Support + Schiff base derived from 2-picolyl amine and 2-mercapto-4-methyl-benzaldehyde	Mesh size 16–45 mm	[992]

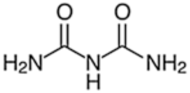
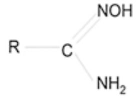
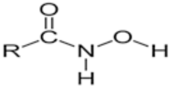
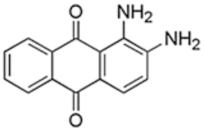
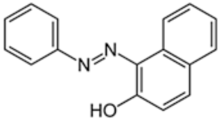
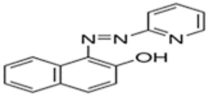
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Copolymer	CoP	St + 2-(2′-hydroxy-4′-ethenylphenyl)imidazole		[993]
	4-acryloxybenzaldehyde-*co*-DVB	PPM	Support + salicyloyl hydrazine	Yield = 51%	[994]
	Poly(methyl vinyl ether-*alt*-maleic anhydride)	PPM	Support + a Schiff base obtained in condensation of 2-acetylpyridine and 4-aminobenzoic hydrazide	$M_w = 216{,}000$, $S_{BET} = 2.051$, $V_{pore} = 0.008$, $D_{pore} = 4.45$ nm	[995]
	4-acryloxyacetophenone-*co*-DVB	PPM	Support + benzoyl hydrazone	Yield = 52%, the average particle size is 86.12 μm	[996]
	4-methacryloxy-acetophenone-*co*-MMA	PPM	Support + isonicotinoyl hydrazine	Yield = 41%	[997]
	PCS	PPM	Support + *N*,*N*′-bis(4-amino-o-hydroxy acetophenone) hydrazine	[CF] = 3.436	[998]
	Polycondensate	PC	Benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid + dihydrazides in ionic liquids	[η] = 0.21–0.47 dL g^{-1}, soluble	[44]
	Homopolymer	HP	Acryloyl benzoic hydrazide	Insoluble, yield = 55%	[999]

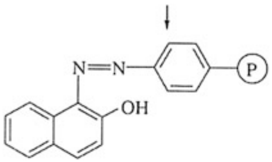
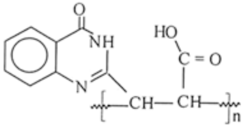
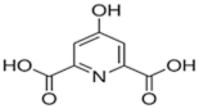
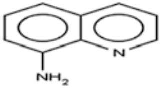
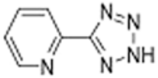
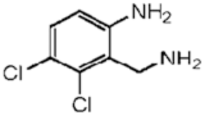
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Polycondensate	PC	Biuret + formaldehyde + 4-hydroxyacetophenone	Yield = 60–76%, M_n = 5230–12,019, [η] = 0.074–0.091 dL g^{-1}	[1000]
Amidoxime-hydroxamic acid  	PAN	PPM	Support + amidoxime (or hydroxylamine)		[1001]
	Poly(AN-*co*-ethylacrylate)	PPM	Support + hydroxylamine (*N*-methylhydroxylamine)	T_m = 240 °C (260 °C)	[1002]
	PEI	PPM	Support + *N*-methylacrylamide	Soluble in water, yield = 64.0%	[274]
	Poly(GMA)	PPM	Support + iminodiacetonitrile + hydroxylamine		[236]
	PAN-co-DVB	PPM	Support + hydroxylamine	[CF] = 3.0	[1003]
	Homopolymer	EP	1-amino-9,10-anthraquinone	Film	[730, 731]
	Poly-2-hydroxyethyl-methacrylate	PPM	Support + 1,2-diaminoantraquinone		[1004]
	Polycondensate	PC	*o*-phenylazonaphthol linked with a phenylene or fluorine unit		[1005]
	PCD (Amberlite XAD-16)	PPM	Support + α-pyridylazo-β-naphthol	S_{BET} = 66	[235, 1006]

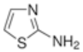
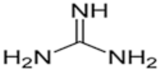
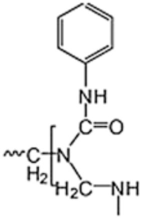
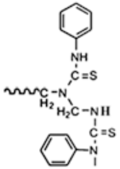
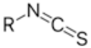
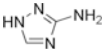
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Aminated PS	PPM	Support + 1-nitroso-2-naphthol		[1007]
	Homopolymer	HP	2-acrolyl-quinazoline		[81]
	Polycondensate	PC	Chelidamic acid + Jeffamin ED® (polyester with end isopropylamino-groups)		[1008]
$RSO_2NHCONH_2$	PCD	PPM	Chlorosulphonated support + urea	3.5 mmol N g^{-1}	[1009]
	Copolymer	Oxidative polymerization	Aminoquinoline + ethylaniline (phenetidine)		[182, 183]
	PCS	PPM	Support + 5-aminopyridine-2-tetrazole	S_{BET} = 23.72, D_{pore} = 18.74, V_{pore} = 0.11	[1010]
	Homopolymer (copolymer)	Oxidative polymerization	*o*-amino benzyl amine (+ aniline)		[181]

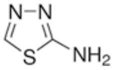
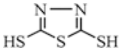
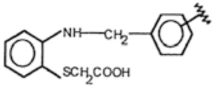
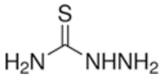
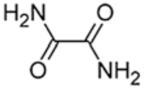
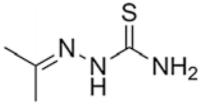
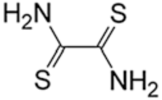
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	PCS	PPM	Support + 2-aminothiazole	[CF] = 2.52	[1011]
	Homopolymer	HP	4-acrylamido benzene sulphonyl guanidine		[1012]
	Polycondensate	PC	Guanidine hydrochloride + hexamethylene diamine + epichlorohydrin	$M_w = 5.8 \times 10^3 - 1.66 \times 10^6$	[1013]
	St-*co*-DVB-*co*-*N*,*N*,*N*′-trimethyl-*N*′-(4-vinylbenzyl) cyanoguanidine	PPM	Support hydration		[1014]
	Polycondensate	PC	Phenylurea + formaldehyde	Yield = 75%, T_m >300 °C	[1015]
	Polycondensate	PC	Phenylthiourea + formaldehyde	Yield = 75%, M_w = 16,800	[1016]
	Polyallylamine with thiourea groups	PPM	Support + methyl isothiocyanate	Water-soluble	[280]
	Homopolymer	EP	3-amino-1,2,4-triazole	Film	[710]
	Polycondensate	PC	3-amino-1,2,4-triazole-5-thiol + glutaraldehyde (thiourea)	$T_m > 300$ °C, $S_{BET} =$ 560 (687)	[1017]

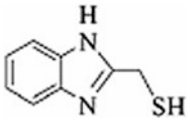
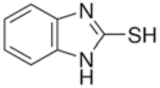
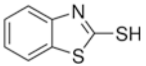
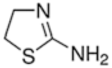
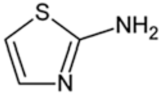
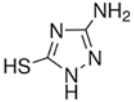
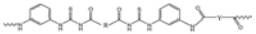
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	PAN (PCS)	PPM	Support + 2-amino-1,3,4-thiadiazole	[CF] = 3.55, yield = 34.92%, S_{BET} = 27.83, D_{pore} = 25.4 ([CF] = 3.65, yield = 88.6%)	[1018, 1019]
	PS-diethylene glycol or PS-triethylene glycol	PPM	Support + 2-amino-5-methylthio-1,3,4-thiadizole		[1020]
	PCS	PPM	Support + 2,5-dimercapto-1,3,4-thiadiazol	[CF] = 2.07	[1021]
	Copolymer	PC	2,5-bis(mercapto-acetichydrazide)-1,3,4-thiadiazole + 4,4′-biphenic, 3,3′-azodibenzoyl, 4,4′-azodibenzoyl dichlorides		[244]
	PCS	PPM	Support + 2-aminothiophenyl-*S*-acetic acid		[199]
	Copolymer	PC	Thiosemicarbazide + formaldehyde		[268]
	Amberlite IRC-50	PPM	Support + thiosemicarbazide		[1022]
	Polycondensate	PC	4-hydroxyacetophenone + oxamide + formaldehyde		[1023]
	PCD	PPM	Support + thiosemicarbazone		[1024]
	PCD	PPM	Support + dithiooxamide	[CF] = 0.97	[1025]

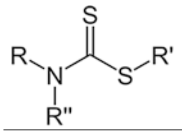
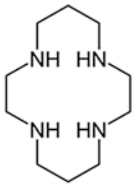
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	PCD	PPM	Support + 2-thiomethylbenzimidazole		[1026]
	Copolymer	CoP	AA + 2-mercaptobenzimidazole		[107]
	PCD (PCS)	PPM	Support + 2-mercaptobenzothiazole	D_{pore} = 875–890, S_{BET} = 10.29–12.22 ([CF] = 3.67)	[232, 233, 1027]
	PAN	PPM	Support + 2-amino-2-thiazoline	S_{BET} = 27.80, D_{pore} = 25.1, [CF] = 2002	[1028]
	Homopolymer	EP	2-aminothiazole	Film	[1029]
	PCD	PPM	Support + 4-amino-5-methyl-3-thio-1,2,4-triazole	[CF] = 0.916	[1030]
	Poly(thiourea-amide)s	PC	Aromatic and aromatic-aliphatic diamines [isophthaloyl bis(3-(3-aminophenyl)thiourea), terephthaloyl bis(3-(3-aminophenyl)thiourea), adipoyl bis(3-(3-aminophenyl) thiourea), sebacoyl bis(3-(3-aminophenyl)thiourea)] + the diacid chlorides such as isophthaloyl, terephthaloyl and adipoyl chloride	0.92–1.56 dL g^{-1}, M_n = 607 × 10^2-851 × 10^2, PDI = 1.62–1.88	[1031]

(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Phenol-formaldehyde resin	PPM	Support + the disulfide carbon	Yield = 70%	[1032]
Ligands of macrocyclic complexes					
DOTA	GL	PPM	Support + DOTA	[CF] = 0.088	[1033]
	Homopolymer	HP	Monomer based on cyclam and acryloyl chloride	Swelling ratio 1400% at pH 12.0	[75]
	Vinylbenzyl chloride-co-DVB	PPM	Support + cyclam		[1034]
Tetraazacyclododecane (cyclen)	Poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline)	PPM	Support + *N*,*N*′,*N*″,*N*‴-tetraazacyclododecane-1,4,7,10-tetraacetic acid	Water-soluble, 4500	[1035]
	Polycondensate	PC	Diester macrocycles + different aliphatic diamines		[1036]
Triazamacrocycle	Copolymer	CoP	(E,E,E)-1-[(4-methylphenyl)sulfonyl]-6-[(2-trimethylsilylethyl)sulfonyl]-11-[(4-vinylphenyl)sulfonyl)]-1,6,11-triazacyclopentadeca-3,8,13-triene + St	[CF] = 1.15	[1037]
12-crown-4	Copolymer	CoP	NIPAM + benzo-12-crown-4-acrylamide		[86]
	Homopolymer	HP	1,4,7,10-tetraoxacyclododecan-2-ylmethyl methacrylate	Soluble, T_g = 35 °C	[1038]
	Polycondensate	PC	Isophthalic diacid-based monomers with 12-crown-4 ether group + aromatic diamines	T_m up to 349 °C, soluble	[1039]
15-crown-4	Copolymer	CoP	2,7-dibromo-9-(15-crown-4)-9H-fluoren + 2,4,7-trivinyl-9,9-dihexylfluoren		[1040]
15-crown-5	Copolymer	CoP	MMA + benzo-15-crown-5	M_n = 33,000–90,000, PDI = 2.1–2.5	[84]

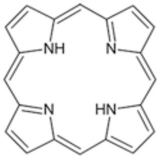
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
18-crown-6	Copolymer	CoP	AA + acrylamidomethyl-18-crown-6 (acrylamidomethyl 15-crown-5)	Yield = 70–72%, M_n = 37,500 (yield = 70%, M_n = 31,500)	[85]
	Copolymer	Oxidative coupling polymerization	Macromonomer containing dibenzo-18-crown-6 + *p*-phenylenediamine		[1041]
	Copolymer	CoP	NIPAM + benzo-18-crown-6-acrylamide		[1042]
	Copolymer	EP	Dibenzo-18-crown-6	Film	[1043]
	PP	PPM	Support + di-*t*-butylbenzo-18-crown-6		[1044]
32-crown-10	Homopolymer (copolymer)	HP (CoP)	5-vinyl-m-phenylene-m'-phenylene-32-crown-10 (+ AN or St)	M_n = 36,000 (M_n = 9900–14,300, T_g = 7–39 °C or M_n = 7300–11,800, T_g = 21–53 °C)	[83]
Azacrown ethers	Homopolymer	HP	16-membered α-methylenemacrolide monomers with monoazacrown ether	M_n > 5000	[1045]
	Copolymer	CoP	Crowned spirobenzopyran vinyl monomer + MMA	$M_n = 5.7 \times 10^3$, 8.1×10^3, and 5.1×10^4	[1046]
	Copolymer	CoP	*N*-2-ethyl-azacrown ether methacrylate (aza-12-crown-4, aza-15-crown-5 or aza-18-crown-6) + 9-anthryl methacrylate	[η] = 1.011, 0.599 or 0.573	[1047]
Monoaza dibenzo-18-crown-6	Amberlite XAD-4	PPM	Support + monoaza dibenzo-18-crown-6	[CF] = 1.34	[1048]
Diaza-18-crown-6	Polycondensate	PC	4,4′-(hexafluoroisopropylidene)diphthalic anhydride + macrocyclic diamine monomers		[1049]
Polymeric pseudo-crown ethers	Homopolymer	Cyclopolymerization	PEG dimethacrylates		[1050]
Polyamine podand	Polycondensate	PC	1,3,5,7-tetrakis(2-glycidyloxypropyl)-1,3,5,7-tetramethylcyclotetrasiloxane + the corresponding amine	Yield = 79–87%, [CF] = 6.43–12.95	[1051]
Thiacrown ethers	Copolymer	ROP	3-thiopentyl glycidyl ether + diethylene glycol bisglycidyl ether	Yield = 74.6–95.1%	[159]

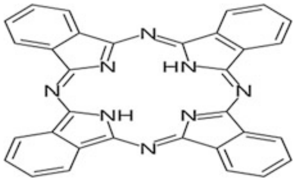
(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Homopolymer	EP	Monomer containing fullerene and Pp units		[757]
	Copolymer	EP	Pp + tetra- or bithiophene		[754]
	Homopolymer	EP	5,10,15,20-tetrakis[3-(*N*-ethylcarbazoyl)]-Pp		[752]
	Homopolymer	EP	Tetra-(4-hydroxyphenyl)-Pp		[755]
	Homopolymer	EP	5-(4′-aminophenylamino)-10,20-diphenyl-Pp		[753]
	Homopolymer	HP	Ethynyl Pp monomers		[1052]
	Homopolymer	Polycycloaddition by click polymerization	Pp-containing dialkyne and 1,4-diazidobenzene		[667]
	Copolymer	ROMP	Pp + alkylnorbornene		[153]
	Block-copolymers	NMP	PSS + 5-(4-acryloyloxyphenyl)-10,15,20-tritolyl-Pp	Water-soluble	[145]
	Copolymer	CoP	Meso-tetrakis(pentafluorophenyl)-Pp + bis(catechol) monomer	S_{NET} = 900–1000	[1053]
	Copolymer	CoP	Pp + dithienothiophene	Soluble, T_m = 330–410 °C, T_g = 130–180 °C	[255]
	Copolymer	CoP	Pp, poly(*p*-phenylenevinylene) and/or a pendant fullerene		[1054]
	Copolymer	CoP	AAm (methacrylic acid) + disodium salt of protoporphyrin IX	6.5×10^4 (2.3×10^5)	[1055]
	Polycondensate	PC	9,9′-dioctylfluorene + tetraphenyl-Pp by Pd-catalyzed Suzuki coupling reaction	M_n = 6000–23,000, PDI = 2.1–2.6	[249]
	Poly(aryl isocyanide)	PPM	Support + tetraphenyl-Pp derivative	M_n = 10,300–19,000, PDI = 1.15–1.16	[217]

(continued)

Table 2.5 (continued)

Chelating fragment	Polymer-support	Preparation method	Initial reagents	PCL characteristics	References
	Homopolymer	Polymeric tetramerization	1,8-diazabicyclo[5.4.0]undec-7-ene + bisphthalonitrile monomer (*N*,*N*′-bis (2-oxyethyl-phthalonitrilo)-4,13-diaza-18-crown-6) (1,11-bis(3,4-dicyanophenylthio)-3,6,9-trithiaundecane or o-bis[3-(3,4-dicyanophenoxy) propyloxy]benzene)	T_m > 300 °C (yield = 70%, PDI = 2.76)	[205, 1056–1058]
	Poly[chlorotrifluoroethylene-*alt*-(2-iodoethyl vinyl ether)]	GP	Support + alkynyl CF_3-containing phthalocyanine		[1059]
	Polycondensate	PC	Tetranitrile monomer + 4,4′-[pyridine-2,6-diylbis (methyleneoxy)]diphthalonitrile	Yield = 51%, T_m > 300 °C	[198]
	Cz-based polymer	PPM	Support + Pc	M_n = 8729, M_w = 27 809, T_g = 97–110 °C, soluble	[1060]
	Allyloxy nonyl-phenoxy propanol polyoxyethylene ether ammonium sulfonate	PPM	Support + Pc		[1061]

Note EP Electropolymerization; *HP* Homopolymerization; *CoP* Copolymerization; *[CF]* Concentration of chelating fragments, mmol g^{-1}; S_{BET} Brunauer-Emmett-Teller (BET) surface area, m^2 g^{-1}; V_{pore} Volume of pores, cm^3 g^{-1}; D_{pore} Average pore diameter, nm

References

1. F. Tian, M.J. Roman, E.A. Decker, J.M. Goddard, J. Appl. Polym. Sci. **132**, 41232 (2015)
2. A.D. Pomogailo, I.E. Uflyand, *Makromolekulayrnye Metallokhelaty (Macromolecular Metal Chelates)* (Khimiya, Moscow, 1991)
3. D. Wohrle, A.D. Pomogailo, *Metal Complexes and Metals in Macromolecules* (Wiley-VCH, Weinheim, 2003)
4. I. Manners, *Synthetic Metal-Containing Polymers* (Wiley-VCH, Weinheim, 2004)
5. V. Chandrasekhar, *Inorganic and Organometallic Polymers* (Springer, Berlin, Heidelberg, 2005)
6. U.S. Schubert, G.R. Newkome, I. Manners (eds.), *Metal-Containing and Metallosupramolecular Polymers and Materials*, ACS Symposium Series, vol 928 (ACS, Washington, 2006)
7. Ch. Carraher Jr., C. Pittman Jr., A. Abd-El-Aziz, M. Zeldin, J. Sheats (eds.), *Metal and Metalloid Containing Macromolecules* (Wiley, NY, 2006)
8. A. Abd-El-Aziz, C.E. Carraher Jr., C.U. Pittman, M. Zeldin (eds.), *Macromolecules Containing Metal and Metal-Like Elements* (Wiley, New Jersey, 2006)
9. J.H. Zagal, F. Bedioui, J.P. Dodelet, *N_4-Macrocyclic Metal Complexes* (Springer, NY, 2006)
10. U.S. Schubert, H. Hofmeier, G.R. Newkome, *Modern Terpyridine Chemistry* (Wiley-VCH, Weinheim, 2006)
11. O.I. Koifman, T.A. Ageeva, *Porphyrinpolymers* (Fizmatlit, Moscow, 2006)
12. A.S. Abd-El-Aziz, I. Manners, *Frontiers in Transition Metal-Containing Polymers* (Wiley, Hoboken, New Jersey, 2007)
13. A.S. Abd-El-Aziz, C.E. Carraher, C.U. Pittman, *Inorganic and Organometallic Macromolecules: Design and Applications* (Springer, NY, 2008)
14. U.S. Schubert, A. Winter, G.R. Newkome, *Terpyridine-Based Materials. For Catalytic, Optoelectronic and Life Science Applications* (Wiley-VCH, Weinheim, 2011)
15. A.D. Pomogailo, Ros. Khim. Zh. (Mendeleev Chem. J.) **46**, 64 (2002)
16. P. Theato, H.-A. Klok (eds.), *Functional Polymers by Post-Polymerization Modification—Concepts, Guidelines, and Applications* (Wiley-VCH, Weinheim, 2012)
17. P. Zinck, F. Bonnet, A. Mortreux, M. Visseaux, Progr. Polym. Sci. **34**, 369 (2009)
18. M. Chanda, S.K. Roy, *Industrial Polymers, Specialty Polymers, and Their Applications* (CRC Press, Boca Raton, 2008)
19. E.A. Campo, *Industrial Polymers* (Hanser-Gardner, Cincinnati, 2008)
20. W. Wu, R. Tang, Q. Li, Z. Li, Chem. Soc. Rev. **44**, 3997 (2015)
21. W. Knoll, R.C. Advincula (eds.), *Functional Polymer Films* (Wiley-VCH, Weinheim, 2013)
22. M.I. Barroso (ed.), *Reactive and Functional Polymers Research Advances* (Nova Science Publishers, NY, 2008)
23. V. Jain, A. Kokil (eds.), *Optical Properties of Functional Polymers and Nano Engineering Applications* (CRC Press, Boca Raton, 2015)
24. J. Hu, *Adaptive and Functional Polymers, Textiles and Their Applications* (Imperial College Press, London, 2011)
25. W.-Y. Wong, A.S. Abd-El-Aziz (eds.), *Molecular Design and Applications of Photofunctional Polymers and Materials* (RSC Press, Cambridge, 2012)
26. H. Zhang, Eur. Polym. J. **49**, 579 (2013)
27. M.R. Aguilar, J.S. Román (eds.), *Smart Polymers and their Applications* (Woodhead Publishing, Cambridge, 2014)
28. E. Khosravi, Y. Yagci, Y. Savelyev (eds.), *New Smart Materials Via Metal Mediated Macromolecular Engineering* (Springer, Dordrecht, 2008)
29. H. Meng, G. Li, Polymer **54**, 2199 (2013)
30. T. Ueki, R. Yoshida, Phys. Chem. Chem. Phys. **16**, 10388 (2014)
31. A. Kumar, A. Srivastava, IYu. Galaev, B. Mattiasson, Prog. Polym. Sci. **32**, 1205 (2007)

32. P.T. Anastas, J.B. Zimmerman (eds.), *Innovations in Green Chemistry and Green Engineering* (Springer, NY, 2013)
33. R.A. Sheldon, I. Arends, U. Hanefeld, *Green Chemistry and Catalysis* (Wiley, Weinheim, 2007)
34. C. Jimenez-Gonzalez, D.J.C. Constable, *Green Chemistry and Engineering* (Wiley, Hoboken, New Jersey, 2011)
35. M. Lancaster, *Green Chemistry: An Introductory Text* (RSC, Cambridge, 2010)
36. S.C. Ameta, R. Ameta (eds.), *Green Chemistry: Fundamentals and Applications* (CRC Press, Boca Raton, 2013)
37. H. Pinkowska, Polimery **51**, 836 (2006)
38. T. Oshima, M. Sato, Y. Shikaze, K. Ohto, K. Inoue, Y. Baba, Biochem. Eng. J. **35**, 66 (2007)
39. Y. Yang, L. Mao, L. Li, X. Liu, J. Shi, S. Cao, Chem. Res. Chin. Univ. **20**, 240 (2004)
40. L. Zhang, J. Lian, J. Solid State Electrochem. **12**, 1 (2008)
41. B. Grignard, C. Jerome, C. Calberg, R. Jerome, C. Detrembleur, Eur. Polym. J. **44**, 861 (2008)
42. T. Ribaut, P. Lacroix-Desmazes, B. Fournel, S. Sarrade, J. Polym. Sci. A **47**, 5448 (2009)
43. J.M. DeSimone, W. Tumas (eds.), *Green Chemistry Using Liquid and Supercritical Carbon Dioxide* (Oxford University Press, Oxford, 2003)
44. A. Abdolmaleki, S.K. Varnamkhasti, J. Appl. Polym. Sci. **113**, 1935 (2009)
45. C.L. McCormick, A.B. Lowe, Acc. Chem. Res. **37**, 312 (2004)
46. D. Braun, H. Cherdron, M. Rehahn, H. Ritter, B. Voit, *Polymer Synthesis: Theory and Practice: Fundamentals, Methods, Experiments* (Springer, Berlin, 2012)
47. P.A. Williams (ed.), *Handbook of Industrial Water Soluble Polymers* (Wiley-Blackwell, Singapore, 2007)
48. B. Rieger, A. Künkel, G.W. Coates, R. Reichardt, E. Dinjus, T.A. Zevaco (eds.), *Synthetic Biodegradable Polymers* (Springer, Heidelberg, 2012)
49. T. Ma, Y. Liu, L. Sun, Gaofenzi Cailiao Kexue Yu Gongcheng **25**, 157 (2009)
50. K. Ishizu, K. Tsubaki, A. Mori, S. Uchida, Prog. Polym. Sci. **28**, 27 (2003)
51. S. Seiffert, Macromol. Chem. Phys. **216**, 9 (2015)
52. U.S. Schubert, A. Winter, *Supramolecular Assemblies: Polymers and Discrete Systems* (Wiley-VCH Verlag, Weinheim, 2015)
53. N. Hadjichristidis, A. Hirao, Y. Tezuka, F. Du Prez (eds.), *Complex Macromolecular Architectures: Synthesis, Characterization, and Self-Assembly* (John Wiley & Sons, Asia, Pte Ltd., 2011)
54. J.-M. Lehn, Chem. Soc. Rev. **36**, 151 (2007)
55. J.-M. Lehn, Aust. J. Chem. **63**, 611 (2010)
56. J.-M. Lehn, Constitutional dynamic chemistry: bridge from supramolecular chemistry to adaptive chemistry, in *Constitutional Dynamic Chemistry*, ed. by M. Barboiu (Springer, Berlin, Heidelberg, 2012)
57. J.-M. Lehn, Angew. Chem. Int. Ed. **127**, 4 (2015)
58. S.J. Rowan, S.J. Cantrill, G.R.L. Cousins, J.K.M. Sanders, J.F. Stoddart, Angew. Chem. Int. Ed. **41**, 898 (2002)
59. L. Hu, F. Schaufelberger, B.J.J. Timmer, M. Abellán Flos, O. Ramström, Constitutional dynamic chemistry, in *Kirk-Othmer Encyclopedia of Chemical Technology*, ed. by Kirk-Othmer (Wiley, NY, 2014)
60. J. Li, P. Nowak, S. Otto, J. Am. Chem. Soc. **135**, 9222 (2013)
61. J.C. Eslick, Q. Ye, J. Park, E.M. Topp, P. Spencer, K.V. Camarda, Comput. Chem. Eng. **33**, 954 (2009)
62. A.D. Pomogailo, I.E. Uflyand, E.F. Vainshtein, Russ. Chem. Rev. **64**, 857 (1995)
63. V.I. Irzhak, *Polymer Architecture* (Nauka, Moscow, 2012)
64. G.V. Korolyov, M.M. Mogilevich, *Three-Dimensional Free-Radical Polymerization* (Springer, Berlin, Heidelberg, 2009)
65. J. Zhao, T. Zhao, K. Qiu, Chin. J. Polym. Sci. **15**, 50 (1997)

66. T. Kaliyappan, S. Rajagopan, P. Kannan, J. Appl. Polym. Sci. **90**, 2083 (2003)
67. P. Kandasamy, M. Sasidaran, N. Janaki, T. Kaliyappan, J. Appl. Polym. Sci. **124**, 3600 (2012)
68. T. Kaliyappan, S. Rajagopan, P. Kannan, J. Appl. Polym. Sci. **91**, 494 (2004)
69. P.G. Ingole, H.C. Bajaj, K. Singh, J. Appl. Polym. Sci. **128**, 66 (2013)
70. R. Sankar, M. Sasidaran, T. Kaliyappan, High Perform. Polym. **23**, 32 (2011)
71. S. Vijayalakshmi, R. Sankar, S. Subramanian, S. Rajagopan, T. Kaliyappan, J. Appl. Polym. Sci. **104**, 797 (2007)
72. S. Vijayalakshmi, S. Subramanian, S. Rajagopan, T. Kaliyappan, J. Appl. Polym. Sci. **99**, 1516 (2006)
73. S. Vijayalakshmi, R. Sankar, S. Subramanian, S. Rajagopan, T. Kaliyappan, Des. Monomers Polym. **9**, 425 (2006)
74. R. Sankar, S. Vijayalakshmi, S. Subramanian, S. Rajagopan, T. Kaliyappan, Eur. Polym. J. **43**, 4639 (2007)
75. B. Salih, J. Appl. Polym. Sci. **83**, 1406 (2002)
76. M.V. Arsenyev, M.P. Shurygina, A.I. Poddel’sky, N.O. Druzhkov, S.A. Chesnokov, G.K. Fukin, V.K. Cherkasov, G.A. Abakumov, J. Polym. Res. **20**, 98 (2013)
77. A. Khazaei, D. Soudbar, M. Sadri, S.M.S. Mohaghegh, Iran. Polym. J. **16**, 309 (2007)
78. A.A. Khalil, J. Polym. Res. **20**, 28 (2013)
79. A.A. Khalil, J. Appl. Polym. Sci. **121**, 1160 (2011)
80. R.M. Issa, A.Z. El-Sonbati, A.A. El-Bindary, H.M. Kera, Eur. Polym. J. **38**, 561 (2002)
81. E.H. El-Mossalamy, Zaštita Materijala **49**, 23 (2008)
82. L.Y. Jin, T. Chien, M. Fang, S. Mah, B. Yin, Fibers Polym. **8**, 143 (2007)
83. L.Y. Jin, S. Mah, J. Appl. Polym. Sci. **84**, 2372 (2002)
84. A. Aydogan, D.J. Coady, K.S. Kuk, A. Akar, C.W. Bielawski, M. Marquez, J.L. Sessler, Angew. Chem. Int. Ed. **47**, 9648 (2008)
85. G.J. Price, P.L. Drake, React. Funct. Polym. **66**, 109 (2006)
86. Y.M. Wang, X.J. Ju, Z. Liu, R. Xie, W. Wang, J.F. Wu, Y.Q. Zhang, L.Y. Chu, Macromol. Rapid Commun. **35**, 1280 (2014)
87. P. Mi, L.Y. Chu, X.J. Ju, C.H. Niu, Macromol. Rapid Commun. **29**, 27 (2008)
88. H.R. Yu, X.J. Ju, R. Xie, W. Wang, B. Zhang, L.Y. Chu, Anal. Chem. **85**, 6477 (2013)
89. B. Zhang, X.J. Ju, R. Xie, Z. Liu, S.W. Pi, L.Y. Chu, J. Phys. Chem. B **116**, 5527 (2012)
90. R.M. Patel, M.B. Patel, P.M. Patel, K.J. Patel, Orient. J. Chem. **17**, 233 (2001)
91. S.A. Patel, B.S. Shah, R.M. Patel, P.M. Patel, Iran. Polym. J. **13**, 445 (2004)
92. P. Patel, B. Shah, A. Ray, R. Patel, J. Polym. Res. **11**, 65 (2004)
93. H.M. Zalloum, B. El-Eswed, R.M. Zalloum, M.S. Mubarak, J. Appl. Polym. Sci. **126**, 1008 (2012)
94. J. Bernard, C. Branger, I. Beurroies, R. Denoyel, S. Blanc, A. Margaillan, Polymer **51**, 2472 (2010)
95. C.-H. Yuan, S.-B. Lin, B. Liu, A.-R. Ke, Z.-L. Quan, Sens. Actuators B Chem. **140**, 155 (2009)
96. R.M. Zalloum, M.S. Mubarak, J. Appl. Polym. Sci. **109**, 3180 (2008)
97. L. Hauser, A.-C. Knall, M. Roth, G. Trimmel, M. Edler, T. Griesser, W. Kern, Monatsh. Chem. **143**, 1551 (2012)
98. T. Bilig, Y. Koyama, T. Takata, Chem. Lett. **37**, 468 (2008)
99. A.Z. Albayrak, D. Avci, J. Appl. Polym. Sci. **109**, 459 (2008)
100. S. Masuda, T. Tomida, M. Tanaka, Y. Asahi, Macromol. Chem. Phys. **196**, 621 (1995)
101. T. Tomida, M. Tomida, Y. Nishihara, I. Nakabayashi, T. Okazaki, S. Masuda, Polymer **31**, 102 (1990)
102. H.R. Kricheldorf, N. Lomadze, G. Schwarz, J. Macromol. Sci. Part A **46**, 346 (2009)
103. D.-F. Wei, R.-H. Zhou, Y.-W. Zhang, Y. Guan, A.-N. Zheng, J. Appl. Polym. Sci. **130**, 419 (2013)
104. C.-C. Wang, C.-Y. Chen, C.-Y. Chang, J. Appl. Polym. Sci. **84**, 1353 (2002)
105. R. Say, S. Emir, B. Garipcan, S. Patir, A. Denizli, Adv. Polym. Technol. **22**, 355 (2003)

106. A. Denizli, B. Garipean, A. Karabakan, R. Say, S. Emir, S. Patir, Sep. Purif. Technol. **30**, 3 (2003)
107. H.M.M.N. El-Din, J. Appl. Polym. Sci. **86**, 1607 (2002)
108. H.A. Hanafi, M. Abd Elsamad, Open J. Inorg. Chem. **5**, 19 (2015)
109. N. Şahiner, Ö. Çelikbıçak, S. Malc, Ö. Kantoğlu, B. Salih, J. Appl. Polym. Sci. **99**, 1657 (2006)
110. S. Döker, Ö. Çelikbıçak, M. Doğan, B. Salih, Microchem. J. **84**, 80 (2006)
111. N. Sandor, D. Gyorgy, K. Sandor, Z. Miklos, Magy. Kem. Lap. **57**, 410 (2002)
112. J. Jagur-Grodzinski (ed.), *Living and Controlled Polymerization, Synthesis, Characterization and Properties of the Respective Polymers and Copolymers* (Nova Science Publishers, NY, 2006)
113. N.V. Tsarevsky, B.S. Sumerlin (eds.), *Fundamentals of Controlled/Living Radical Polymerization* (RSC Publications, Cambridge, 2012)
114. K. Matyjaszewski, T.P. Davis, *Handbook of Radical Polymerization* (Wiley, Hoboken, 2002)
115. K.A. Aamer, G.N. Tew, Macromolecules **37**, 1990 (2004)
116. Y.-N. Zhou, Q. Zhang, Z.-H. Luo, Langmuir **30**, 1489 (2014)
117. K. Matyjaszewski, J. Xia, Chem. Rev. **101**, 2921 (2001)
118. M. Kamigaito, T. Ando, M. Sawamoto, Chem. Rev. **101**, 3689 (2001)
119. G. Moad, E. Rizzardo, S.H. Thang, Polymer **49**, 1079 (2008)
120. S. Perrier, P. Takolpuckdee, J. Polym. Sci. Part A Polym. Chem. **43**, 5347 (2005)
121. J.B. Mcleary, B. Klumperman, Soft Matter **2**, 45 (2006)
122. G. Moad, M. Chen, M. Häussler, A. Postma, E. Rizzardo, S.H. Thang, Polym. Chem. **2**, 492 (2011)
123. G. Moad, E. Rizzardo, S.H. Thang, Aust. J. Chem. **62**, 1402 (2009)
124. C.J. Hawker, A.W. Bosman, E. Harth, Chem. Rev. **101**, 3661 (2001)
125. Z. Yang, J. Lu, Gaofenzi Xuebao 838 (2008)
126. Z. Yang, J. Lu, L. Wang, Polym. Bull. **53**, 249 (2005)
127. C.-M. Liu, J.-J. Qiu, R. Bao, Y. Xu, X.-J. Cheng, F. Hu, Polymer **47**, 2962 (2006)
128. J. Zhou, L. Wang, X. Dong, T. Chen, Q. Yang, Q. Tan, J. Wang, Eur. Polym. J. **43**, 2088 (2007)
129. S. Li, H. Li, J. Guo, Huagong xuebao. SIESC J. **63**, 1967 (2012)
130. C. Wang, W. Zhang, N. Zhou, Y. Qiu, Z. Cheng, X. Zhu, Int. J. Polym. Sci. **2010**, article ID 340926 (2010)
131. J. Xu, X. Xiao, Y. Zhang, W. Zhang, J. Polym. Sci. Part A Polym. Chem. **51**, 1147 (2013)
132. H. Hofmeier, A. El-Ghayoury, U.S. Schubert, J. Polym. Sci. A **42**, 4028 (2004)
133. F.D. Jochum, J. Brassinne, C.-A. Fustin, J.-F. Gohy, Soft Matter **9**, 2314 (2013)
134. Q. He, J. Huang, H. Liang, J. Lu, Polym. Chem. **5**, 4348 (2014)
135. G. Zhou, I.I. Harruna, Macromolecules **37**, 7132 (2004)
136. G. Zhou, I.I. Harruna, Macromolecules **38**, 4114 (2005)
137. J. Zhang, L. Wang, C. Li, Y. Li, J. Liu, Y. Tu, W. Zhang, N. Zhou, X. Zhu, J. Polym. Sci. Part A Polym. Chem. **52**, 691 (2014)
138. S. Mukherjee, A.P. Bapat, M.R. Hill, B.S. Sumerlin, Polym. Chem. **5**, 6923 (2014)
139. S. Wang, B. Wu, F. Liu, Y. Gao, W. Zhang, Polym. Chem. **6**, 1127 (2015)
140. M. Demetriou, T. Krasia-Christoforou, J. Polym. Sci. Part A Polym. Chem. **50**, 52 (2012)
141. T. Krasia, R. Soula, H.G. Börner, H. Schlaad, Chem. Commun. **4**, 538 (2003)
142. T. Otsu, J. Polym. Sci. Part A Polym. Chem. **38**, 2121 (2000)
143. N. Metz, P. Theato, Eur. Polym. J. **43**, 1202 (2007)
144. U. Mansfeld, A. Winter, M.D. Hager, W. Günther, E. Altuntaş, U.S. Schubert, J. Polym. Sci. Part A Polym. Chem. **51**, 2006 (2013)
145. M. Nowakowska, A. Karewicz, M. Klos, Macromolecules **36**, 4134 (2003)
146. R. Shunmugam, K.A. Aamer, G.N. Tew, Polym. Prepr. **48**, 635 (2007)
147. B.G.G. Lohmeijer, U.S. Schubert, J. Polym. Sci. Part A Polym. Chem. **42**, 4016 (2004)

148. H.W. Gibson, Z. Ge, F. Huang, J.W. Jones, H. Lefebvre, M.J. Vergne, D.M. Hercules, Macromolecule **38**, 2626 (2005)
149. A. Farcas, M. Pinteala, V. Harabagiu, Rev. Roum. Chim. **52**, 143 (2007)
150. C.W. Bielawski, R.H. Grubbs, Prog. Polym. Sci. **32**, 1 (2007)
151. A.V. Rozhkov, L.N. Bochkarev, G.V. Basova, G.A. Abakumova, Zh. Prikl. Khim. **85**, 2046 (2012)
152. A.V. Rozhkov, L.N. Bochkarev, G.V. Basova, I.P. Malysheva, Y.E. Begantsova, E.O. Platonova, E.V. Baranov, Y.A. Kurskii, V.A. Il'ichev, M.A. Lopatin, G.A. Abakumov, M. N. Bochkarev, Zh. Obsch. Khim. **82**, 1937 (2012)
153. H. Li, K. Feng, L. Zhou, B. Chen, L. Zhang, Z. Tong (C. Tung), L. Wu, Yingxiang kexue yu guanghuaxue. Imaging Sci. Photochem. **30**, 429 (2012)
154. J.L. Bender, Q.-D. Shen, C.L. Fraser, Tetrahedron **60**, 7277 (2004)
155. A.A. Farah, W.J. Pietro, Can. J. Chem. **82**, 595 (2004)
156. H. Hofmeier, R. Hoogenboom, M.E.L. Wouters, U.S. Schubert, J. Am. Chem. Soc. **127**, 2913 (2005)
157. R.P. Sijbesma, F.H. Beier, L. Brunsveld, B.J.B. Folmer, J.H.K.K. Hirschberg, R.F.M. Lange, J.K.L. Lowe, E.W. Meijer, Science **278**, 1601 (1997)
158. R. Hoogenboom, D. Wouters, U.S. Schubert, Macromolecules **36**, 4743 (2003)
159. L.-Z. Meng, S.-L. Gong, Y.-H. Yin, Y.-Y. Chen, Y.-W. Wang, J. Appl. Polym. Sci. **87**, 1445 (2003)
160. J. Hu, J. He, M. Zhang, P. Ni, Gaofenzi Xuebao. Acta Polym. Sin. 300 (2013)
161. P. Espeel, F.E. Du Prez, Macromolecules **48**, 2 (2015)
162. H. Struthers, T.L. Mindt, R. Schibli, Dalton Trans. **39**, 675 (2010)
163. H. Chen, J. Zeng, F. Deng, X. Luo, Z. Lei, H. Li, J. Polym. Res. **19**, 9880 (2012)
164. W.H. Daly, S. Moulay, J. Polym. Sci. Polym. Symp. **74**, 227 (1986)
165. S.V. Amosova, L.P. Shaulina, G.V. Ratovskii, I.P. Golentovskaya, M.I. Smagunova, E.I. Birukova, S.A. Zhivetjeva, Khim. Inter. Ustoich. Razv. **11**, 831 (2003)
166. S. Habaue, M. Morita, Y. Okamoto, Kobunshi Ronbunshu **59**, 717 (2002)
167. H. Higashimura, S. Kobayashi, Oxidative polymerization, in *Encyclopedia of Polymer Science and Technology*, ed. by H.F. Mark, J.I. Kroschwitz (Wiley, Hoboken, 2002)
168. Z. Chen, C. Duanmu, L. Xiao, Wuhan Univ. J. Nat. Sci. **9**, 503 (2004)
169. T.C. Chang, C.C. Shih, C.P. Yin, H.B. Chen, T.R. Wu, Polym. Degrad. Stab. **87**, 87 (2005)
170. X.-G. Li, M.-R. Huang, Y.-M. Hua, M.-F. Zhu, Q. Chen, Polymer **45**, 4693 (2004)
171. X.-G. Li, M.-R. Huang, Y. Jin, Y.L. Yang, Polymer **42**, 3427 (2001)
172. X.-G. Li, M.-R. Huang, F. Li, W.J. Cai, Z. Jin, Y.L. Yang, J. Polym. Sci. Part A Polym. Chem. **38**, 4407 (2000)
173. C.O. Sánchez, B.L. Rivas, J. Appl. Polym. Sci. **85**, 2564 (2002)
174. H. Wang, A. Miyamoto, T. Hirano, M. Seno, T. Sato, Eur. Polym. J. **40**, 2287 (2004)
175. P. Savitha, P.S. Rao, D.N. Sathyanarayana, Polym. Int. **54**, 1243 (2005)
176. H.J. Salavagione, D.F. Acevedo, M.C. Miras, C. Barbero, Port. Electrochim. Acta **21**, 245 (2003)
177. B.L. Rivas, C.O. Sanchez, J. Appl. Polym. Sci. **89**, 2641 (2003)
178. J. Rutkowska, K. Kilian, K. Pyrzynska, Eur. Polym. J. **44**, 2108 (2008)
179. Z. Liu, Q. Liu, X. Dai, C. Shen-Tu, C. Yao, Y. Kong, ECS Electrochem. Lett. **2**, G1 (2013)
180. S. Huang, P. Du, C. Min, Y. Liao, H. Sun, Y. Jiang, J. Fluoresc. **23**, 621 (2013)
181. B.L. Rivas, C.O. Sanchez, J. Appl. Polym. Sci. **92**, 31 (2004)
182. X.-G. Li, Y.-M. Hua, M.-R. Huang, Chem. Eur. J. **11**, 4247 (2005)
183. X.-G. Li, M.-R. Huang, Y.-M. Hua, Macromolecules **38**, 4211 (2005)
184. X. Lu, H. Mao, D. Chao, X. Zhao, W. Zhang, Y. Wei, Mater. Lett. **61**, 1400 (2007)
185. X.-G. Li, M.-R. Huang, S.-X. Li, Acta Mater. **52**, 5363 (2004)
186. S. Huang, C. Min, Y. Liao, P. Du, H. Sun, Y. Zhu, A. Ren, RSC Adv. **4**, 47657 (2014)
187. J. Stejskal, Prog. Polym. Sci. **41**, 1 (2015)
188. S. Almeida, E. Rivera, J.M. Reyna-González, G. Huerta, F. Tapia, M. Aguilar-Martínez, Synth. Metals **159**, 1215 (2009)

189. A. Vázquez-Arce, G. Zaragoza-Galán, E. Aguilar-Ortíz, E.G. Morales-Espinoza, E. Rodríguez-Alba, E. Rivera, Des. Monom. Polym. **17**, 78 (2014)
190. E. Aguilar-Ortíz, G. Zaragoza-Galán, N. Solladié, R. Rein, M. Aguilar-Martínez, N. Macías-Ruvalcaba, E. Rivera, Synth. Metals **162**, 1000 (2012)
191. S.-M. Lee, S. Jung, C.-S. Ha, I. Chung, W.-K. Lee, Y.-H. Park, Macromol. Res. **16**, 510 (2008)
192. S.-M. Lee, N.-J. Lee, C.-S. Ha, W.-J. Cho, J. Appl. Polym. Sci. **94**, 57 (2004)
193. C. Ebner, T. Bodner, F. Stelzer, F. Wiesbrock, Macromol. Rapid Commun. **32**, 254 (2011)
194. S. Mallakpour, Z. Rafiee, Prog. Polym. Sci. **36**, 1754 (2011)
195. S. Mallakpour, M. Dinari, Polym. Adv. Technol. **19**, 1334 (2008)
196. S.D. Kukade, R.R. Naik, S.V. Bawankar, Orbital Electron. J. Chem. **6**, 240 (2014)
197. H. Kantekin, Z. Biyiklioğlu, Dyes Pigm. **77**, 432 (2008)
198. Y. Yang, D. Yu, Y. Liu, Y. Zhao, H. Fan, L. Jin, J. Zhou, Q. Jin, Liaoning Shiyou Huagong Daxue xuebao **26**, 56 (2006)
199. B.C. Mondal, A.K. Das, React. Funct. Polym. **53**, 45 (2002)
200. K. Faghihi, K. Zamani, A. Mirsamie, S.M. Reza, Eur. Polym. J. **39**, 247 (2003)
201. İ. Değirmencioğlu, R. Bayrak, M. Er, K. Serbest, Dyes Pigm. **83**, 51 (2009)
202. Q. Li, Q. Gao, H. Peng, Z. Xu, C. Yi, Gaofenzi Cailiao Kexue Yu Gongcheng **24**, 34 (2008)
203. A. Mahapatro, T.D.M. Negrón, Microwave-assisted biocatalytic polymerizations, in *Green Polymer Chemistry: Biocatalysis and Materials II*, ACS Symposium Series, vol. 1144, ed. by H.N. Cheng, R.A. Gross, P.B. Smith (ACS, Washington, 2013)
204. R. Kakuchi, R. Sakai, I. Otsuka, T. Satoh, H. Kaga, T. Kakuchi, Macromolecules **38**, 9441 (2005)
205. A. Bilgin, D. Yanmaz, C. Yagci, Turk. J. Chem. **38**, 1135 (2014)
206. K. Naka, T. Uemura, Y. Chujo, J. Polym. Sci. A **39**, 4083 (2001)
207. T. Narita, H. Hamana, M. Takeshita, H. Fujiwara, J. Fluorine Chem. **124**, 197 (2003)
208. M.H. Weston, O.K. Farha, B.G. Hauser, J.T. Hupp, S.T. Nguyen, Chem. Mater. **24**, 1292 (2012)
209. V. Borovkov, Symmetry **6**, 256 (2014)
210. M. Heller, U.S. Schubert, e-Polymers **2**, 375 (2002)
211. M. Azechi, K. Yamabuki, K. Onimura, T. Oishi, Polym. J. **42**, 632 (2010)
212. L. Feng, F.B. Zhao, Z.L. Liu, J.P. Sun, J.W. Hu, Chin. Chem. Lett. **18**, 875 (2007)
213. C. Zhang, Y. Zhang, H. Zhang, Y. Hu, X. Zhang, T. Masuda, React. Funct. Polym. **87**, 46 (2015)
214. Y. Zhang, K. Gao, Z. Zhao, D. Yue, Y. Hu, T. Masuda, J. Polym. Sci. Part A Polym. Chem. **51**, 5248 (2013)
215. R. Sakai, I. Otsuka, T. Satoh, R. Kakuchi, H. Kaga, T. Kakuchi, J. Polym. Sci. A **44**, 325 (2006)
216. R. Sakai, I. Otsuka, T. Satoh, R. Kakuchi, H. Kaga, T. Kakuchi, Macromolecules **39**, 4032 (2006)
217. F. Takei, H. Hayashi, K. Onitsuka, N. Kobayashi, S. Takahashi, Angew. Chem. Int. Ed. **40**, 4092 (2001)
218. P.A.J. De Witte, M. Castriciano, J.J.L.M. Cornelissen, L.M. Scolaro, R.J.M. Nolte, A.E. Rowan, Chem. Eur. J. **9**, 1775 (2003)
219. J. Tabei, M. Shiotsuki, F. Sanda, T. Masuda, Macromolecules **38**, 9448 (2005)
220. R. Sakai, T. Yonekawa, I. Otsuka, R. Kakuchi, T. Satoh, T. Kakuchi, J. Polym. Sci. A **48**, 1197 (2010)
221. S. Sakthivel, T. Punniyamurthy, Tetrahedron Asymmetry **23**, 570 (2012)
222. K. Günay, P. Theato, H.-A. Klok, J. Polym. Sci. A **51**, 1 (2013)
223. P.J. Roth, Macromol. Chem. Phys. **215**, 825 (2014)
224. M.D. Hossain, Z. Jia, M.J. Monteiro, Macromolecules **47**, 4955 (2014)
225. J. Romulus, J.T. Henssler, M. Weck, Macromolecules **47**, 5437 (2014)
226. N. Bensacia, S. Moulay, Int. J. Polym. Mater. **61**, 699 (2012)

227. I.M. Henderson, R.C. Hayward, Macromolecules **43**, 3249 (2010)
228. K. Uzun, E. Çevik, M. Şenel, Amer. J. Chem. **1**, 16 (2011)
229. H.A. Saadeh, E.A. Abu Shairah, N. Charef, M.S. Mubarak, J. Appl. Polym. Sci. **124**, 2717 (2012)
230. J.F. Lovell, A. Roxin, K.K. Ng, Q. Qi, J.D. McMullen, R.S. DaCosta, G. Zheng, Biomacromol **12**, 3115 (2011)
231. Y. de Gaetano, I. Clarota, J.-B. Regnouf-de-Vains, New J. Chem. **36**, 1339 (2012)
232. X. Wang, X. Zhang, H. Guo, L. Yuan, P. Liu, Polym. Eng. Sci. **52**, 972 (2012)
233. L.X. Yuan, X.M. Wang, X. Zhang, P.G. Liu, W.D. Yan, Chin. Chem. Lett. **21**, 1493 (2010)
234. R. Kumar, S.K. Jain, R.K. Misra, M. Kachchwaha, P.K. Khatri, Int. J. Environ. Sci. Technol. **9**, 79 (2012)
235. M.Y. Abdelaal, I.M.M. Kenawy, M.A.H. Hafez, J. Appl. Polym. Sci. **77**, 3044 (2000)
236. T. Çaykara, Ş.Ş. Alaslan, J. Appl. Polym. Sci. **106**, 2126 (2007)
237. K. Bester, A. Bukowska, W. Bukowski, J. Mol. Catal. A Chem. **378**, 124 (2013)
238. B. Gao, J. Zhang, J. Guo, J. Polym. Res. **17**, 301 (2010)
239. S.V. Vinogradova, V.A. Vasnev, Russ. Chem. Rev. **73**, 487 (2004)
240. S.V. Vinogradova, V.A. Vasnev, M.L. Keshtov, Vysokomol. Soedin. **49**, 2010 (2007)
241. S.S. Butoliya, A.B. Zade, W.B. Gurnule, J. Appl. Polym. Sci. **113**, 1 (2009)
242. A.S. Amarasekara, D. Green, L.D. Williams, Eur. Polym. J. **45**, 595 (2009)
243. H. Al-Adwani, A. Bishara, H. Shaban, J. Appl. Polym. Sci. **89**, 1 (2003)
244. N.S. Al-Muaikel, T.I. El-Emary, Eur. Polym. J. **39**, 211 (2003)
245. S. Lugovskoy, M. Nisnevitch, M. Zinigrad, D. Wolf, Clean Technol. Environ. Policy **10**, 279 (2008)
246. Y. Zhang, C.B. Murphy, W.E. Jones Jr., Macromolecules **35**, 630 (2002)
247. R.C. Smith, A.G. Tennyson, A.C. Won, S.J. Lippard, Inorg. Chem. **45**, 9367 (2006)
248. H. Huang, Q. Miao, Y. Kang, X. Huang, J. Xu, Y. Cheng, Bull. Chem. Soc. Jpn. **81**, 1116 (2008)
249. Q. Hou, Y. Zhang, R.Q. Yang, W. Yang, Y. Cao, Synth. Metals **153**, 193 (2005)
250. I. Welterlich, B. Tieke, Macromolecules **44**, 4194 (2011)
251. A.R. Rabindranath, A. Maier, M. Schafer, B. Tieke, Macromol. Chem. Phys. **210**, 659 (2009)
252. Q. Sun, H. Wang, C. Yang, Y. Li, J. Mater. Chem. **13**, 800 (2003)
253. M. Chiper, R. Hoogenboom, U.S. Schubert, Eur. Polym. J. **46**, 260 (2010)
254. H. Huang, Z. Cao, Z. Gu, X. Li, B. Zhao, P. Shen, S. Tan, Eur. Polym. J. **10**, 1805 (2012)
255. X. Huang, C. Zhu, S. Zhang, W. Li, Y. Guo, X. Zhan, Y. Liu, Macromolecules **41**, 6895 (2008)
256. Q.-H. Chu, Y. Pang, J. Polym. Sci. Part A Polym. Chem. **44**, 2338 (2006)
257. L. Florea, D. Diamond, F. Benito-Lopez, Macromol. Mater. Eng. **297**, 1148 (2012)
258. L. Bao, J. Sun, Q. Li, J. Polym. Res. **21**, 575 (2014)
259. H. Komber, S. Müllers, F. Lombeck, A. Held, M. Walter, M. Sommer, Polym. Chem. **5**, 443 (2014)
260. M. Sommer, H. Komber, Macromol. Rapid Commun. **34**, 57 (2013)
261. L. Metzler, T. Reichenbach, O. Brügner, H. Komber, F. Lombeck, S. Müllers, R. Hanselmann, H. Hillebrecht, M. Walter, M. Sommer, Polym. Chem. **6**, 3694 (2015)
262. S. Kobayashi, Adv. Polym. Sci. **262**, 141 (2013)
263. R. Mosurkal, S. Roy, J. Kumar, L.A. Samuelson, S.K. Tripathy, J. Macromol. Sci. A **39**, 1195 (2002)
264. L.N. Monsalve, F.M. Kaniz, H. Nonami, R. Erra-Balsells, A. Baldessari, Polymer **51**, 2998 (2010)
265. H. Kawakita, S. Nakano, K. Hamamoto, Y. Matsunaga, Y. Yoshimura, K. Ohto, K. Inoue, J. Appl. Polym. Sci. **118**, 247 (2010)
266. H. Duan, K. Zheng, Y. Cui, Y. Li, L. Zhang, Chin. J. Polym. Sci. **32**, 906 (2014)

267. D.-H. Yao, G.-J. Li, T. Kuila, P. Li, N.-H. Kim, S.-I. Kim, J.-H. Lee, J. Appl. Polym. Sci. **120**, 1114 (2011)
268. A. Mahapatro, B. Kalra, A. Kumar, R.A. Gross, Biomacromolecules **4**, 544 (2003)
269. A. Asati, D. Lehmkuhl, D. Diaz, J.M. Perez, Langmuir **36**, 13066 (2012)
270. T. Naolou, K. Busse, J. Kressler, Biomacromolecules **11**, 3660 (2010)
271. J. Zhang, H. Shi, D. Wu, Z. Xing, A. Zhang, Y. Yang, Q. Li, Process Biochem. **49**, 797 (2014)
272. E.A. Bekturov, *Polymeric Electrolytes, Hydrogels, Complexes and Catalysts* (Print-S, Almaty, Kazakhstan, 2007)
273. C.-Y. Chen, C.-Y. Chen, Eur. Polym. J. **39**, 991 (2003)
274. W. Bisset, H. Jacobs, N. Koshti, P. Stark, A. Gopalan, React. Funct. Polym. **55**, 109 (2003)
275. Y. Chen, Q.-L. Fan, P. Wang, B. Zhang, Y.-Q. Huang, G.-W. Zhang, X.-M. Lu, H.S.O. Chan, W. Huang, Polymer **47**, 5228 (2006)
276. Y. Chen, K.-Y. Pu, Q.-L. Fan, X.-Y. Qi, Y.-Q. Huang, X.-M. Lu, W. Huang, J. Polym. Sci. A **47**, 5057 (2009)
277. L. Zhang, C. Ni, C. Zhu, X. Jiang, Y. Liu, B. Huang, J. Appl. Polym. Sci. **112**, 2455 (2009)
278. H. Zhao, M. Deng, Synthesis. J. Mater. Civ. Eng. **25**, 112 (2013)
279. B. Zhou, J.Z. Li, C.H. He, S.Y. Qin, Chin. Chem. Lett. **16**, 27 (2005)
280. D. Nagai, M. Yoshida, T. Kishi, H. Morinaga, Y. Hara, M. Mori, S. Kawakami, K. Inoue, Chem. Commun. **49**, 6852 (2013)
281. B.L. Rivas, A. Maureira, Inorg. Chem. Commun. **10**, 151 (2007)
282. B.L. Rivas, C. Muñoz, Macromol. Symp. **304**, 40 (2011)
283. K. Ding, F. Wang, F. Wu, Chin. J. Polym. Sci. **30**, 63 (2012)
284. L. Do, R.C. Smith, A.G. Tennyson, S.J. Lippard, Inorg. Chem. **45**, 8998 (2006)
285. F. Gasc, S. Clerc, E. Gayon, J.-M. Campagne, P. Lacroix-Desmazes, J. Supercrit. Fluids **105**, 136 (2015)
286. L. Erdmann, K.E. Uhrich, Biomaterials **21**, 1941 (2000)
287. S.J. Choi, K.E. Geckeler, J. Appl. Polym. Sci. **90**, 650 (2003)
288. A. Okamura, T. Hirai, M. Tanihara, T. Yamaoka, Polymer **43**, 3549 (2002)
289. A.L. Carbone-Howell, N. Stebbins, K.E. Uhrich, Biomacromolecules **15**, 1889 (2014)
290. M.A. Rogers, Y.-F. Yan, K. Ben-Elazar, Y. Lan, J. Faig, K. Smith, K.E. Uhrich, Biomacromolecules **15**, 3406 (2014)
291. Y. Chandorkar, R.K. Bhagat, G. Madras, B. Basu, Biomacromolecules **15**, 863 (2014)
292. A. Zintchenko, L.J. van der Aa, J.F. Engbersen, Macromol. Rapid Commun. **32**, 321 (2011)
293. A.D. Pomogailo, *Catalysis by Polymer-Immobilized Metal Complexes* (Gordon & Breach Science Publishers, Amsterdam, 1998)
294. C. Feng, Y. Li, D. Yang, J. Hu, X. Zhang, X. Huang, Chem. Soc. Rev. **40**, 1282 (2011)
295. N. Hadjichristidis, S. Pispas, H. Iatrou, D.J. Lohse, Graft copolymers, in *Encyclopedia of Polymer Science and Technology*, ed. by K. Matyjaszewski (Wiley, Hoboken, 2007)
296. A. Bhattacharya, J.W. Rawlins, P. Ray (eds.), *Polymer Grafting and Crosslinking* (Wiley, Hoboken, New Jersey, 2009)
297. A. Bhattacharya, B.N. Misra, Prog. Polym. Sci. **29**, 767 (2004)
298. C.J. Galvin, J. Genzer, Prog. Polym. Sci. **37**, 871 (2012)
299. K. Kato, E. Uchida, E.-T. Kang, Y. Uyama, Y. Ikada, Prog. Polym. Sci. **28**, 209 (2003)
300. G. Gu, P. An, Gaofenzi Cailiao Kexue Yu Gongcheng **19**, 1 (2003)
301. H. Gao, K. Matyjaszewski, J. Am. Chem. Soc. **129**, 6633 (2007)
302. L. Wu, J. Baghdachi (eds.), *Functional Polymer Coatings: Principles, Methods, and Applications* (Wiley, Hoboken, NY, 2015)
303. F. Zhisheng, Z. Liang, Z. Jingxing, P. Huijie, S. Hongfu, W. Hua, J. Senyang, F. Zhiqiang, Suliao Keji. Plast. Sci. Technol. **38**, 89 (2010)
304. Y. Zeng, R. Jia, H. Yan, Suliao Keji. Plast. Sci. Technol. **40**, 123 (2012)
305. C. Pichot, Curr. Opin. Colloid Interface Sci. **9**, 213 (2004)
306. H. Wang, H. Zhang, Y. Lv, F. Svec, T. Tan, J. Chromatogr. A **1343**, 128 (2014)

307. L. Malovic, A. Nastasovic, Z. Sandic, J. Markovic, D. Dordevic, Z. Vukovic, J. Mater. Sci. **42**, 3326 (2007)
308. G. Bayramoğlu, M.Y. Arıca, Sep. Purif. Technol. **45**, 192 (2005)
309. J. Zu, S. He, Y.C. Nho, J.J. Pyo, F. Yan, J. Appl. Polym. Sci. **116**, 1414 (2010)
310. M. Barsbay, P.A. Kavakli, O. Güven, Radiat. Phys. Chem. **79**, 227 (2010)
311. K. Miyazaki, K. Hisada, T. Hori, Fiber **56**, 227 (2000)
312. M.J. Roman, E.A. Decker, J.M. Goddard, A.C.S. Appl, Mater. Interfaces **6**, 5383 (2014)
313. T. Shiraishi, M. Tamada, K. Saito, T. Sugo, Radiat. Phys. Chem. **66**, 43 (2003)
314. S. Das, A.K. Pandey, A. Athawale, V. Kumar, Y.K. Bhardwaj, S. Sabharwal, V.K. Manchanda, Desalination **232**, 243 (2008)
315. K. Saito, K. Saito, K. Sugita, M. Tamada, T. Sugo, Ind. Eng. Chem. Res. **41**, 5686 (2002)
316. I. Ozawa, K. Saito, K. Sugita, K. Sato, M. Akiba, T. Sugo, J. Chromatogr. A **888**, 43 (2000)
317. S.-Y. Nishiyama, K. Saito, K. Saito, K. Sugita, K. Sato, M. Akiba, T. Saito, S. Tsuneda, A. Hirata, M. Tamada, T. Sugo, J. Membr. Sci. **214**, 275 (2003)
318. A. Jyo, J. Kugara, H. Trobradovic, K. Yamabe, T. Sugo, M. Tamada, T. Kume, Ind. Eng. Chem. Res. **43**, 1599 (2004)
319. K. Saito, K. Saito, K. Sugita, M. Tamada, T. Sugo, J. Chromatogr. A **954**, 277 (2002)
320. P.A. Kavakli, C. Kavakli, O. Güven, Radiat. Phys. Chem. **94**, 105 (2014)
321. K. Ikeda, D. Umeno, K. Saito, F. Koide, E. Miyata, T. Sugo, Ind. Eng. Chem. Res. **50**, 5727 (2011)
322. G. Depecker, C. Branger, A. Margaillan, T. Pigot, S. Blanc, F. Robert-Peillard, B. Coulomb, J.-L. Boudenne, React. Funct. Polym. **69**, 877 (2009)
323. J. Bernard, C. Branger, I. Beurroies, R. Denoyel, A. Margaillan, React. Funct. Polym. **72**, 98 (2012)
324. X. Qiao, B. Yan, J. Phys. Chem. B **112**, 14742 (2008)
325. I.E. Uflyand, A.D. Pomogailo, J. Inorg. Organomet. Polym. **2**, 373 (1992)
326. S. Boussetta, C. Branger, A. Margaillan, J.-L. Boudenne, B. Coulomb, Eur. Polym. J. **43**, 416 (2007)
327. S. Boussetta, C. Branger, A. Margaillan, J.-L. Boudenne, B. Coulomb, React. Funct. Polym. **68**, 775 (2008)
328. N.M. Alotaibi, S. Lahsasni, T. Aouak, J. Appl. Polym. Sci. **127**, 1338 (2013)
329. I.E. Uflyand, A.S. Kuzharov, M.O. Gorbunova, V.N. Sheinker, A.D. Pomogailo, React. Polym. **13**, 145 (1990)
330. J. Feng, Q. Zhang, W. Li, Y. Li, M. Yang, Y. Cao, J. Appl. Polym. Sci. **109**, 2283 (2008)
331. S.D. Alexandratos, C.L. Stine, React. Funct. Polym. **60**, 3 (2004)
332. A. Khazaei, S. Saednia, M.K. Borazjani, J. Saien, M. Kiani, A. Afkhami, Supramol. Chem. **26** (2014)
333. A. Murugesan, B. Meenarathi, L. Kannammal, S. Palanikumar, R. Anbarasan, Synth. Metals **189**, 143 (2014)
334. L.-F. Wang, J.-C. Duan, W.-H. Miao, R.-J. Zhang, S.-Y. Pan, X.-Y. Xu, J. Hazard. Mater. **186**, 1681 (2011)
335. H.H. Abdel-Razik, M. Abbo, H.A. Almahy, J. Appl. Polym. Sci. **125**, 2102 (2012)
336. S. Liu, B. Gao, H. Fu, Gaofenzi Xuebao 727 (2010)
337. D. Madge, J. Ruhe, PMSE Prepr. 255 (2003)
338. P. Murugan, M. Krishnamurthy, S.N. Jaisankar, D. Samanta, A.B. Mandal, Chem. Soc. Rev. **44**, 3212 (2015)
339. S. Çetin, T. Tinçer, J. Appl. Polym. Sci. **108**, 414 (2008)
340. V.Y. Kabanov, V.N. Kudryavtsev, High Energy Chem. **37**, 1 (2003)
341. M.M. Nasef, O. Güven, Prog. Polym. Sci. **37**, 1597 (2012)
342. J.G. Drobny (ed.), *Radiation Technology for Polymers*, 2nd edn. (CRC Press, Boca Raton, London, NY, 2010)
343. B.I. Kharisov, O.V. Kharisova, U.O. Mendez (eds.), *Radiation Synthesis of Materials and Compounds* (CRC Press, Boca Raton, London, NY, 2013)

344. K. Yamashiro, K. Miyoshi, R. Ishihara, D. Umeno, K. Saito, T. Sugo, S. Yamada, H. Fukunaga, M. Nagai, J. Chromatogr. A **1176**, 37 (2007)
345. Y. Yang, N. Ma, Q. Zhang, S. Chen, J. Appl. Polym. Sci. **113**, 3638 (2009)
346. S. Francis, L. Varshney, Radiat. Phys. Chem. **74**, 310 (2005)
347. K. Yamada, R. Nagano, M. Hirata, J. Appl. Polym. Sci. **99**, 1895 (2006)
348. M. Taniguchi, G. Belfort, J. Membr. Sci. **231**, 147 (2004)
349. Z.P. Zhao, J.D. Li, D.X. Zhang, C.X. Chen, J. Membr. Sci. **232**, 1 (2004)
350. S. Ershov, F. Khelifa, M.-E. Druart, Y. Habibi, M.-G. Olivier, R. Snyders, P. Dubois, RSC Adv. **5**, 14256 (2015)
351. V.A. Titov, E.S. Krivykh, T.A. Ageeva, T.G. Shikova, A.B. Solov'eva, V.A. Timofeeva, I. A. Vershinina, V.V. Rybkin, H.-S. Choi, Polym. Sci. A **50**, 841 (2008)
352. Z.M. Liu, Z.K. Xu, J.Q. Wang, Q. Yang, J. Wu, P. Seta, Eur. Polym. J. **39**, 2291 (2003)
353. T. Ito, T. Hioki, T. Yamaguchi, T. Shinbo, S.-I. Nakao, S. Kimura, J. Am. Chem. Soc. **124**, 7840 (2002)
354. S. Edmondson, V.L. Osborne, W.T.S. Huck, Chem. Soc. Rev. **33**, 14 (2004)
355. R. Barbey, L. Lavanant, D. Paripovic, N. Schüwer, C. Sugnaux, S. Tugulu, H.-A. Klok, Chem. Rev. **109**, 5437 (2009)
356. H. Arslan, Block and graft copolymerization by controlled/living radical polymerization methods, in *Polymerization*, ed. by A. De Souza Gomes (InTech, Rijeka, Croatia, 2012)
357. R.R. Bhat, M.R. Tomlinson, J.J. Genzer, Polym. Sci. Part B Polym. Phys. **43**, 3384 (2005)
358. S. Banerjee, T.K. Paira, T.K. Mandal, Polym. Chem. **5**, 4153 (2014)
359. Q.-H. Wang, C.-Z. Wang, Y.-M. Wei, Gaodeng xuexiao huaxun xuebao. Chem. J. Chin. Univ. **33**, 2579 (2012)
360. F.J. Xu, J.P. Zhao, E.T. Kang, K.G. Neoh, J. Li, Langmuir **23**, 8585 (2007)
361. K. Matyjaszewski, D. Hongchen, W. Jakubowski, J. Pietrasik, A. Kusumo, Langmuir **23**, 4528 (2007)
362. M.P. Weir, A.J. Parnell, Polymers **3**, 2107 (2011)
363. G.-P. Jin, Y. Fu, X.-C. Bao, X.-S. Feng, Y. Wang, W.-H. Liu, J. Appl. Electrochem. **44**, 621 (2014)
364. Y. Inoue, T. Matsugi, N. Kashiwa, K. Matyjaszewski, Macromolecules **37**, 3651 (2004)
365. V. Percec, F. Asgarzadeh, J. Polym. Sci. Part A Polym. Chem. **39**, 1120 (2001)
366. S.C. Hong, T. Pakula, K. Matyjaszewski, Macromol. Chem. Phys. **202**, 3392 (2001)
367. S. Harrisson, X. Liu, J.-N. Ollagnier, O. Coutelier, J.-D. Marty, M. Destarac, Polymers **6**, 1437 (2014)
368. J. Bernard, A. Favier, T.P. Davis, C. Barner-Kowollik, M.H. Stenzel, Polymer **47**, 1073 (2006)
369. A. Nese, Y. Kwak, R. Nicolay, M. Barrett, S.S. Sheiko, K. Matyjaszewski, Macromolecules **43**, 4016 (2010)
370. A. Nese, Y. Li, S. Averick, Y. Kwak, D. Konkolewicz, S.S. Sheiko, K. Matyjaszewski, ACS Macro Lett. **1**, 227 (2011)
371. W. Zhang, M. Shiotsuki, T. Masuda, Macromol. Rapid Commun. **28**, 1115 (2007)
372. K. Maeda, N. Kamiya, E. Yashima, Chem. Eur. J. **10**, 4000 (2004)
373. V. Percec, E. Aqad, M. Peterca, J.G. Rudick, L. Lemon, J.C. Ronda, B.B. De, P.A. Heiney, E.W. Meijer, J. Am. Chem. Soc. **128**, 16365 (2006)
374. A. Bakandritsos, N. Bouropoulos, R. Zboril, K. Iliopoulos, N. Boukos, G. Chatzikyriakos, S. Couris, Adv. Funct. Mater. **18**, 1694 (2008)
375. L. Ding, Y.Y. Huang, Y.Y. Zhang, J.P. Deng, W.T. Yang, Macromolecules **44**, 736 (2011)
376. W. Sheng, B. Li, X. Wang, B. Dai, B. Yu, X. Jia, F. Zhou, Chem. Sci. **6**, 2068 (2015)
377. I. Gitsov, C. Zhu, J. Am. Chem. Soc. **125**, 11228 (2003)
378. Q. Li, X. Xiao, X. Zhang, W. Zhang, Polymer **54**, 3230 (2013)
379. N. Hadjichristidis, M. Pitsikalis, H. Iatrou, S. Pispas, Macromol. Rapid Commun. **24**, 979 (2003)
380. D. Neugebauer, Y. Zhang, T. Pakula, S.S. Sheiko, K. Matyjaszewski, Macromolecules **36**, 6746 (2003)

381. Z. Li, K. Zhang, J. Ma, C. Cheng, K.L. Wooley, J. Polym. Sci. Part A Polym. Chem. **47**, 5557 (2009)
382. J.-F. Lutz, N. Jahed, K. Matyjaszewski, J. Polym. Sci. Part A Polym. Chem. **42**, 1939 (2004)
383. R. Ranjan, W.J. Brittain, Macromolecules **40**, 6217 (2007)
384. R.M. Arnold, D.L. Patton, V.V. Popik, J. Locklin, Acc. Chem. Res. **47**, 2999 (2014)
385. Q. Fu, C. Liu, W. Lin, J. Huang, J. Polym. Sci. Part A Polym. Chem. **46**, 6770 (2008)
386. Y.-C. Li, A. Nese, N.V. Lebedeva, T. Davis, K. Matyjaszewski, S.S. Sheiko, J. Am. Chem. Soc. **133**, 17479 (2011)
387. J. Yin, Z.S. Ge, H. Liu, S.Y. Liu, J. Polym. Sci. Part A Polym. Chem. **47**, 2608 (2009)
388. D.H. Han, X. Tong, Y. Zhao, Macromolecules **44**, 5531 (2011)
389. N. Xu, R. Wang, F.S. Du, Z.C. Li, J. Polym. Sci. Part A Polym. Chem. **47**, 3583 (2009)
390. Y.Y. Yuan, Q. Du, Y.C. Wang, J. Wang, Macromolecules **43**, 1739 (2010)
391. A. Dag, H. Sahin, H. Durmaz, G. Hizal, U. Tunca, J. Polym. Sci. Part A Polym. Chem. **49**, 886 (2011)
392. Y. Li, M. Beija, S. Laurent, L. van der Elst, R.N. Muller, H.T.T. Duong, A.B. Lowe, T.P. Davis, C. Boyer, Macromolecules **45**, 4196 (2012)
393. X.S. Fan, G.W. Wang, J.L. Huang, J. Polym. Sci. Part A Polym. Chem. **49**, 1361 (2011)
394. M. Bertoldo, G. Zampano, F. Terra, V. Villari, V. Castelvetro, Biomacromolecules **12**, 388 (2011)
395. L. Ding, C. Chen, J. Deng, W. Yang, Polym. Bull. **69**, 1023 (2012)
396. H.Q. Huang, S.E. Rankin, L.S. Penn, R.P. Quirk, T.H. Cheong, Langmuir **20**, 5770 (2004)
397. V. Mittal (ed.), *Polymer Brushes: Substrates, Technologies, and Properties* (CRC Press, Boca Raton, 2013)
398. R.C. Advincula, W.J. Brittain, K.C. Caster, J. Rühe (eds.), *Polymer Brushes* (Wiley-VCH, Hoboken, New Jersey, 2004)
399. S.V. Orski, R.J. Sheridan, E.P. Chan, K.L. Beers, Polymer **72**, 471 (2015)
400. S.A. Egorov, H.-P. Hsu, A. Milchev, K. Binder, Soft Matter **11**, 2604 (2015)
401. J. Bünsow, T.S. Kelby, W.T.S. Huck, Acc. Chem. Res. **43**, 466 (2009)
402. O. Azzaroni, J. Polym. Sci. Part A Polym. Chem. **50**, 3225 (2012)
403. G. Liu, G. Zhang (eds.), *QCM-D Studies on Polymer Behavior at Interfaces* (Springer, Heidelberg, 2013)
404. S. Kawaguchi, K. Ito, Adv. Polym. Sci. **175**, 299 (2005)
405. R. Verduzco, X. Li, S.L. Pesek, G.E. Stein, Chem. Soc. Rev. **44**, 2405 (2015)
406. S.G. Boyes, A.M. Granville, M. Baum, B. Akgun, B.K. Mirous, W.J. Brittain, Surf. Sci. **570**, 1 (2004)
407. E. Mastan, L. Xu, S. Zhu, Macromol. Theor. Simul. **24**, 89 (2015)
408. J.R. Boyce, D. Shirvanyants, S.S. Sheiko, D.A. Ivanov, S. Qin, H. Boerner, K. Matyjaszewski, Langmuir **20**, 6005 (2004)
409. K. Fries, S. Samanta, S. Orski, J. Locklin, Chem. Commun. 6288 (2008)
410. R. Klajn, Chem. Soc. Rev. **43**, 148 (2014)
411. W.-H. Wang, J.-L. Dong, G.L. Baker, M.L. Bruening, Analyst **136**, 3595 (2011)
412. S. Rathgeber, T. Pakula, A. Wilk, K. Matyjaszewski, K.L. Beers, J. Chem. Phys. **122**, 124904/124901 (2005)
413. R. Djalali, S.-Y. Li, M. Schmidt, Macromolecules **35**, 4282 (2002)
414. J. Rzayev, Macromolecules **42**, 2135 (2009)
415. K. Ishizu, J. Satoh, A. Sogabe, J. Coll. Interface Sci. **274**, 472 (2004)
416. D. Neugebauer, Y. Zhang, T. Pakula, K. Matyjaszewski, Polymer **44**, 6863 (2003)
417. D. Neugebauer, M. Theis, T. Pakula, G. Wegner, K. Matyjaszewski, Macromolecules **39**, 584 (2006)
418. H.G. Boerner, K. Beers, K. Matyjaszewski, S.S. Sheiko, M. Moeller, Macromolecules **34**, 4375 (2001)
419. H.G. Boerner, D. Duran, K. Matyjaszewski, M. da Silva, S.S. Sheiko, Macromolecules **35**, 3387 (2002)

420. A. Kajiwara, K. Matyjaszewski, M. Kamachi, ACS Symp. Ser. **768**, 68 (2000)
421. S. Ohno, A. Nese, B. Cusick, T. Kowalski, K. Matyjaszewski, Vysokomol. Soedin. Ser. A Ser. B **51**, 1947 (2009)
422. C. Chen, P. Tang, F. Qiu, J. Polym. Sci. Part B Polym. Phys. **52**, 1583 (2014)
423. Y.-C. Chung, J.S. Park, C.H. Shin, J.W. Choi, B.C. Chun, Macromol. Res. **20**, 66 (2012)
424. D.A. Tomalia, J.B. Christensen, U. Boas, *Dendrimers, Dendrons, and Dendritic Polymers: Discovery, Applications, and the Future* (Cambridge University Press, Cambridge, 2012)
425. D.A. Tomalia, S.A. Henderson, M.S. Diallo, Ch. 24. Dendrimers—an enabling synthetic science to controlled organic nanostructures, in *Handbook of Nanoscience, Engineering, and Technology*, Second edn. ed. by W.A. Goddard III, D.W. Brenner, S.E. Lyshevski, G. J. Iafrate (CRC Press, Boca Raton, 2007)
426. V. Sujitha, B. Sayani, P. Kalyani, Int. Res. J. Pharm. **2**, 25 (2011)
427. Y. Cheng (ed.), *Dendrimer-based drug delivery systems: from theory to practice* (Wiley, Hoboken, New Jersey, 2012)
428. L.Y. Sklyarov, *Synthesis of Multifunctional Dendrimers and Their Precursors* (LAP LAMBERT Academic Publishing, Germany, 2014)
429. J.M.J. Frechet, D.A. Tomalia (eds.), *Dendrimers and Other Dendritic Polymers* (Wiley, NY, 2002)
430. G.R. Newkome, C.N. Moorefield, F. Vögtle, *Dendrimers and Dendrons: Concepts, Syntheses, Applications* (Wiley-VCH, Weinheim, 2001)
431. F. Vögtle, S. Gestermann, R. Hesse, H. Schwierz, B. Windisch, Prog. Polym. Sci. **25**, 987 (2000)
432. D.A. Tomalia, Progr. Polym. Sci. **30**, 294 (2005)
433. U. Gupta, H.B. Agashe, A. Asthana, N.K. Jain, Biomacromoles **7**, 649 (2006)
434. T. Furukawa, K. Ishizu, Multibranched polymers in solution: stars, dendrimers and hyperbranched polymers, in *Encyclopedia of Surface and Colloid Science*, vol. 1, ed. by P. Somasundara (CRC Press, Boca Raton, 2006)
435. M.V. Walter, M. Malkoch, Accelerated approaches to dendrimers, in *Synthesis of Polymers: New Structures and Methods*, ed. by D.A. Schlüter, C. Hawker, J. Sakamoto (Wiley-VCH, Hoboken, New Jersey, 2012)
436. K. Inoue, Progr. Polym. Sci. **25**, 453 (2000)
437. U. Singh, M. Maqbool Dar, A. Adil Hashmi, Orient. J. Chem. **30**, 911 (2014)
438. R.V. Tambe, S.S. Pakhare, M.G. Jadhav, S.S. Tiwari, C.R. Rai, IJRRPAS **2**, 513 (2010)
439. P.P. Takalkar, V.N. Deshmukh, D.M. Sakarkar, IJPRS **3**, 733 (2014)
440. F. Vögtle, G. Richardt, N. Werner, A.J. Rackstraw, *Dendrimer Chemistry* (Wiley-VCH, Hoboken, New Jersey, 2009)
441. D.A. Tomalia, I. Majoros, J. Macromol. Sci. C **43**, 411 (2003)
442. M. Seiler, Chem. Eng. Technol. **25**, 237 (2002)
443. R. Ceña-Diez, P. García-Broncano, F.J. de la Mata, R. Gómez, M.A. Muñoz-Fernández, Int. J. Nanomed. **11**, 2443 (2016)
444. A. Kimoto, J.-S. Cho, M. Higuchi, K. Yamamoto, Macromolecules **37**, 5531 (2004)
445. M. Arseneault, C. Wafer, J.-F. Morin, Molecules **20**, 9263 (2015)
446. L.P. Balogh, Dendrimer 101, in *Bio-Applications of Nanoparticles*, ed. by W.C.W. Chan, Adv. Exp. Med. Biol. **620**, 136 (2007)
447. R. Prajapat, B. Soni, S. Jain, A. Bhandari, WebmedCentral Pharm. Sci. **1**, WMC00745 (2010)
448. M. Galán, E. Fuentes-Paniagua, F. Javier de la Mata, R. Gómez, Organometallics **33**, 3977 (2014)
449. D.A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, Macromolecules **19**, 2466 (1986)
450. F. Aulenta, W. Hayes, S. Rannard, Eur. Polym. J. **39**, 1741 (2003)
451. D.A. Tomalia, H.M. Brothers, L.T. Piehler, Y.D. Durst, D.R. Swanson, Proc. Nat. Acad. Sci. U S A **99**, 5081 (2002)
452. P.M. Welch, C.F. Welch, Macromolecules **42**, 7571 (2009)

453. A. Malik, S. Chaudhary, G. Garg, A. Tomar, Adv. Biol. Res. **6**, 165 (2012)
454. G.R. Newkome, C.N. Moorefield, F. Vögtle, Chiral dendritic macromolecules, in *Dendritic Molecules: Concepts, Syntheses, Perspectives*, ed. by G.R. Newkome, C.N. Moorefield, F. Vögtle (Wiley, NY, 2007)
455. B. Romagnoli, W. Hayes, J. Mater. Chem. **12**, 767 (2002)
456. A. Ritzén, T. Frejd, Chem. Commun. 207 (1999)
457. R. Stangenberg, D. Türp, K. Müllen, Tetrahedron **70**, 3178 (2014)
458. K. Kono, Polymer J. **44**, 531 (2012)
459. D. Konkolewicz, M.J. Monteiro, S. Perrier, Macromolecules **44**, 7067 (2011)
460. Z. Wang, M. Gao, J. Sun, D. Liang, X. Jia, Macromolecules **46**, 1723 (2013)
461. K. Aoi, A. Motoda, M. Ohno, K. Tsutsumiuchi, M. Okada, T. Imae, Polym. J. **11**, 1071 (1999)
462. A. Harada, K. Nakanishi, S. Ichimura, C. Kojima, K. Kono, J. Polym. Sci. A **47**, 1217 (2009)
463. X. Xiong, Y. Chen, S. Feng, W. Wang, J. Polym. Sci. A **48**, 3515 (2010)
464. I.J. Majoros, B. Keszler, S. Woehler, T. Bull, J.R. Baker, Macromolecules **36**, 5526 (2003)
465. K. Kono, T. Fukui, T. Takagishi, S. Sakurai, C. Kojima, Polymer **49**, 2832 (2008)
466. K. Kono, E. Murakami, Y. Hiranaka, E. Yuba, C. Kojima, A. Harada, K. Sakurai, Angew. Chem. Int. Ed. **50**, 6332 (2011)
467. E. Yuba, Y. Nakajima, K. Tsukamoto, S. Iwashita, C. Kojima, A. Harada, K. Kono, J. Control. Rel. **160**, 552 (2012)
468. S.J. Teertstra, M. Gauthier, Prog. Polym. Sci. **29**, 277 (2004)
469. S.R. Vinukonda, Dendritic copolymers, in *Synthesis and Applications of Copolymers*, ed. by A. Parthiban (Wiley, Hoboken, New Jersey, 2014)
470. S.K. Ghosh, S. Kawaguchi, Y. Jinbo, Y. Izumi, K. Yamaguchi, T. Taniguchi, K. Nagai, K. Koyama, Macromolecules **36**, 9162 (2003)
471. B.-B. Wang, X. Zhang, X.-R. Jia, Z.-C. Li, Y. Ji, Y. Wei, J. Polym. Sci. A **43**, 5512 (2005)
472. M. Tülü, M. Şenel, J. Appl. Polym. Sci. **109**, 2808 (2008)
473. V. Percec, D.A. Wilson, P. Leowanawat, C.J. Wilson, A.D. Hughes, M.S. Kaucher, D.A. Hammer, D.H. Levine, A.J. Kim, F.S. Bates, K.P. Davis, T.P. Lodge, M.L. Klein, R.H. DeVane, E. Aqad, B.M. Rosen, A.O. Argintaru, M.J. Sienkowska, K. Rissanen, S. Nummelin, J. Ropponen, Science **328**, 1009 (2010)
474. D. Guillon, R. Deschenaux, Curr. Opin. Solid State Mater. Sci. **6**, 515 (2002)
475. B. Donnio, S. Buathong, I. Bury, D. Guillon, Chem. Soc. Rev. **36**, 1495 (2007)
476. N. Gimeno, J. Vergara, M. Cano, J.L. Serrano, M.B. Ros, J. Ortega, C.L. Folcia, S. Rodríguez-Conde, G. Sanz-Enguita, J. Etxebarria, Chem. Mater. **25**, 286 (2013)
477. S.M. Grayson, J.M.J. Frechet, Chem. Rev. **101**, 3819 (2001)
478. S.J. Guillaudeu, M.E. Fox, Y.M. Haidar, E.E. Dy, F.C. Szoka, J.M. Fréchet, Bioconjug. Chem. **19**, 461 (2008)
479. A.-M. Stadler, Cryst. Growth Des. **10**, 5050 (2010)
480. J.W. Lee, J.H. Kim, B.-K. Kim, W.S. Shin, S.-H. Jin, Tetrahedron **62**, 894 (2006)
481. P.R. Dvornic, A.M. de Leuze-Jallouli, M.J. Owen, S.V. Perz, Macromolecules **33**, 5366 (2000)
482. P.R. Dvornic, M.J. Owen, in *Advances in Silicones and Silicone-Modified Materials*, ACS Symposium Series, vol. 1051 (ACS, Washington, 2010)
483. E.A. Rebrov, A.M. Muzafarov, A.A. Zhdanov, Dokl. Akad. Nauk **302**, 346 (1988)
484. A.M. Muzafarov, E.A. Rebrov, V.S. Pashkov, Uspehi Khim. **60**, 1596 (1991)
485. A.M. Muzafarov, E.A. Rebrov, J. Polym. Sci. Part A Polym. Chem. **46**, 4935 (2008)
486. A.-M. Caminade, A. Ouali, R. Laurent, C.-O. Turrin, J.-P. Majoral, Chem. Soc. Rev. **44**, 3890 (2015)
487. A.-M. Caminade, A. Ouali, R. Laurent, C.-O. Turrin, J.-P. Majoral, Coord. Chem. Rev. **308**, 478 (2016)
488. A.-M. Caminade, A. Ouali, R. Laurent, J.-P. Majoral, Inorg. Chim. Acta **431**, 3 (2015)
489. A.-M. Caminade, A. Hameau, J.-P. Majoral, Dalton Trans. **45**, 1810 (2016)

490. S. Gottis, L.-I. Rodriguez, R. Laurent, I. Angurell, M. Seco, O. Rossell, J.-P. Majoral, A.-M. Caminade, Tetrahedron Lett. **54**, 6864 (2013)
491. J. Liu, Y. Feng, B. Ma, Y.-M. He, Q.-H. Fan, Eur. J. Org. Chem. **2012**, 6737 (2012)
492. M. Sowinska, Z. Urbanczyk-Lipkowska, New J. Chem. **38**, 2168 (2014)
493. C. Jahier, S. Nlate, J. Organomet. Chem. **694**, 637 (2009)
494. A. Ossenbach, H. Rüegger, A. Zhang, K. Fischer, A.D. Schlüter, M. Schmidt, Macromolecules **42**, 8781 (2009)
495. J. Roeser, B. Heinrich, C. Bourgogne, M. Rawiso, S. Michel, V. Hubscher-Bruder, F. Arnaud-Neu, S. Méry, Macromolecules **46**, 7075 (2013)
496. M.S. Diallo, S. Christie, P. Swaminathan, L. Balogh, X. Shi, W. Um, C. Papelis, W.A. Goddard III, J.H. Johnson Jr., Langmuir **20**, 2640 (2004)
497. H.D.F. Winkler, D.P. Weimann, A. Springer, C.A. Schalley, Angew. Chem. Int. Ed. **48**, 7246 (2009)
498. W.P.L. Maurice, A. Baars, E.W. Meijer, Host-guest chemistry of dendritic molecules, in *Dendrimers II—Architecture, Nanostructure and Supramolecular Chemistry*, ed. by F. Vögtle (Springer, Berlin, Heidelberg, NY, 2000)
499. W.-S. Li, T. Aida, Chem. Rev. **109**, 6047 (2009)
500. D. Wang, M. Sun, H. Zhang, J. Wang, Jilin Daxue Xuebao. Lixue Ban **43**, 524 (2005)
501. S.C. Zimmerman, I. Zharov, M.S. Wendland, N.A. Rakow, K.S. Suslick, J. Am. Chem. Soc. **44**, 13504 (2003)
502. Z. Fei, Y. Han, Z. Bo, J. Polym. Sci. A **46**, 4030 (2008)
503. J.W. Lee, H.J. Kim, S.C. Han, J.H. Kim, S.-H. Jin, J. Nanosci. Nanotechnol. **8**, 4635 (2008)
504. M.V. Walter, M. Malkoch, Chem. Soc. Rev. **41**, 4593 (2012)
505. T. Kawaguchi, K.L. Walker, C.L. Wilkins, J.S. Moore, J. Am. Chem. Soc. **117**, 2159 (1995)
506. A.V. Hopper (ed.), *Recent Developments in Polymer Research* (Nova Science Publishers, NY, 2007)
507. F. Zeng, S.C. Zimmerman, J. Am. Chem. Soc. **118**, 5326 (1996)
508. X.-X. Deng, F.-S. Du, Z.-C. Li, ACS Macro Lett. **3**, 667 (2014)
509. K.L. Wooley, C.J. Hawker, J.M.J. Frechet, Angew. Chem. Int. Ed. **33**, 82 (1994)
510. R. Spindler, J.M.J. Fréchet, J. Chem. Soc. Perkin Trans. **1**, 913 (1993)
511. N.J. Wells, A. Basso, M. Bradlet, Biopolymers **47**, 381 (1998)
512. S.C. Stinson, Chem. Eng. News 28 (1997)
513. C.O. Kappe, D. Dallinger, S. Murphree, in *Practical Microwave Synthesis for Organic Chemists: Strategies, Instruments, and Protocols* (Wiley VCH: Weinheim, 2008)
514. C.O. Kappe, Chem. Soc. Rev. **37**, 1127 (2008)
515. S.C. Ameta, P.B. Punjabi, R. Ameta, C. Ameta (eds.), *Microwave-Assisted Organic Synthesis. A Green Chemical Approach* (Apple Academic Press, CRC Press, Toronto, New Jersey, 2014)
516. J. López-Andarias, J. Guerra, G. Castañeda, S. Merino, V. Ceña, P. Sánchez-Verdú, Eur. J. Org. Chem. **12**, 2331 (2012)
517. A.S. Ertürk, M. Tülü, A.E. Bozdoğan, T. Parali, Eur. Polym. J. **52**, 218 (2014)
518. A.S. Ertürk, M.U. Gürbüz, M. Tülü, A.E. Bozdoğan, RSC Adv. **5**, 60581 (2015)
519. A.E. Enciso, Z.M. Abid, E.E. Simanek, Polym. Chem. **5**, 4635 (2014)
520. A.E. Enciso, F. Ramirez-Crescencio, M. Zeiser, R. Redón, E.E. Simanek, Polym. Chem. **6**, 5219 (2015)
521. T. Kawauchi, Y. Oguchi, J. Sawayama, K. Nagai, T. Iyoda, Macromolecules **48**, 8090 (2015)
522. B. Wang, Y. Luo, X. Jia, Y. Gong, Y. Ji, L. Yang, W. Yen, Gaofenzi Xuebao 304 (2004)
523. G. Zhou, H. Tan, Y. Luo, Gaofenzi Cailiao Kexue Yu Gongcheng **21**, 85 (2005)
524. A.Y.-T. Huang, C.-H. Tsai, H.-Y. Chen, H.-T. Chen, C.-Y. Lu, Y.-T. Lin, C.-L. Kao, Chem. Commun. **49**, 5784 (2013)
525. D. Kushwaha, V.K. Tiwari, J. Org. Chem. **78**, 8184 (2013)

526. D.Q. McNerny, D.G. Mullen, I.J. Majoros, M.M. Banaszak Holl, J.R. Baker, Dendrimer synthesis and functionalization by click chemistry for biomedical applications. in *Click Chemistry for Biotechnology and Materials Science*, ed. by J. Lahann (Wiley, Singapore, 2009)
527. A. Carlmark, C. Hawker, A. Hult, M. Malkoch, Chem. Soc. Rev. **38**, 352 (2009)
528. G. Franc, A.K. Kakkar, Chem. Eur. J. **15**, 5630 (2009)
529. K.L. Killops, L.M. Campos, C.J. Hawker, J. Am. Chem. Soc. **130**, 5062 (2008)
530. S.P. Rannard, N.J. Davis, J. Am. Chem. Soc. **122**, 11729 (2000)
531. W.H. Binder, R. Sachsenhofer, Click chemistry on supramolecular materials, in *Click Chemistry for Biotechnology and Materials Science*, ed. by J. Lahann (Wiley, Singapore, 2009)
532. G. Franc, A. Kakkar, Chem. Commun. 5267 (2008)
533. A. Vieyres, T. Lam, R. Gillet, G. Franc, A. Castonguay, A. Kakkar, Chem. Commun. **46**, 1875 (2010)
534. K. Kempe, A. Krieg, C.R. Becer, U.S. Schubert, Chem. Soc. Rev. **41**, 176 (2012)
535. D. Astruc, L. Liang, A. Rapakousiou, J. Ruiz, Acc. Chem. Res. **45**, 630 (2012)
536. C.Y. Lee, R. Held, A. Sharma, R. Baral, C. Nanah, D. Dumas, S. Jenkins, S. Upadhaya, W. Du, J. Org. Chem. **78**, 11221 (2013)
537. A. Sharma, A. Kakkar, Molecules **20**, 16987 (2015)
538. A. Nazemi, E.R. Gillies, Braz. J. Pharm. Sci. **49**, 42 (2013)
539. X.Y. Shi, W. Lesniak, M.T. Islam, M.C. Muniz, L.P. Balogh, J.R. Baker, Colloids Surf. A Phys. Eng. Aspects **272**, 139 (2006)
540. C. Kojima, Y. Haba, T. Fukui, K. Kono, T. Takagishi, Macromolecules **36**, 2183 (2003)
541. X. Shi, I. Bányai, M.T. Islam, W. Lesniak, D.Z. Davis, J.R. Baker Jr., L.P. Balogh, Polymer **46**, 3022 (2005)
542. R.C. van Duijvenbode, A. Rajanayagam, G.J.M. Koper, M.W.P.L. Baars, B.F.M. de Waal, E.W. Meijer, M. Borkovec, Macromolecules **33**, 46 (2000)
543. A. Rether, M. Schuster, React. Funct. Polym. **57**, 13 (2003)
544. X.M. He, W. Zheng, P.X. Yang, H.P. Xia, Chin. Chem. Lett. **17**, 1251 (2006)
545. G. Smith, R. Chen, S. Mapolie, J. Organomet. Chem. **673**, 111 (2003)
546. H. Stephan, G. Geipel, G. Bernhard, P. Comba, G. Rajaraman, U. Hahn, F. Vogtle, Eur. J. Inorg. Chem. **22**, 4501 (2005)
547. M. Dasgupta, P.M. Brad, A.K. Kakkar, Coord. Chem. Rev. **233–234**, 223 (2002)
548. I.J. Majoros, C.R. Williams, D.A. Tomalia, J.R. Baker, Jr. Macromolecules **41**, 8372 (2008)
549. Y. Lu, J. Chen, Y. Lu, P. Gai, H. Zhong, J. Appl. Polym. Sci. **127**, 282 (2013)
550. U.E. Berndt, T. Zhou, R.C. Hider, Z.D. Liu, H. Neubert, J. Mass Spectrom. **40**, 1203 (2005)
551. S.M. Cohen, S. Petoud, K.N. Raymond, Chem. Eur. J. **7**, 272 (2001)
552. P. Ilaiyaraja, A.K.S. Deb, D. Ponraju, B. Venkatraman, J. Envir. Chem. Eng. **3**, 1047 (2015)
553. J. Rull, M. Casals, R.M. Sebastián, A. Vallribera, J.-P. Majoral, A.-M. Caminade, ChemCatChem **7**, 2698 (2015)
554. B. Gonzalez, B. Alonso, J. Losada, M.P. Garcia-Armada, C.M. Casado, Organometallics **25**, 3558 (2006)
555. C. Ornelas, J. Broichhagen, M. Weck, J. Am. Chem. Soc. **132**, 3923 (2010)
556. K. Yoon, P. Goyal, M. Weck, Org. Lett. **9**, 2051 (2007)
557. T.S. Dirk, G. Rijkers, W. van Esse, R. Merkx, A.J. Brouwer, H.J.F. Jacobs, R.J. Pieters, R.M.J. Liskamp, Chem. Commun. **36**, 4581 (2005)
558. P. Antoni, Y. Hed, A. Nordberg, D. Nyström, H. von Holst, A. Hult, M. Malkoch, Angew. Chem. Int. Ed. **48**, 2126 (2009)
559. F. Zeng, S.C. Zimmerman, S.V. Kolotuchin, D.E.C. Reichert, Y. Ma, Tetrahedron **58**, 825 (2002)

560. I.V. Lijanova, R.G. Monter, N.V. Likhanova, F.V. Garibay, X.O.C. Olivares, Supramol. Chem. **24**, 56 (2012)
561. Y. Takaguchi, Kagaku to Kogyo **78**, 25 (2004)
562. B.-L. Li, Z.-T. Liu, G.-J. Deng, Q.-H. Fan, Eur. J. Org. Chem. 508 (2007)
563. J. Li, J. Wang, T. Wang, L. Liu, Huaxue yanjiu **15**, 31 (2004)
564. C.K. Jang, J.Y. Jaung, J. Porphyrins Phthalocyanines **13**, 939 (2009)
565. Y. Pan, M. Lu, Z. Peng, J.S. Melinger, Org. Biomol. Chem. **1**, 4465 (2003)
566. Y.-M. He, Y. Feng, Q.-H. Fan, Acc. Chem. Res. **47**, 2894 (2014)
567. C. Ornelas, Macromol. Chem. Phys. **217**, 149 (2016)
568. X. Yang, H. Shang, C. Ding, J. Li, Polym. Chem. **6**, 668 (2015)
569. K. Goren, M. Portnoy, Dendritic molecules on solid support: solid-phase synthesis and applications, in *Solid-Phase Organic Synthesis: Concepts, Strategies, and Applications*, ed. by P.H. Toy, Y. Lam (Wiley, Hoboken, New Jersey, 2012)
570. B. Pan, D. Cui, F. Gao, R. He, Nanotechnology **17**, 2483 (2006)
571. I. Grabchev, J.-M. Chovelon, V. Bojinov, Polymer **44**, 4421 (2003)
572. I. Grabchev, J.-M. Chovelon, V. Bojinov, G. Ivanova, Tetrahedron **59**, 9591 (2003)
573. A. Olivas, T.A. Zepeda, D. Madrigal Peralta, Mater. Res. Innov. **12**, 12 (2008)
574. C. Zhang, P. Su, M.U. Farooq, Y. Yang, X. Gao, E. Hongjun, React. Funct. Polym. **70**, 129 (2010)
575. M.A. Andrade Jr., H.O. Pastore, A.C.S. Appl, Mater. Interfaces **27**, 1884 (2016)
576. F. Zhang, B. Wang, S. He, R. Man, J. Chem. Eng. Data **59**, 1719 (2014)
577. A.M. Caminade, R. Laurent, J.P. Majoral, Adv. Drug Deliv. Rev. **57**, 2130 (2005)
578. M. Ballauff, C.N. Likos, Angew. Chem. Int. Ed. **43**, 2998 (2004)
579. S. Uppuluri, F.A. Morrison, P.R. Dvornic, Macromolecules **33**, 2551 (2000)
580. P.K. Maiti, T. Cagin, S.T. Lin, W.A. Goddard III, Macromolecules **38**, 979 (2005)
581. D.A. Tomalia, H. Baker, J.R. Dewald, Polym. J. **17**, 117 (1985)
582. B.I. Voit, A. Lederer, Chem. Rev. **109**, 5924 (2009)
583. H. Mori, A.H.E. Müller, P.F.W. Simon, in *Macromolecular Engineering: Precise Synthesis, Materials, Properties, Applications*, vol. 2, ed. by K. Matyjaszewski, Y. Gnanou, L. Leibler (Wiley-VCH, Weinheim, 2007)
584. M.G. McKee, S. Unal, G.L. Wilkes, T.E. Long, Prog. Polym. Sci. **30**, 507 (2005)
585. M. Jikei, M.-A. Kakimoto, in *Progress in Polycondensation*, ed. by T. Matsumoto (Research Signpost, Trivandrum, India, 2002)
586. W. Burchard, Adv. Polym. Sci. **143**, 113 (1999)
587. V. Balzani, P. Ceroni, M. Maestri, C. Saudan, V. Vicinelli, Top. Curr. Chem. **228**, 159 (2003)
588. D.A. Tomalia, Soft Matter **6**, 456 (2010)
589. D.A. Tomalia, J. Nanopart. Res. **11**, 1251 (2009)
590. T. Zhong, P. Ai, J. Zhou, Fluid Phase Equilib. **302**, 43 (2011)
591. C.N. Moorefield, A. Schultz, G.R. Newkome, Braz. J. Pharm. Sci. **49**, 67 (2013)
592. M.S. Shinde, M.B. Bhalerao, S. Thakre, J. Franklin, A. Jain, Asian J. Pharm. Res. Dev. **2**, 24 (2014)
593. P. Bhattacharya, D. Du, Y. Lin, J.R. Soc, Interface **11**, 20131067 (2014)
594. C. Gao, D. Yan, Prog. Polym. Sci. **29**, 183 (2004)
595. D. Wang, T. Zhao, X. Zhu, D. Yan, W. Wang, Chem. Soc. Rev. **21**, 4023 (2015)
596. Q. Zhu, F. Qiu, B. Zhu, X. Zhu, RSC Adv. **3**, 2071 (2014)
597. I.N. Kurniasih, J. Keilitz, R. Haag, Chem. Soc. Rev. **44**, 4145 (2015)
598. D.A. Markelov, Yu.Ya. Gotlib, A.A. Darinskii, A.V. Lulin, S.V. Lulin, Vysokomol. Soedin. **51**, 469 (2009)
599. B.K. Nanjwade, H.M. Bechraa, G.K. Derkara, F.V. Manvia, V.K. Nanjwade, Eur. J. Pharm. Sci. **38**, 185 (2009)
600. P. Kesharwani, K. Jain, N.K. Jain, Prog. Polym. Sci. **39**, 268 (2014)
601. K. Madaan, S. Kumar, N. Poonia, V. Lather, D. Pandita, J. Pharm. Bioallied Sci. **6**, 139 (2014)

602. D. Yan, C. Gao, H. Frey (eds.), *Hyperbranched Polymers: Synthesis, Properties, and Applications* (Wiley, Hoboken, New Jersey, 2011)
603. X. Huang, S. Zheng, I. Kim, J. Nanosci. Nanotechnol. **14**, 1631 (2014)
604. M. Mishra, S. Kobayashi, *Star and Hyperbranched Polymers* (CRC Press, NY, Basel, 1999)
605. A. Lederer, W. Burchard, *Hyperbranched Polymers: Macromolecules in between Deterministic Linear Chains and Dendrimer Structures*, RSC Polymer Chemistry Series (RSC Publishing, Cambridge, 2015)
606. N. Karak, S. Maiti, *Dendrimers and Hyperbranched Polymers: Synthesis to Applications* (MD Publications Pvt Ltd, New Delhi, 2008)
607. J. Vukovic, *Hyperbranched Polymers Based on Aliphatic Polyesters, Synthesis and Characterization* (VDM Verlag Dr. Müller, Germany, 2008)
608. W.A. Braunecker, K. Matyjaszewski, Prog. Polym. Sci. **32**, 93 (2007)
609. S. Kuchanov, H. Slot, A. Stroeks, Prog. Polym. Sci. **29**, 563 (2004)
610. Y. Zheng, S. Li, Z. Weng, C. Gao, Chem. Soc. Rev. **44**, 4091 (2015)
611. J. Han, S. Li, A. Tang, C. Gao, Macromolecules **45**, 4966 (2012)
612. A. Hult, M. Johannson, E. Malmström, Adv. Polym. Sci. **143**, 1 (1999)
613. P. Froehling, J. Polym. Sci. Part A Polym. Chem. **42**, 3110 (2004)
614. B. Voit, J. Polym. Sci. Part A Polym. Chem. **38**, 2505 (2000)
615. M. Jikei, M. Kakimoto, J. Polym. Sci. Part A Polym. Chem. **42**, 1293 (2004)
616. J.-F. Stumbé, B. Bruchmann, Macromol. Rapid Commun. **25**, 921 (2004)
617. B. Bruchmann, Macromol. Mater. Eng. **292**, 981 (2007)
618. B. Bruchmann, R. Koeniger, H. Renz, Macromol. Symp. **187**, 271 (2002)
619. H. Holter, A. Burgath, H. Frey, Acta Polym. **48**, 30 (1997)
620. N. Hadjichristidis, M. Pitsikalis, S. Pispas, H. Iatrou, Chem. Rev. **101**, 3747 (2001)
621. C. Wei, H. Gao, Star polymers as unimolecular containers, in *Encyclopedia of Polymeric Nanomaterials*, ed. by S. Kobayashi, K. Müllen (Springer, Berlin, Heidelberg, 2013)
622. K. Khanna, S. Varshney, A. Kakkar, Polym. Chem. **1**, 1171 (2010)
623. A. Blencowe, J.F. Tan, T.K. Goh, G.G. Qiao, Polymer **50**, 5 (2009)
624. F.K. Wolf, A.M. Fischer, H. Frey, Beilstein J. Org. Chem. **6**, 67 (2010)
625. C. Gao, X. Zheng, Soft Matter **5**, 4788 (2009)
626. A. Kowalczuk, A. Vandendriessche, B. Trzebicka, B. Mendrek, U. Szeluga, G. Cholewiński, M. Smet, A. Dworak, W. Dehaen, J. Polym. Sci. Part A Polym. Chem. **47**, 1120 (2009)
627. H. Hong, Y. Mai, Y. Zhou, D. Yan, Y. Chen, J. Polym. Sci. Part A Polym. Chem. **46**, 668 (2008)
628. A. Hirao, H.-S. Yoo, Polymer J. **43**, 2 (2011)
629. M. Morell, A. Lederer, X. Ramis, B. Voit, A. Serra, J. Polym. Sci. Part A Polym. Chem. **49**, 2395 (2011)
630. M.A. Quadir, R. Haag, J. Control. Release **161**, 484 (2012)
631. M. Caldéron, M.A. Quadir, S.K. Sharma, R. Haag, Adv. Mater. **22**, 190 (2010)
632. C.R. Yates, W. Hayes, Eur. Polym. J. **40**, 1257 (2004)
633. A. Khan, M. Malkoch, M.F. Montague, C.J. Hawker, J. Polym. Sci. Polym. Chem. **46**, 6238 (2008)
634. B. Voit, H. Komber, A. Lederer, Hyperbranched polymers: synthesis and characterization aspects, in *Materials Science and Technology*, 701 (2013)
635. Y. Shi, R.W. Graff, X. Cao, X. Wang, H. Gao, Angew. Chem. Int. Ed. **54**, 7631 (2015)
636. F. Huang, H.W. Gibson, J. Am. Chem. Soc. **126**, 14738 (2004)
637. L.J. Twyman, A.S.H. King, J. Burnett, I.K. Martin, Tetrahedron Lett. **45**, 433 (2004)
638. A.S. Nasar, M. Jikei, M.A. Kakimoto, Eur. Polym. J. **39**, 1201 (2003)
639. Y.B. Kim, H.K. Kim, H. Nishida, T. Endo, Macromol. Mater. Eng. **289**, 923 (2004)
640. A.V. Ambade, A. Kumar, J. Polym. Sci. A **42**, 5134 (2004)
641. Y. Ohta, Y. Kamijyo, A. Yokoyama, T. Yokozawa, Polymer **4**, 1170 (2012)
642. X. Li, J. Zhan, Y. Li, Macromolecules **37**, 7584 (2004)
643. Y. Segawa, T. Higashihara, M. Ueda, Polym. Chem. **4**, 1746 (2013)

644. K. Onitsuka, N. Ohshiro, M. Fujimoto, F. Takei, S. Takahashi, Mol. Cryst. Liq. Cryst. **342**, 159 (2000)
645. T. Higashihara, Y. Segawa, W. Sinananwanich, M. Ueda, Polymer J. **44**, 14 (2012)
646. A.S. Abd-El-Aziz, S.A. Carruthers, P.M. Aguiar, S. Kroeker, J. Inorg. Organomet. Polym. **15**, 349 (2005)
647. H. Magnusson, E. Malmstrom, A. Hult, Macromolecules **33**, 3099 (2000)
648. L. Song, C. Tu, Y. Shi, F. Qiu, Y. Jiang, Q. Zhu, B. Zhu, D. Yan, X. Zhu, Macromol. Rapid Commun. **31**, 443 (2010)
649. J. Feng, Y. Li, M. Yang, Eur. Polym. J. **44**, 3314 (2008)
650. J. Feng, Y. Li, M. Yang, J. Polym. Sci. A **47**, 222 (2009)
651. Y. Jiang, Y. Wang, J. Hua, S. Qu, S. Qian, H. Tian, J. Polym. Sci. A **47**, 4400 (2009)
652. C. Liu, C. Gao, D. Yan, Chem. Res. Chin. Univ. **21**, 345 (2005)
653. L. Xu, Z. Ye, Chem. Commun. **49**, 8800 (2013)
654. J.-B. Baek, J.B. Ferguson, L.-S. Tan, Macromolecules **36**, 4385 (2003)
655. S. Li, J. Han, C. Gao, Polym. Chem. **4**, 1774 (2013)
656. M. Smet, C. Gottschalk, S. Skaria, H. Frey, Macromol. Chem. Phys. **206**, 2421 (2005)
657. I. Gadwal, S. Binder, M.C. Stuparu, A. Khan, Macromolecules **47**, 5070 (2014)
658. R.R. Barzegar, S. Akbari, M.H. Kish, Polym. Int. **62**, 1767 (2013)
659. F. Sun, X. Luo, L. Kang, X. Peng, C. Lu, Polym. Chem. **6**, 1214 (2015)
660. F. Xu, J. Zhong, X. Qian, Y. Li, X. Lin, Q. Wu, Polym. Chem. **4**, 3480 (2013)
661. R. Barbey, S. Perrier, Macromolecules **47**, 6697 (2014)
662. A.B. Cook, R. Barbey, J.A. Burns, S. Perrier, Macromolecules **49**, 1296 (2016)
663. J.-J. Yan, J.-T. Sun, Y.-Z. You, D.-C. Wu, C.-Y. Hong, Sci. Rep. **3**, Article number 2841 (2013)
664. R. Salazar, L. Fomina, S. Fomine, Polym. Bull. **47**, 151 (2001)
665. R. Reul, J. Nguyen, T. Kissel, J. Biomaterial. **30**, 5815 (2009)
666. G. Prevec, E. Zagar, M. Zigon, Chem. Ind. **55**, 365 (2006)
667. S. Chen, X.Z. Zhang, S.X. Cheng, R. Zhuo, Z.W. Gu, Biomacromolecules **9**, 2578 (2008)
668. N.S. Klimenko, A.V. Shevchuk, M.Ya. Vortman, E.G. Privalko, V.V. Shevchenko, Vysokomol. Soedin. Ser. A. **50**, 268 (2008)
669. Z. Feng, L. Lin, Sci. Photochem. **24**, 36 (2006)
670. T. Qiu, L. Tang, Z. Fu, X. Tuo, Y. Li, D. Liu, W. Yang, Polym. Adv. Technol. **15**, 65 (2004)
671. K. Fukukawa, R. Rossin, A. Hagooly, E.D. Pressly, J.N. Hunt, B.W. Messmore, K.L. Wooley, M.J. Welch, C.J. Hawker, Biomacromolecules **9**, 1329 (2008)
672. X. Wang, R.W. Graff, Y. Shi, H. Gao, Polym. Chem. **6**, 6739 (2015)
673. H. Xiaohua, Y. Deyue, M. Yiyong, Eur. Polym. J. **40**, 1759 (2004)
674. C. Schüll, H. Rabbel, F. Schmid, H. Frey, Macromolecules **46**, 5823 (2013)
675. P. Fan, C. Lu, Polym. Adv. Technol. **23**, 48 (2012)
676. Y. Liu, L. Xu, J. Liu, X. Liu, C. Chen, G. Li, Y. Meng, Chem. Eng. J. **285**, 698 (2016)
677. H. Yang, J. Xu, S. Pispas, G. Zhang, RSC Adv. **3**, 6853 (2013)
678. G.G. Wallace, P.R. Teasdale, G.M. Spinks, L.A.P. Kane-Maguire, *Conductive Electroactive Polymers: Intelligent Polymer Systems*, 3rd edn. (CRC Press, Boca Raton, 2008)
679. G. Inzelt, *Conducting Polymers: A New Era in Electrochemistry* (Springer, Heidenberg, 2012)
680. R. Tucceri, *Poly(o-aminophenol) Film Electrodes: Synthesis, Transport Properties and Practical Applications* (Springer, Cham, Heidelberg, NY, Dordrecht, London, 2013)
681. M.W. Urban (ed.), *Stimuli-Responsive Polymeric Films and Coatings*, ACS Symposium Series, vol. 912 (American Chemical Society, Washington, 2005)
682. A. Singh, *Structure and Dynamics of Ultrathin Polymeric Films* (Lap Lambert Academic Publishing, Germany, 2013)
683. H. Biederman (ed.), *Plasma Polymer Films* (Imperial College Press, London, 2004)
684. A. Heilmann, *Polymer Films with Embedded Metal Nanoparticles* (Springer, Berlin, 2003)

685. O.C. Tsui, T.P. Russell, *Polymer Thin Films* (World Scientific Publishing Co., Singapore, 2008)
686. D.R. Baer, P.E. Burrows, A.A. El-Azab, Prog. Org. Coat. **47**, 342 (2003)
687. L.A. Felton, Int. J. Pharm. **457**, 423 (2013)
688. J. Zhou, H. Wang, Zhongnan Minzu Daxue Xuebao. Ziran Kexue Ban **23**, 5 (2004)
689. M.G. Zolotukhin, M.C.G. Hernandez, A.M. Lopez, L. Fomina, G. Cedillo, A. Nogales, T. Ezquerra, D. Rueda, H.M. Colquhoun, K.M. Fromm, A. Ruiz-Trevino, M. Ree, Macromolecules **39**, 4696 (2006)
690. V. Calderon, F.C. Garcia, J.L. De la Pena, E.M. Maya, J.M. Garcia, J. Polym. Sci. A **44**, 2270 (2006)
691. B.I. Podlovchenko, V.N. Andreev, Uspekhi Khim. **71**, 950 (2002)
692. L. Tian, M. Zhang, P. Lu, W. Zhang, B. Yang, Y. Ma, Chin. Sci. Bull. **49**, 246 (2004)
693. S. Panozzo, F. Lafolet, L. Trouillet, J.-C. Vial, S. Guillerez, Synth. Metals **142**, 201 (2004)
694. S. Basak, Y.S.L.V. Narayana, M. Baumgarten, K. Müllen, R. Chandrasekar, Macromolecules **46**, 362 (2013)
695. S.A. Shin, J.B. Park, J.-H. Kim, D.-H. Hwang, Synth. Metals **172**, 54 (2013)
696. D.R. Rueda, A. Nogales, J.J. Hernández, M.-C. García-Gutiérrez, T.A. Ezquerra, S.V. Roth, M.G. Zolotukhin, R. Serna, Langmuir **23**, 12677 (2007)
697. C.-H. Yang, L.-R. Huang, Y.-K. Chih, S.-L. Chung, J. Phys. Chem. C **111**, 3786 (2007)
698. K. Fukuda, S. Lee, Polym. Prepr. (Japan) Engl. Ed. **45**, E 396 (1996)
699. E.J. Onah, U. Oertel, L. Hauszler, D. Voigt, C. Froeck, H. Komber, B.I. Voit, K. Lunkwitz, Eur. Polym. J. **39**, 127 (2003)
700. T. Akiyama, M. Matsushita, K. Kakutani, S. Yamada, K. Takechi, T. Shiga, T. Motohiro, H. Nakayama, K. Kohama, Jpn. J. Appl. Phys. Part 1 **44**, 2799 (2005)
701. M. Tagowska, B. PaLys, M. Mazur, M. Skompska, K. Jackowska, Electrochim. Acta **50**, 2363 (2005)
702. J. Zhang, D. Shan, S. Mu, J. Polym. Sci. A **45**, 5573 (2007)
703. M.M. Ayad, N.A. Salahuddin, A.K. Abou-Seif, M.O. Alghaysh, Eur. Polym. J. **44**, 426 (2008)
704. M.Y. Abed, A.M. Mazrouaa, Z. Abdeen, A. Ashery, Periodica Polytech. **58**, 35 (2014)
705. X.-G. Li, H.-Y. Wang, M.-R. Huang, Macromolecules **40**, 1489 (2007)
706. S. Cosnier, A. Karyakin (eds.), *Electropolymerization: Concepts, Materials and Applications* (Wiley, Weinheim, 2011)
707. S. Mu, Electrochim. Acta **56**, 3764 (2011)
708. J.A. Cobos-Murcia, L. Galicia, A. Rojas-Hernandez, M.T. Ramirez-Silva, R. Alvarez-Bustamante, M. Romero-Romo, G. Rosquete-Pina, M. Palomar-Pardave, Polymer **46**, 9053 (2005)
709. W. Badawy, K. Ismail, S. Medany, Z. Phys. Chem. **237**, 1741 (2013)
710. S.B. Revin, S.A. John, Electrochim. Acta **56**, 8934 (2011)
711. W.A. Badawy, K.M. Ismail, Z.M. Khalifa, J. Appl. Electrochem. **37**, 593 (2007)
712. H. Liu, G. Zhang, Y. Zhou, M. Gao, F. Yang, J. Mater. Chem. A **1**, 13902 (2013)
713. A.H.A. Shah, R. Holze, J. Electroanal. Chem. **597**, 95 (2006)
714. S.M. Sayyah, M.M. El-Deeb, S.M. Kamal, R.E. Azooz, J. Appl. Polym. Sci. **112**, 3695 (2009)
715. J. Hwang, J.I. Son, Y.-B. Shim, Sol. Energy Mater. Sol. Cells **94**, 1286 (2010)
716. G. Shul, M. Weissmann, D. Bélanger, Langmuir **30**, 6612 (2014)
717. Y.F. Du, X.M. Qi, P. Zhao, J.X. Lu, M.Y. He, Chin. Chem. Lett. **15**, 1098 (2004)
718. M. Ates, Mater. Sci. Eng. C **33**, 1853 (2013)
719. Z.M. Zain, N. Zakaria, Malays. J. Anal. Sci. **18**, 107 (2014)
720. W. Zhai, X. Tian, Y. Yan, Y. Zhao, Y. Liu, Canad. J. Chem. **91**, 1077 (2013)
721. A. Curulli, Sensor Lett. **6**, 682 (2008)
722. S.P. Luo, Q.X. Liu, Z. Liu, A.J. Xie, Y. Kong, X. Dai, Chin. Chem. Lett. **23**, 1311 (2012)
723. S.R. Cao, R. Yuan, Y.Q. Chai, L.Y. Zhang, X.L. Li, R. Chai, J. Electrochem. Soc. **153**, H223 (2006)

724. S.R. Cao, R. Yuan, Y.Q. Chai, L.Y. Zhang, X.L. Li, F.X. Gao, Bioproc. Biosyst. Eng. **30**, 71 (2007)
725. A. Merz, S. Anikin, B. Lieser, J. Heinze, H. John, Chem. Eur. J. **9**, 449 (2003)
726. Y. Oztekin, Z. Yazicigil, A.O. Solak, Z. Ustundag, Z. Kilic, S. Bilge, Surf. Interface Anal. **43**, 923 (2011)
727. Y. Oztekin, Z. Yazicigil, A.O. Solak, Z. Ustundag, A. Okumus, Z. Kilic, A. Ramanaviciene, A. Ramanavicius, Sens. Actuators B Chem. **166–167**, 117 (2012)
728. G. Shul, M. Weissmann, D. Bélanger, Electrochim. Acta **162**, 146 (2015)
729. B.D. Mert, M.E. Mert, G̈. Kardaş, B. Yazici, Appl. Surf. Sci. **258**, 9668 (2012)
730. W.A. Badawy, K.M. Ismail, S.S. Medany, Electrochim. Acta **51**, 6353 (2006)
731. K.M. Ismail, Z.M. Khalifa, M.A. Azzem, W.A. Badawy, Electrochim. Acta **47**, 1867 (2002)
732. W.A. Badawy, K.M. Ismail, S.S. Medany, Int. J. Chem. Kinet. **43**, 141 (2011)
733. Z. Algharaibeh, P.G. Pickup, Electrochim. Acta **93**, 87 (2013)
734. L.A. Hernández, M.A. del Valle, F.R. Díaz, D.J. Fermin, T.A.G. Risbridger, Electrochim. Acta **166**, 163 (2015)
735. I.M. Burguete, V. Fabregat, F. Galindo, A.M. Izquierdo, S.V. Luis, Eur. Polym. J. **45**, 1516 (2009)
736. Z. Xu, M. Wang, W. Fan, J. Zhao, H. Wang, Electrochim. Acta **160**, 271 (2015)
737. S.M. Sayyah, M.M. El-Rabiey, S.S. Abd El-Rehim, R.E. Azooz, J. Appl. Polym. Sci. **99**, 3093 (2006)
738. A.M. Golyakov, A.N. Borisov, G.A. Shagisultanova, F.L. Shpikev, Zh. Obsch. Khim. **81**, 1529 (2011)
739. A.M. Golyakov, A.V. Schukarev, V.N. Pak, G.A. Shagisultanova, A.N. Borisov, Zh. Prikl. Khim. **84**, 321 (2011)
740. B.C. Thompson, K.A. Abboud, J.R. Reynolds, K. Nakatani, P. Audebert, New J. Chem. **29**, 1128 (2005)
741. X. Tan, S. Zhang, X. Song, C. Li, Nanosci. Nanotechn. Lett. **6**, 333 (2014)
742. R. Solmaz, G. Kardas, Prog. Org. Coat. **64**, 81 (2009)
743. M. Yildirim, İ. Kaya, Synth. Metals **162**, 834 (2012)
744. F.R. Diaz, M.A. Del Valle, C. Nunez, A. Godoy, J.L. Mondaca, A. Toro-Labbe, J.C. Bernede, Polym. Bull. **56**, 155 (2006)
745. E.N. Esmer, S. Tarkuc, Y.A. Udum, L. Toppare, Mater. Chem. Phys. **131**, 519 (2011)
746. M. Mahmut, T. Awut, I. Nurulla, M. Mijit, J. Polym. Res. **21**, 403 (2014)
747. M. Mahmut, T. Awut, I. Nurulla, M. Mijit, J. Appl. Polym. Sci. **131**, 40861 (2014)
748. B.B. Carbas, A. Kivrak, M. Zora, A.M. Önal, J. Electroanal. Chem. **677–680**, 9 (2012)
749. K.A. Koparkar, B.B. ECarbaEs, A. Kivrak, M. Zora, A.M. Onal, React. Funct. Polym. **71**, 579 (2011)
750. B. Duong, R. Arechabaleta, N.J. Tao, J. Electroanal. Chem. **447**, 63 (1998)
751. M.V. Tesakova, I.A. Popov, V.I. Parfenyuk, Russ. J. Electrochem. **50**, 517 (2014)
752. J. Durantini, G.M. Morales, M. Santo, M. Funes, E.N. Durantini, F. Fungo, T. Dittrich, L. Otero, M. Gervaldo, Org. Electron. **13**, 604 (2012)
753. A. Uygun, R. Myjavcova, A.G. Yavuz, J.V. Ruppel, K.B. Fields, A. Frankhauser, X.P. Zhang, V.R. Bhethanbotla, P. Bednar, Electroanalysis **23**, 1158 (2011)
754. K. Takechi, T. Shiga, T. Akiyama, S. Yamada, Photochem. Photobiol. Sci. **9**, 1085 (2010)
755. P. Veerender, S.P. Koiry, V. Saxena, P. Jha, A.K. Chauhan, D.K. Aswal, S.K. Gupta, AIP Conf. Proc. **1447**, 727 (2012)
756. K. Iwasaki, A. Kimoto, S. Naya, F. Iwahori, J. Abe, Synth. Metals **159**, 880 (2009)
757. M. Gervaldo, P.A. Liddell, G. Kodis, B.J. Brennan, C.R. Johnson, J.W. Bridqewater, A.L. Moore, T.A. Moore, D. Gust, Photochem. Photobiol. Sci. **9**, 890 (2010)
758. J.-M. Pernaut, K. Zong, J.R. Reynolds, Synth. Metals **130**, 1 (2002)
759. S. Bilal, A.H.A. Shah, R. Holze, J. Electrochem. Soc. **155**, P89 (2008)
760. S. Bilal, R. Holze, J. Electroanal. Chem. **592**, 1 (2006)
761. S. Bilal, R. Holze, Electrochim. Acta **52**, 1247 (2006)

762. S. Bilal, R. Holze, Electrochim. Acta **52**, 5346 (2007)
763. S. Bilal, A. Ali Shah, R. Holze, Electrochim. Acta **97**, 364 (2013)
764. S. Bilal, A.H.A. Shah, R. Holze, Electrochim. Acta **85**, 358 (2012)
765. L.A. Hernandez, M.A. Del Valle, F.J. Armijo, F.R. Diaz, G. Louarn, Electrochemistry **81**, 954 (2013)
766. S. Palaniappan, P. Manisankar, J. Polym. Res. **18**, 311 (2011)
767. A.H.A. Shah, R. Holze, Electrochim. Acta **52**, 1374 (2006)
768. Y. Zhang, X. Liu, Q. Li, J. Appl. Polym. Sci. **128**, 1625 (2013)
769. S. Mu, Synth. Metals **143**, 259 (2004)
770. A. Benyoucef, S. Boussalem, M.I. Ferrahi, M. Belbachir, Synth. Metals **160**, 1591 (2010)
771. H.S.O. Chan, S.C. Ng, W.S. Sim, K.L. Tan, B.T.G. Tan, Macromolecules **25**, 6029 (1992)
772. W.C. Chen, T.C. Wen, A. Gopalan, J. Electrochem. Soc. **148**, E427 (2001)
773. C.-F. Chang, W.-C. Chen, T.-C. Wen, A. Gopalan, Acid J. Electrochem. Soc. **149**, E298 (2002)
774. M.S. Wu, T.C. Wen, A. Gopalan, Mat. Chem. Phys. **74**, 58 (2002)
775. M.S. Wu, T.C. Wen, A. Gopalan, J. Electrochem. Soc. **148**, D65 (2001)
776. L. Zhang, B. Hou, Q. Lang, Amer. J. Anal. Chem. **2**, 182 (2011)
777. S.M. Sayyah, M.M. El-Rabiey, S.S. Abd El-Rehim, R.E. Azooz, J. Appl. Polym. Sci. **109**, 1643 (2008)
778. Y. Wang, F. Teng, Z. Xu, Y. Hou, Y. Wang, X. Xu, Eur. Polym. J. **41**, 1020 (2005)
779. K. Wagner, M. Zanoni, A.B.S. Elliott, P. Wagner, R. Byrne, L.E. Florea, D. Diamond, K.C. Gordon, G.G. Wallace, D.L. Officer, J. Mater. Chem. C **1**, 3913 (2013)
780. J. Wang, B. Lu, C. Liu, J. Xu, M. Pei, J. Mater. Sci. **45**, 5769 (2010)
781. K.H. Fries, G.R. Sheppard, J.A. Bilbrey, J. Locklin, Polym. Chem. **5**, 2094 (2014)
782. K.A. Koparkar, Sens. Transducers J. **143**, 10 (2012)
783. K.L. Jarvis, P. Majewski, Plasma Proc. Polym. **10**, 619 (2013)
784. A.I. Drachev, A.B. Gil'man, E.S. Obolonkova, A.A. Kuznetsov, Synth. Metals **142**, 35 (2004)
785. K. Lintinen, L. Storbacka, A. Efimov, S. Hietala, R. Ahorinta, N. Tkachenko, H. Lemmetyinen, J. Polym. Sci. A **47**, 6095 (2009)
786. K. Lintinen, L. Storbacka, A. Efimov, A. Tolkki, N. Tkachenko, H. Lemmetyinen, Solar Energy Mater. Solar Cells **95**, 909 (2011)
787. F. Tian, E.A. Decker, J.M. Goddard, J. Agr. Food Chem. **60**, 2046 (2012)
788. M.J. Roman, F. Tian, E.A. Decker, J.M. Goddard, J. Appl. Polym. Sci. **131**, 39948 (2014)
789. G. Bayramoglu, M.Y. Arica, Fibers Polym. **13**, 1225 (2012)
790. A. Joseph, S. Subramanian, P.C. Ramamurthy, S. Sampath, R.V. Kumar, C. Schwandt, Electrochim. Acta **137**, 557 (2014)
791. H. Březnová, R. Volf, V. Král, J.L. Sessler, A.C. Try, T.V. Shishkanova, Anal. Bioanal. Chem. **375**, 1193 (2003)
792. T.R. Aslamazova, V.A. Kotenev, YuA Plachev, AYu. Tsivadze, Prot. Met. Phys. Chem. Surf. **48**, 627 (2012)
793. A.M. Donald, A.H. Windle, S. Hanna (eds.), *Liquid Crystalline Polymers*, 2nd edn. (Cambridge University Press, Cambridge, 2006)
794. D. Broer, G.P. Crawford, S. Zumer (eds.), *Cross-Linked Liquid Crystalline Systems: From Rigid Polymer Networks to Elastomers* (CRC Press, Boca Raton, London, NY, 2011)
795. V.P. Shibaev, L. Lam (eds.), *Liquid Crystalline and Mesomorphic Polymers* (Springer, NY, 1994)
796. X. Wang, Q. Zhou, Liquid crystalline polymers, in *Thermoplastic Materials: Properties, Manufacturing Methods, and Applications*, ed. by C.C. Ibeh (CRC Press, Boca Raton, 2011)
797. W.H. de Jeu (ed.), *Liquid Crystal Elastomers: Materials and Applications* (Springer, Berlin, 2012)
798. S. Kumar, *Chemistry of Discotic Liquid Crystals: From Monomers to Polymers* (CRC Press, Boca Raton, 2010)

799. S.J. Woltman, G.D. Jay, G.P. Crawford (eds.), *Liquid Crystals: Frontiers in Biomedical Applications* (World Scientific Publishing Co., Singapore, 2007)
800. P. Oswald, P. Pieranski, *Nematic and Cholesteric Liquid Crystals* (CRC Press, Boca Raton, 2005)
801. T. Rasing, I. Musevic (eds.), *Surfaces and Interfaces of Liquid Crystals* (Springer, Berlin, Heidelberg, 2004)
802. S.V. Pasechnik, V.G. Chigrinov, D.V. Shmeliova, *Liquid Crystals: Viscous and Elastic Properties in Theory and Applications* (Wiley, Weinheim, 2009)
803. S. Sudhakar, T. Narasimhaswamy, K.S.V. Srinivasan, Liq. Cryst. **27**, 1525 (2000)
804. B.B. Sauer, W.G. Kampert, R.S. McLean, Polymer **44**, 2721 (2003)
805. J.M. Adell, M.P. Alonso, J. Barbera, L. Oriol, M. Pinol, J.L. Serrano, Polymer **44**, 7829 (2003)
806. D. Pucci, A. Bellusci, A. Crispini, M. Ghedini, M. La Deda, Inorg. Chim. Acta **357**, 495 (2004)
807. P. Kannan, S. Raja, P. Sakthivel, Polymer **45**, 7895 (2004)
808. K.I. Aly, A.A. Khalaf, I.A. Alkskas, J. Appl. Polym. Sci. **88**, 153 (2003)
809. E.-J. Choi, J.-C. Ahn, L.-C. Chien, C.-K. Lee, W.-C. Zin, D.-C. Kim, S.-T. Shin, Macromolecules **37**, 71 (2004)
810. E.J. Choi, J.C. Ahn, C.K. Lee, J.I. Jin, Polymer **41**, 7617 (2000)
811. D. Ribera, A. Mantecon, A. Serra, Macromol. Symp. **199**, 267 (2003)
812. K.S.V. Srinivasan, T. Padmavathy, Macromol. Symp. **199**, 277 (2003)
813. M. Cano, L. Oriol, M. Pinol, J.L. Serrano, Chem. Mater. **11**, 94 (1999)
814. T. Sasaki, G. Fukunaga, Chem. Mater. **17**, 3433 (2005)
815. B. Donnio, J. Barbera, R. Gimenez, D. Guillon, M. Marcos, J.L. Serrano, Macromolecules **35**, 370 (2002)
816. J. Barbera, M. Marcos, J.L. Serrano, Chem. Eur. J. **5**, 1834 (1999)
817. J. Barbera, M. Marcos, A. Omenat, J.L. Serrano, J.I. Martinez, P.J. Alonso, Liq. Cryst. **27**, 255 (2000)
818. M. Marcos, R. Gimenez, J.L. Serrano, B. Donnio, B. Heinrich, D. Guillon, Chem. Eur. J. **7**, 1006 (2001)
819. V. Cozan, M. Gaspar, E. Butuc, A. Stoleriu, Eur. Polym. J. **37**, 1 (2001)
820. P.A. Henderson, C.T. Imrie, Macromolecules **38**, 3307 (2005)
821. H. Hioki, M. Fukutaka, H. Takahashi, M. Kubo, K. Matsushita, M. Kodama, K. Kubo, K. Ideta, A. Mori, Tetrahedron **61**, 10643 (2005)
822. T. Narasimhaswamy, N. Somanathan, D.K. Lee, A. Ramamoorthy, Chem. Mater. **17**, 2013 (2005)
823. J.A. Smith, R.A. DiStasio, N.A. Hannah, R.W. Winter, T.J.R. Weakley, G.L. Gard, S.B. Rananavare, J. Phys. Chem. B **108**, 19940 (2004)
824. R. Paschke, S. Liebsch, C. Tschierske, M.A. Oakley, E. Sinn, Inorg. Chem. **42**, 8230 (2003)
825. M. Grigoras, C.O. Catanescu, J. Macromol. Sci. C **44**, 131 (2004)
826. I.O. Savchenko, V.G. Siromyatnikov, Ukr. Khim. Zh. **80**, 44 (2014)
827. J.J. Wie, S. Chatterjee, D.H. Wang, L.-S. Tan, M.R. Shankar, T.J. White, Polymer **55**, 5915 (2014)
828. G. Rabilloud, High-performance polymers. Chemistry and applications, in *Polyquinoxalines and Polyimides*, vol. 2. (Editions Technip, Paris, 1997–2000)
829. D.-J. Liaw, K.-L. Wang, Y.-C. Huang, K.-R. Lee, J.-Y. Lai, C.-S. Ha, Prog. Polym. Sci. **37**, 907 (2012)
830. U. Shukla, K.V. Rao, A.K. Rakshit, J. Appl. Polym. Sci. **88**, 153 (2003)
831. V.P. Malinovskaya, T.I. Borisova, N.M. Geller, S.V. Fedorova, S.S. Skorokhodov, Vysokomol. Soedin. **48**, 34 (2006)
832. C.-L. Liu, F.-C. Tsai, C.-C. Chang, K.-H. Hsieh, J.-L. Lin, W.-C. Chen, Polymer **46**, 4950 (2005)

833. H. Ocak, B. Bilgin-Eran, C. Tschierske, U. Baumeister, G. Pelzl, J. Mater. Chem. **19**, 6995 (2009)
834. B.J. Vasanthi, L. Ravikumar, Open J. Polym. Chem. **3**, 70 (2013)
835. M. Kaller, S. Laschat, Top. Curr. Chem. **318**, 109 (2012)
836. S. Zhang, X. Zhang, T. Jia, G. Hao, Z. Li, Gaofenzi Xuebao 403 (2009)
837. S. Zheng, K. Guo, M. Niu, S. Zhang, Z. Li, Q. Zhou, L. Li, Gaofenzi Xuebao 32 (2004)
838. Z. Li, W. Zhu, K. Guo, S. Zhang, S. Zheng, Gaofenzi Cailiao Kexue Yu Gongcheng **20**, 81 (2004)
839. L. Marin, E. Perju, M.D. Damaceanu, Eur. Polym. J. **47**, 1284 (2011)
840. A. Iwan, D. Sek, Progr. Polym. Sci. **33**, 289 (2008)
841. E.A. Soto-Bustamante, C.M. Gonzalez-Henriquez, G.A. Rodriguez-Lehyt, R.O. Vergara-Toloza, Liq. Cryst. **31**, 1115 (2004)
842. E.A. Soto-Bustamante, D. Saldaño-Hurtado, R.O. Vergara-Toloza, P.A. Navarrete-Encina, M.A. Athanassopoulou, Liq. Cryst. **30**, 17 (2003)
843. A. Iwan, M. Palewicz, A. Sikora, J. Chmielowiec, A. Hreniak, G. Pasciak, P. Bilski, Synth. Met. **160**, 1856 (2010)
844. H.E. Gulbas, H. Ocak, Y.H. Gursel, B. Bilgin-Eran, Mol. Cryst. Liq. Cryst. **574**, 40 (2013)
845. H.E. Gulbas, D.G. Coskun, Y.H. Gurse, B. Bilgin-Eran, Adv. Mat. Lett. **5**, 333 (2014)
846. J.W. Brown, G.J. Lambe, P.J.S. Foot, J.A. Clipson, Macromol. Rapid Commun. **25**, 1000 (2004)
847. P. Castell, A. Serra, M. Galia, J. Polym. Sci. A **42**, 3631 (2004)
848. J. Kim, B.M. Novak, A.J. Waddon, Macromolecules **37**, 8286 (2004)
849. Z. Li, K. Guo, X. Zhang, T. Zhang, S. Zheng, S. Zhang, Q. Zhou, L. Li, Gaofenzi Xuebao 175 (2003)
850. A. Ryabchun, A. Bobrovsky, A. Medvedev, V. Shibaev, J. Polym. Sci. A **49**, 625 (2011)
851. S.-J. Wang, R.-Y. Zhao, S. Yang, Z.-Q. Yu, E.-Q. Chen, Chem. Commun. **50**, 8378 (2014)
852. V. Shibaev, A. Medvedev, A. Bobrovsky, J. Polym. Sci. A **46**, 6532 (2008)
853. H. Zhang, Y. Tu, X. Wan, Q.-F. Zhou, E.M. Woo, J. Polym. Res. **9**, 11 (2002)
854. X. He, W. Sun, D. Yan, L. Liang, Eur. Polym. J. **44**, 42 (2008)
855. J.E. Stumpel, E.R. Gil, A.B. Spoelstra, C.W.M. Bastiaansen, D.J. Broer, A.P.H. J. Schenning, Adv. Funct. Mater. **25**, 3314 (2015)
856. D. Zhao, Q. Wang, L. Guo, H. Yang, Liq. Cryst. **41**, 1510 (2014)
857. J.J. Wie, K.M. Lee, T.H. Ware, T.J. White, Macromolecules **48**, 1087 (2015)
858. M.E. McConney, A. Martinez, V.P. Tondiglia, K.M. Lee, D. Langley, I.I. Smalyukh, T.J. White, Adv. Mater. **25**, 5880 (2013)
859. D. Iqbal, M.H. Samiullah, Materials **6**, 116 (2013)
860. T. Seki, Polym. J. **46**, 751 (2014)
861. G. Fernández, Nature Mater. **12**, 12 (2013)
862. B. Donnio, D. Guillon, Adv. Polym. Sci. **201**, 45 (2006)
863. M. Higuchi, M. Tsuruta, H. Chiba, S. Shiki, K. Yamamoto, J. Am. Chem. Soc. **125**, 9988 (2003)
864. J.S. Cho, K. Takanashi, M. Higuchi, K. Yamamoto, Synth. Met. **150**, 79 (2005)
865. A. Kimoto, K. Masachika, J.S. Cho, M. Higuchi, K. Yamamoto, Chem. Mater. **16**, 5706 (2004)
866. X. Yan, T. Goodson, T. Imaoka, K. Yamamoto, J. Phys. Chem. B **109**, 9321 (2005)
867. M. Marcos, R. Martín-Rapún, A. Omenat, J.L. Serrano, Chem. Soc. Rev. **36**, 1889 (2007)
868. I. Gracia, B. Feringán, J.L. Serrano, R. Termine, A. Golemme, A. Omenat, J. Barbera, Chemistry **21**, 1359 (2015)
869. Y. Sagara, T. Kato, Angew. Chem. Int. Ed. **47**, 5175 (2008)
870. B.I. Ostrovskii, S.N. Sulyanov, N.A. Boiko, V.P. Shibaev, S.B. Astaf'ev, L.G. Yanusova, W.H. de Jeu, Eur. Phys. J. E. **36**, 134 (2013)
871. A. Belaissaoui, I.M. Saez, S.J. Cowling, J.W. Goodby, Macromolecules **46**, 1268 (2013)
872. V.P. Shibaev, Polym. Sci. Ser. A **51**, 1131 (2009)
873. V.P. Shibaev, Polym. Sci. Ser. A **56**, 727 (2014)

874. P. Argurio, R. Molinari, T. Poerio, Desalination **162**, 217 (2004)
875. I. Kaya, M. Yildiz, S. Koyuncu, Synth. Met. **128**, 267 (2002)
876. M.A.R. Ahamed, R. Subha, D. Jeyakumar, A.R. Burkanudeend, Polym. Int. **64**, 126 (2015)
877. H. Kasgoz, S. Ozgumus, M. Orbay, Polymer **44**, 1785 (2003)
878. M.-A. Kwon, G.-J. Kim, Catal. Today **87**, 145 (2003)
879. X. Liu, Y. Hu, B. Wang, Z. Su, Synth. Met. **159**, 1557 (2009)
880. R. Qu, C. Sun, J. Chen, H. Chen, C. Wang, C. Ji, L. Xu, Polym. Eng. Sci. 721 (2007)
881. K.H. Reddy, A.R. Reddy, J. Appl. Polym. Sci. **88**, 414 (2003)
882. Y. Kwak, A.J.D. Magenau, K. Matyajaszewski, Macromolecules **44**, 811 (2011)
883. Y. Xu, W. Bai, Z. Luo, Y. Jin, B. Peng, L. Feng, B. Hu, J. Lin, Appl. Surf. Sci. **258**, 5141 (2012)
884. Y.Q. Wang, Y.X. Sun, X.L. Xong, X.Z. Zhang, G.Y. Zhang, Mol. BioSyst. **6**, 256 (2010)
885. D. Kumar, P.K. Gupta, A. Syamal, J. Chem. Sci. **117**, 247 (2005)
886. A.M. Albu, M. Mocioi, C.D. Mateescu, A. Iosif, J. Appl. Polym. Sci. **121**, 1867 (2011)
887. P.U. Belsare, A.B. Zade, Der Pharma Chem. **5**, 325 (2013)
888. M.K. Othman, F.A. Al-Qadri, F.A. Al-Yusufy, Spectrochim. Acta Part A **78**, 1342 (2011)
889. F. Bakhtiarzaden, S.A. Ghani, Electroanalysis **22**, 549 (2010)
890. C. Sun, G. Zhang, R. Qu, Y. Yu, Chem. Eng. J. **170**, 250 (2011)
891. N.P. Tzanetos, A.K. Andreopoulou, J.K. Kallitsis, J. Polym. Sci. Part A Polym. Chem. **43**, 4838 (2005)
892. Y. Cui, Q. Chen, D.-D. Zhang, J. Cao, B.-H. Han, J. Polym. Sci. Part A Polym. Chem. **48**, 1310 (2010)
893. K.J. Calzia, G.N. Tew, Macromolecules **35**, 6090 (2002)
894. M.A.R. Meier, U.S. Schubert, J. Polym. Sci. Part A Polym. Chem. **41**, 2964 (2003)
895. D.-W. Yoo, S.-K. Yoo, C. Kim, J.-K. Lee, J. Chem. Soc. Dalton Trans. 3931 (2002)
896. E. Holder, V. Marin, M.A.R. Meier, U.S. Schubert, Macromol. Rapid Commun. **25**, 1491 (2004)
897. Q. Luo, Y. Guan, Y. Zhang, M. Siddiq, J. Polym. Sci. Part A Polym. Chem. **48**, 4120 (2010)
898. T. Yamamoto, Y. Saitoh, K. Anzai, H. Fukumoto, T. Yasuda, Y. Fujiwara, B.-K. Choi, K. Kubota, T. Miyamae, Macromolecules **36**, 6722 (2003)
899. N. Kang, A.S. Hay, J. Macromol. Sci. Part A Pure Appl. Chem. **40**, 881 (2003)
900. P. Yan, H. Jing, Adv. Synth. Catal. **351**, 1325 (2009)
901. T. Ahamad, S.M. Alshehri, Adv. Polym. Technol. **32**, 21350 (2013)
902. J. Ritchie, A. Ruseckas, P. Andre, C. Munther, M. Van Ryssen, D.E. Vize, J.A. Crayston, I. D.W. Samuel, Synth. Met. **159**, 583 (2009)
903. S.M. Islam, M. Mobarok, P. Mondal, A.S. Roy, S. Mondal, D. Hossain, J. Appl. Polym. Sci. **123**, 3789 (2012)
904. M. Nagy, M. Zsuga, D. Racz, S. Keki, J. Polym. Sci. Part A Polym. Chem. **48**, 2709 (2010)
905. S. He, A.A. Buelt, J.M. Hanley, B.P. Morgan, A.G. Tennyson, R.C. Smith, Macromolecules **45**, 6344 (2012)
906. B. Liu, W.-L. Yu, J. Pei, S.-Y. Liu, Y.-H. Lai, W. Huang, Macromolecules **34**, 7932 (2001)
907. L. Zong, Q. Miao, Y. Liu, J. Xu, X. Huang, Y. Cheng, Chin. J. Chem. **27**, 1179 (2009)
908. S.-I. Kato, K. Takagi, K. Suzuki, T. Kinoshita, Y. Yuki, J. Polym. Sci. Part A Polym. Chem. **42**, 2631 (2004)
909. Y. de Gaetano, I. Clarot, J.-B. Regnouf-de-Vains, Tetrahedron Lett. **50**, 5793 (2009)
910. A.V. Pestov, P.A. Slepukhin, Y.G. Yatluk, V.N. Charushin, O.N. Chupakhin, J. Appl. Polym. Sci. **125**, 1970 (2012)
911. A. de Bettencourt-Dias, J.S.K. Rossini, Inorg. Chem. **55**, 9954 (2016)
912. C. Ji, S. Song, C. Wang, C. Sun, R. Qu, C. Wang, H. Chen, Chem. Eng. J. **165**, 573 (2010)
913. C. Ji, R. Qu, C. Sun, C. Wang, Q. Xu, Y. Sun, C. Li, S. Guo, J. Appl. Polym. Sci. **103**, 3220 (2007)
914. C. Ji, R. Qu, Q. Xu, C. Sun, C. Wang, Y. Cheng, Y. Song, J. Appl. Polym. Sci. **111**, 2148 (2009)

915. T. Ahamad, S.M. Alshehri, Polym. Int. **61**, 1640 (2012)
916. J. Weng, L.M. Jiang, W.L. Sun, Z.Q. Shen, S.Q. Liang, Polymer **42**, 5491 (2001)
917. C. Bianchini, M. Frediani, G. Mantovani, F. Vizza, Organometallics **20**, 2660 (2001)
918. S. Moulay, R. Mehdaoui, React. Funct. Polym. **61**, 265 (2004)
919. A. Stepuk, J.G. Halter, A. Schaetz, R.N. Grass, W.J. Stark, Chem. Commun. **48**, 6238 (2012)
920. C. Dai, Y. Wang, Y. Quan, Q. Chen, Y. Cheng, C. Zhu, J. Polym. Sci. Part A Polym. Chem. **52**, 3080 (2014)
921. I.A. Alkskas, I.S. Moosa, Int. J. Polym. Mat. **61**, 1142 (2012)
922. R. Qu, C. Wang, C. Ji, C. Sun, X. Sun, G. Cheng, J. Appl. Polym. Sci. **95**, 1558 (2005)
923. M.M. Patel, M.A. Kapadia, G.P. Patel, J.D. Joshi, React. Funct. Polym. **67**, 746 (2007)
924. M.M. Patel, M.A. Kapadia, J.D. Joshi, Eur. Polym. J. **45**, 426 (2009)
925. S.S. Rahangdale, World Appl. Sci. J. **1**, 237 (2013)
926. G. Alagumuthu, P. Mariselvi, Int. J. Chem. Stud. **1**, 157 (2013)
927. Z. Yang, J. Lu, Acta Polym. Sinica **1**, 838 (2008)
928. J. Lai, L.-Q. Wang, K. Tu, C. Zhao, W. Sun, J. Appl. Polym. Sci. **26**, 1572 (2005)
929. W.B. Gurnule, H.D. Juneja, L.J. Paliwal, React. Funct. Polym. **50**, 95 (2002)
930. J. Dontulwar, K. Nandekara, W. Gurnule, Der Pharma Chem. **5**, 160 (2013)
931. M.S. Dhore, S.S. Butoliya, A.B. Zade1, ISRN Polym. Sci. **2014**, Article ID 873520 (2014)
932. B. Gao, W. Zhang, Z. Zhang, Q. Lei, J. Lumin. **132**, 2005 (2012)
933. A. El-Dissouky, A.-Z. Elassar, A.-H. Bu-Olian, J. Chem. Eng. Data **56**, 1827 (2011)
934. M.S. Hosseini, H. Raissi, S. Madarshahian, React. Funct. Polym. **66**, 1539 (2006)
935. A. Islam, A. Ahmad, M.A. Laskar, J. Appl. Polym. Sci. **123**, 3448 (2012)
936. I. Kaya, D. Senol, J. Appl. Polym. Sci. **90**, 442 (2003)
937. G. Pina-Luis, G.A. Rosquete Pina, A.C.V. Gonzalez, A.O. Teran, I.R. Espejel, M.E. Diaz-Garcia, React. Funct. Polym. **72**, 61 (2012)
938. C.-Y. Chen, C.-Y. Chen, J. Appl. Polym. Sci. **86**, 1986 (2002)
939. B. Gao, X. Wei, Y. Zhang, Opt. Mater. **35**, 536 (2013)
940. C.-Y. Chen, S.-Y. Chen, J. Appl. Polym. Sci. **94**, 2123 (2004)
941. G. Iyer, L.M.V. Tillekeratne, M.R. Coleman, A. Nadarajah, Polymer **49**, 3744 (2008)
942. G. Iyer, L.M.V. Tillekeratne, M.R. Coleman, A. Nadarajah, Polymer **49**, 3737 (2008)
943. L. Yang, Y. Li, X. Jin, Z. Yeb, X. Ma, L. Wang, Y. Liu, Chem. Eng. J. **168**, 115 (2011)
944. L.Q. Yang, Y.F. Li, L.Y. Wang, Y. Zhang, X.J. Ma, Z.F. Ye, J. Hazard. Mater. **180**, 98 (2010)
945. N. Illy, D. Majonis, I. Herrera, O. Ornatsky, M.A. Winnik, Biomacromolecules **13**, 2359 (2012)
946. D. Majonis, I. Herrera, O. Ornatsky, M. Schulze, X. Lou, M. Soleimani, M. Nitz, M.A. Winnik, Anal. Chem. **82**, 8961 (2010)
947. C. Sun, R. Qu, C. Ji, Q. Wang, C. Wang, Y. Sun, G. Cheng, Eur. Polym. J. **42**, 188 (2006)
948. B.L. Rivas, A. Maureira, C. Guzman, M.A. Mondaca, J. Appl. Polym. Sci. **111**, 78 (2009)
949. A. Denizli, R. Say, B. Garipcan, S. Patir, React. Funct. Polym. **58**, 123 (2004)
950. I. Kaya, A.R. Vilayetoglu, H. Topak, J. Appl. Polym. Sci. **85**, 2004 (2002)
951. X. Ma, Y. Li, Z. Ye, L. Yang, L. Zhou, L. Wang, J. Hazard. Mater. **185**, 1348 (2011)
952. J.X. Luo, C.L. Yang, J. Zheng, J.Y. Ma, L.Y. Liang, M.G. Lu, Eur. Polym. J. **47**, 385 (2011)
953. N.M. Salem, K.A.K. Ebraheem, M.S. Mubarak, React. Funct. Polym. **59**, 63 (2004)
954. S.S. Katkamwar, A.B. Zade, S.S. Rahangdale, W.B. Gurnule, J. Appl. Polym. Sci. **113**, 3330 (2009)
955. S. Gharbi, J. Khiari, B. Jamoussi, J. Chem. Eng. Process Technol. **5**, 198 (2014)
956. W.B. Gurnule, S.S. Katkamwar, Der Pharm. Lett. **4**, 1360 (2012)
957. R.S. Azarudeen, M.A.R. Ahamed, A.R. Burkanudeen, Desalination **268**, 90 (2011)
958. V.D. Mane, N.J. Wahane, W.B. Gurnule, J. Appl. Polym. Sci. **111**, 3039 (2009)
959. S.K. Mandavgade, J.R. Dontulwar, W.B. Gurnule, Der Pharma Chem. **4**, 1695 (2012)
960. W. Zhang, B. Gao, Y. Chen, Acta Polym. Sinica 1382 (2011)

961. M.N.A. Al-Jibouri, T.M. Musa, M. Mubarak, W.M. Al-Jibouri, Sci. J. Chem. **1**, 38 (2013)
962. H. Askun, B. Gülbakan, O. Celikbicak, C. Uzun, O. Güven, B. Salih, J. Appl. Polym. Sci. **107**, 2714 (2008)
963. H. Dierssen, W. Balzer, W.M. Landing, Mar. Chem. **73**, 173 (2001)
964. M. Hruby, J. Hradil, M.J. Bene, React. Funct. Polym. **59**, 105 (2004)
965. C. Sun, C. Li, C. Wang, R. Qu, Y. Niu, H. Geng, Chem. Eng. J. **200–202**, 291 (2012)
966. W.B. Gurnule, D.B. Patle, Elixir Appl. Chem. **50**, 10338 (2012)
967. S.M. Islam, A.S. Roy, P. Mondal, S. Paul, N. Salam, Inorg. Chem. Commun. **24**, 170 (2012)
968. S. Samal, S. Acharya, R.K. Dey, A.R. Ray, J. Appl. Polym. Sci. **88**, 570 (2003)
969. N. Samadi, R. Hasanzadeh, M. Rasad, J. Appl. Polym. Sci. **132**, 41642 (2015)
970. S.M. Islam, N. Salam, P. Mondal, A.S. Roy, J. Mol. Catal. A Chem. **366**, 321 (2013)
971. O. Melad, M. Esleem, Open J. Org. Polym. Mater. **5**, Article ID: 54864 (2015)
972. M.R. Nateghi, M. Borhani, React. Funct. Polym. **68**, 153 (2008)
973. R.S. Azarudeen, M.A.R. Ahamed, D. Jeyakumar, A.R. Burkanudeen, Iran. Polym. J. **18**, 821 (2009)
974. R.S. Azarudeen, M.A.R. Ahamed, N. Prabu, N.M. Kani, Appl. Organomet. Chem. **28**, 773 (2014)
975. I. Kaya, H.O. Demir, A.R. Vilayetoglu, Synth. Met. **126**, 183 (2002)
976. A. Ercag, I. Kaya, D. Senol, S. Koyunci, Polym. Plast. Technol. Eng. **44**, 265 (2005)
977. J. Hou, F. Song, L. Wang, G. Wei, Y. Cheng, C. Zhu, Macromolecules **45**, 7835 (2012)
978. S. Keesara, M.R. Mandapati, S. Parvathaneni, Appl. Catal. A Gen. **496**, 58 (2015)
979. J.P. Gangwar, P.N. Saxena, Orient. J. Chem. **27**, 119 (2011)
980. D. Kumar, P.K. Gupta, A. Syamal, J. Chil. Chem. Soc. **59**, 2260 (2014)
981. Y. Feng, M.E. Lydon, C.W. Jones, ChemCatChem **5**, 3636 (2013)
982. G.S.V. Kumar, B. Mathew, J. Appl. Polym. Sci. **92**, 1271 (2004)
983. I. Kaya, M. Yildirim, A. Avci, Synth. Met. **160**, 911 (2010)
984. F. Dogan, I. Kaya, A. Bilici, Synth. Met. **161**, 79 (2011)
985. H. Fukumoto, K. Yamane, Y. Kase, T. Yamamoto, Macromolecules **43**, 10366 (2010)
986. B. Liu, Y. Bao, F. Du, H. Wang, J. Tian, R. Bai, Chem. Commun. **47**, 1731 (2011)
987. R. Sankar, S. Vijayalakshmi, S. Rajagopan, T. Kaliyappan, J. Appl. Polym. Sci. **117**, 2146 (2010)
988. I. Kaya, F. Dogana, A. Bilici, Polym. Int. **58**, 570 (2009)
989. N. Sarı, S. Özcan, Chin. J. Polym. Sci. **27**, 675 (2009)
990. M. Sasidaran, R. Sankar, P. Kandasamy, S. Vijayalakshmi, T. Kaliyappan, High Perform. Polym. **23**, 602 (2011)
991. I. Kaya, A. Bilici, M. Sacak, Synth. Met. **159**, 1414 (2009)
992. M.N. Al-jibouri, T.M. Musa, IOSR J. Appl. Chem. (IOSR-JAC) **7**, 46 (2014)
993. R.S. Walmsley, C. Litwinski, E. Antunes, P. Hlangothi, E. Hosten, C. McCleland, T. Nyokong, N. Torto, Z.R. Tshentu, J. Mol. Catal. A Chem. **379**, 94 (2013)
994. T.R. Sankar, P.V. Ramana, J. Appl. Chem. **2**, 1459 (2013)
995. M. Cegłowski, G. Schroeder, Chem. Eng. J. **263**, 402 (2015)
996. T.R. Sankar, K. Kesavulu, P.V. Ramana, J. Chem. Sci. **126**, 597 (2014)
997. K. Kesavulu, T.R. Sankar, P.V. Ramana, Chem. Sci. Trans. **2**, 1318 (2013)
998. K.C. Gupta, A.K. Sutar, J. Mol. Catal. A Chem. **280**, 173 (2008)
999. A.M. Gad, A. El-Dissouky, E.M. Mansour, A. El-Maghraby, Polym. Degrad. Stab. **68**, 153 (2000)
1000. W.B. Gurnule, P.K. Rahangdale, L.J. Paliwal, R.B. Kharat, React. Funct. Polym. **55**, 255 (2003)
1001. S.M. Badawy, H.H. Sokker, A.M. Dessouki, J. Appl. Polym. Sci. **99**, 1180 (2006)
1002. F.A. Alakhras, K.A. Dari, M.S. Mubarak, J. Appl. Polym. Sci. **97**, 691 (2005)
1003. G. Zong, J. Ma, H. Chen, C. Wang, N. Ji, D. Liu, J. Appl. Polym. Sci. **124**, 2179 (2012)
1004. M. Bru, M.I. Burguete, F. Galindo, S.V. Luis, M.J, Marin, L. Vigara, Tetrahedron Lett. **47**, 1787 (2006)

1005. M.S. Choi, J.H. Lee, D.W. Kim, T.S. Lee, J. Polym. Sci. Part A Polym. Chem. **45**, 4430 (2007)
1006. M.B. Amran, A.S. Panggabean, A. Sulaeman, M. Rusnadi, Int. J. Environ. Res. **5**, 531 (2011)
1007. S.M. Islam, P. Mondal, A.S. Roy, S. Mondal, D. Hossain, Tetrahedron Lett. **51**, 2067 (2010)
1008. M. Ignatova, M. Sepulchre, N. Manolova, Eur. Polym. J. **38**, 33 (2002)
1009. B.F. Senkal, E. Yavuz, Monatsh. Chem. **137**, 929 (2006)
1010. Y. Zhang, Y. Chen, C. Wang, Y. Wei, J. Hazard. Mater. **276**, 129 (2014)
1011. C. Xiong, S. Zhou, X. Liu, Q. Jia, C. Ma, X. Zheng, Ind. Eng. Chem. Res. **53**, 2441 (2014)
1012. M.A. Diab, A.Z. El-Sonbati, R.H. Mohamed, Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **77**, 795 (2010)
1013. L. Qian, Y. Guan, B. He, H. Xiao, Polymer **49**, 2471 (2008)
1014. M. Hatanaka, M. Hoshi, R. Shiba, Kobunshi Ronbunshu **63**, 745 (2006)
1015. T. Ahamad, S.M. Alshehri, Spectrochim. Acta. Part A Mol. Biomol. Spectr. **96**, 179 (2012)
1016. T. Ahamad, S.M. Alshehri, Spectrochim. Acta. Part A Mol. Biomol. Spectr. **108**, 26 (2012)
1017. M.A.A. El-Ghaffar, M.H. Mohamed, K.Z. Elwakeel, Chem. Eng. J. **151**, 30 (2009)
1018. C. Xiong, Y. Zheng, Y. Feng, C. Yao, C. Ma, X. Zheng, J. Jiang, J. Mater. Chem. A **2**, 5379 (2014)
1019. C. Xiong, Y. Li, G. Wang, L. Fang, S. Zhou, C. Yao, Q. Chen, X. Zheng, D. Qi, Y. Fu, Y. Zhu, Chem. Eng. J. **259**, 257 (2015)
1020. C. Wang, C. Ji, Y. Meng, L. Liu, R. Qu, C. Wang, J. Appl. Polym. Sci. **116**, 636 (2010)
1021. R. Qu, C. Sun, C. Ji, C. Wang, Q. Xu, S. Lu, C. Li, G. Xu, G. Cheng, J. Appl. Polym. Sci. **101**, 631 (2006)
1022. K. Roy, S. Basu, Ind. J. Chem. **44A**, 531 (2005)
1023. W.B. Gurnule, P.K. Rahangdale, L.J. Paliwal, R.B. Kharat, J. Appl. Polym. Sci. **89**, 787 (2003)
1024. K.S. Chettiyar, K. Sreekumar, Ind. J. Chem. **42A**, 499 (2003)
1025. S. Dutta, A.K. Das, J. Appl. Polym. Sci. **103**, 2281 (2007)
1026. M.R. Maurya, A. Arya, P. Adao, J.C. Pessoa, Appl. Catal. A Gen. **351**, 239 (2008)
1027. C. Ji, R. Qu, C. Sun, C. Wang, Y. Sun, N. Zhao, H. Xie, J. Appl. Polym. Sci. **100**, 5034 (2006)
1028. Y. Chen, Y. Zhao, React. Funct. Polym. **55**, 89 (2003)
1029. H. Ciftci, H.N. Testereci, Z. Oktem, Polym. Bull. **66**, 747 (2011)
1030. M. Bakherad, A. Keivanloo, B. Bahramian, S. Jajarmi, J. Organomet. Chem. **724**, 206 (2013)
1031. A. Kausar, S. Zulfiqar, Z. Ahmad, M. Ishaq, M.I. Sarwar, J. Appl. Polym. Sci. **124**, 373 (2012)
1032. A.R. Reddy, K.H. Reddy, J. Appl. Polym. Sci. **91**, 1932 (2004)
1033. M. Hruby, M. Skodova, H. Mackova, J. Skopal, M. Tomes, M. Kropacek, J. Zimova, J. Kucka, React. Funct. Polym. **71**, 1155 (2011)
1034. D. Jermakowicz-Bartkowiak, React. Funct. Polym. **67**, 1505 (2007)
1035. F.C. Gaertner, R. Luxenhofer, B. Blechert, R. Jordan, M. Essler, J. Control. Rel. **119**, 291 (2007)
1036. H. Mouaziz, J.-C. Soutif, V. Montembault, Eur. Polym. J. **39**, 1773 (2003)
1037. L. Garcia, A. Torrent, E. Anticó, C. Fontas, A. Roglans, React. Funct. Polym. **68**, 1088 (2008)
1038. M.J. Tapia, H.D. Burrows, J.M. Garcia, F. Garcia, A.A.C.C. Pais, Macromolecules **37**, 856 (2004)
1039. V. Calderon, F. Serna, F. Garcıa, J.L. de la Pena, J.M. Garcia, J. Appl. Polym. Sci. **106**, 2875 (2007)
1040. J.-M. Yu, Y. Chen, Macromolecules **42**, 8052 (2009)
1041. L. Cui, D. Chao, J. Zhang, H. Mao, Y. Li, C. Wang, Synth. Metals **160**, 400 (2010)
1042. X. Han, P. Xiao, H. Zhao, C. Zeng, J. Zhou, Appl. Spectrosc. **68**, 879 (2014)

1043. W. Zhou, M. Guo, J. Xu, X. Yuan, Eur. Polym. J. **44**, 656 (2008)
1044. P.K. Mohapatra, S. Lakshmi, D.M. Raju, V.K. Manchanda, J. Membr. Sci. **232**, 133 (2004)
1045. S. Habaue, Y. Akagi, M. Sato, A. Niimi, Polym. Bull. **54**, 237 (2005)
1046. K. Kimura, H. Sakamoto, R.M. Uda, Macromolecules **37**, 1871 (2004)
1047. H. Sakamoto, T. Anase, H. Osuga, K. Kimura, React. Funct. Polym. **71**, 569 (2011)
1048. S.R. Dave, H. Kaur, S.K. Menon, React. Funct. Polym. **70**, 692 (2010)
1049. S.H. Chan, W.T. Wong, W.K. Chan, Chem. Mater. **13**, 4635 (2001)
1050. T. Terashima, M. Kawabe, Y. Miyabara, H. Yoda, M. Sawamoto, Nat. Commun. **4**, 2321 (2013)
1051. B. Gierczyk, G. Schroeder, M. Cegłowski, React. Funct. Polym. **71**, 463 (2011)
1052. Z. Liu, I. Schmidt, P. Thamyongkit, R.S. Loewe, D. Syomin, J.R. Diers, A. Zhao, V. Misra, J.S. Lindsey, D.F. Bocian, Chem. Mater. **17**, 3728 (2005)
1053. N.B. McKeown, S. Hanif, K. Msayib, C.E. Tattershall, P.M. Budd, Chem. Commun. 2782 (2002)
1054. C. Huang, N. Wang, Y. Li, C. Li, J. Li, H. Liu, D. Zhu, Macromolecules **39**, 5319 (2006)
1055. T. Asano, P.-C. Wang, A. Iwasaki, Spectrochim. Acta. Part A **75**, 305 (2010)
1056. A. Bilgin, C. Yagci, A. Mendi, U. Yildiz, Polyhedron **26**, 617 (2007)
1057. A. Bilgin, C. Yagci, U. Yildiz, Macromol. Chem. Phys. **206**, 2257 (2005)
1058. A. Bilgin, A. Mendi, U. Yildiz, Polymer **47**, 8462 (2006)
1059. G. Tillet, P. De Leonardis, A. Alaaeddine, M. Umeda, S. Mori, N. Shibata, S.M. Ali, D. Fortin, P.D. Harvey, B. Ameduri, Macromol. Chem. Phys. **213**, 1559 (2012)
1060. H. Duan, L. Liu, X. Meng, D. Qin, X. Wang, X. Du, C. Wang, J. Tian, Synth. Met. **159**, 1512 (2009)
1061. S. Fu, K. Zhang, M. Zhang, L. Tian, Pigm. Resin Technol. **41**, 3 (2012)