Chapter 20
Discotic Liquid Crystalline Polymers: Structure and Chemistry

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Historically polymers are known for their insulating property, processability, thermal stability and mechanical strength. Discovery of the conducting polymers introduced them to molecular electronics for variety of applications like organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors and biosensors (Lange et al. 2008). Physical and electronic properties of bulk polymer materials are highly dependent on molecular ordering of polymers chains. For example, a light-weight polymer stronger then steel can be prepared in the form of kevlar just by assembling the polymer chains. Again the alignment of the polymer chains has been shown to enhance conductivity of conductive polymers (Ogasawara et al. 1985).

Lots of efforts have been put forth by the scientific community to achieve the control on molecular ordering of polymer chains through various supramolecular approaches. Among all, a well-known approach is attaching the liquid crystal mesogens to the polymer chain. With the advantage of self-assembling tendency of liquid crystals molecules into ordered materials, polymer chains can be influenced to assemble into well-ordered structure by attaching them to polymer back bone. This class of polymers are well known as Liquid crystal polymers (LCPs). Followed by the first discovery of LCPs by Vorlander et al., a variety of LCPs were synthesized and characterized to sooth the scientific curiosity about them. A range of synthetic methods including polymer substitution reactions, free radical polymerizations, optical polymerizations, ring-opening metathesis polymerizations, and condensation polymerizations have been used to prepare such

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polymers. At the ground of liquid crystals materials LCPs can be classified in linear, banana, discotic and mixed mesogen based LCPs. Discotic mesogens based polymers (DLCPs) were first realized by the Ringsdorf group (Kreuder et al.1983). These class of polymers are important, because of their tendency to self-organize into well-ordered, self-healable supramolecular columns, which tends to rearrange in 2D lattices due to π-π stacking of the planar aromatic core and the vander Waals interactions of the peripheral chains. These characteristics of DLC make them potential candidates for optoelectronic applications, because of their high charge conducting capacity along the columns. The electronic properties of DLCPs can be tuned based on various discotic mesogen moieties like, benzene, alkynylbenzene, triphenylene, phthalocyanine, hexabenzocoronene etc. On the other hand change in polymer back bone with different spacer and linkages (ester, ether and amide etc.) provide an opportunity to tune the physical properties of DLCPs. The LCPs literature is rich with examples of linear, banana shaped mesogen based LCPs as compare to DLCPs. Main reason for this is less availability of functionalized discogens units due to the symmetry of these molecules. However, motivated with the various applications in the areas of wide view displays, High-quality carbon products, organic electronics, photovoltaic solar cells, light emitting diodes and field effective transistors, research has shown exponential growth in terms of synthesis and understanding of physical properties of DLCPs. Discotic Liquid Crystalline Polymers (DLCPs) can be further classified into (a) discotic main chain (b) discotic side chain (c) discotic elastomers (d) discotic dendritic (e) discotic hyperbranched and (f) discotic metallomesogenic liquid crystalline polymers (Fig. 20.1), based on the position of discotic mesogens and connectivity.

20.1 Main Chain Discotic Liquid Crystal Polymers

In main chain discotic liquid crystal polymers discotic mesogens are incorporate into the main chain of polymer backbone. So, difunctionalized discotic mesogens are the primary requirement of these class of polymers. These functional groups are often hydroxyl moities to produce polyether or polyester based main chain polymer. In spite of very less literature available, main chain DLCPs are the second most studied DLCPs after side chain DLCPs. These main chain DLCPs can be classified based on various discotic mesogen like Triphenylene, benzene, rufigallol, cycloter-averatrylene etc.

20.1.1 Rufigallol-Based Main Chain Discotic Liquid Crystal Polymers

The unequal reactivity of the six phenolic groups of Rufigallol **1** core presents an advantage of the selective alkylation of four of the phenolic groups, leaving behind the two intramolecular hydrogen-bonded ones. Utilizing this strategy Raja
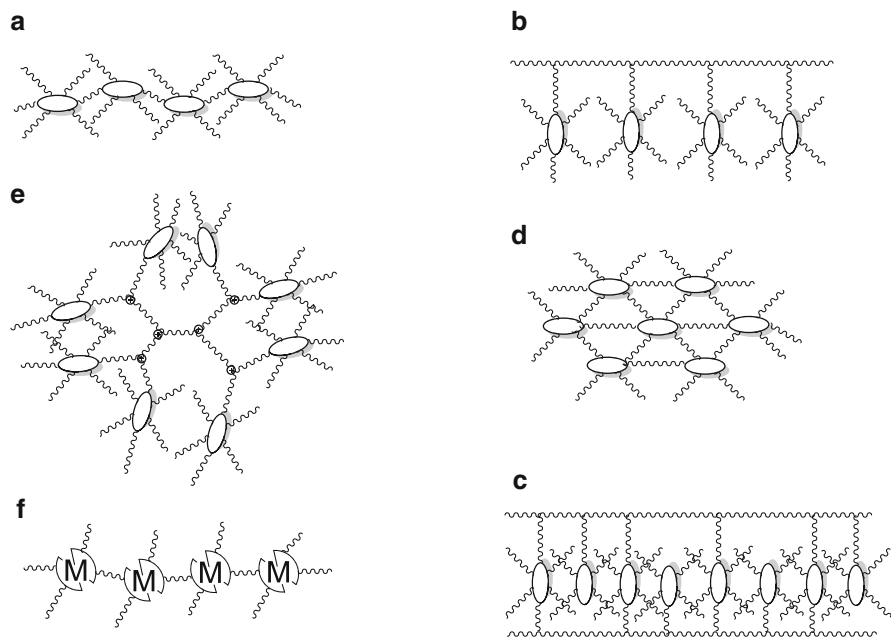
Fig. 20.1 Schematic representation of; (**a**) discotic main chain; (**b**) discotic side chain; (**c**) discotic elastomers; (**d**) discotic dendritic; (**e**) discotic hyperbranched; (**f**) discotic metallomesogenic liquid crystalline polymers

et al. (Raja et al.1998) have been prepared two series of thermotropic main chain discotic liquid crystalline polyether based on rufigallol starting from the symmetric tetraether of rufigallol. The Polyether **2a–h** were synthesized by reacting 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone **2** (Scheme 20.1) with equimolar amount of α,ω-dibromoalkane in the presence of Potassium carbonate (aq) in *o*-dichlorobenzene solvent under nitrogen atmosphere at 90 °C for 14 days. These polyether can also be prepared by heating an equimolar mixture of dihydroxytetraalkoxyanthraquinone **2** and α,ω-dibromoalkane in *o*-dichlorobenzene at 90 °C in the presence of cesium carbonate for 10 days.

The length of the spacer segment in the polyethers was systematically varied. GPC studies revealed that, all polymers have moderate molecular weights varying between 5400 and 17,000. It can be seen from Table 20.1 that spacer to peripheral alkyl chain length ratio highly influenced thermal behaviour of these polymers **2a–h**. The isotropization temperature inversely depends on spacer length, when ratio is more than two. However, trend is quite the opposite when ratio is less than two. Furthermore, the polymers exhibit the hexagonal discotic columnar mesophases when ratio is more than two, while a rectangular lattice has been seen when ratio is less than two. Finally, the polymers have been shown to exhibit liquid crystalline columnar mesophases, while some of their low molar mass analogues are not liquid crystalline.
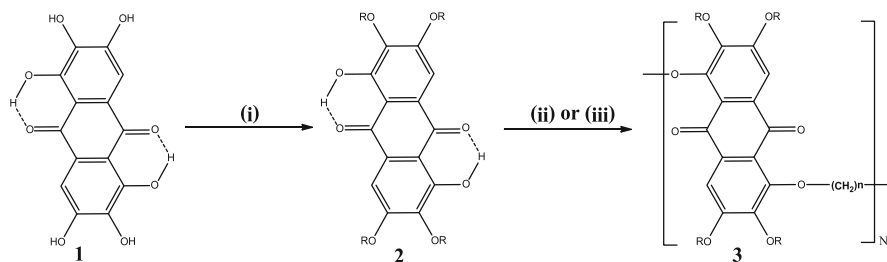
Scheme 20.1 Synthesis of rufigallol-based main-chain polyethers: (*i*) α,ω dibromoalkane, NaOH, DMSO, 90 °C; (*ii*) α,ω-dibromoalkane, o-dichlorobenzene, aq K_2CO_3, tetrabutylammonium bromide (TBAB), 90 °C, 14 days; (*iii*) α,ω dibromoalkane, o-dichlorobenzene, Cs_2CO_3, 90 °C, 10 days

Table 20.1 Thermal behavior of Rufigallol-based main-chain polyethers

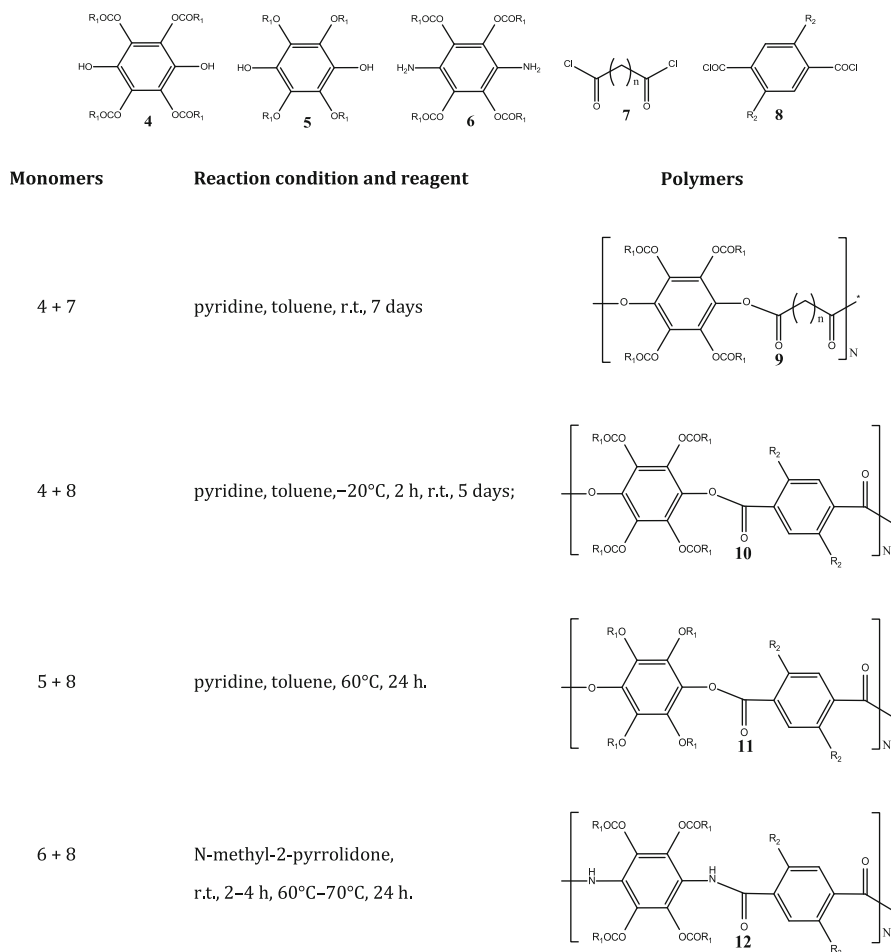| Structure	R	n	M_w	Phase transitions	References
2a	C_4H_9	6	68,00	g 72 Col$_r$ 164 Col$_r$' 175 I	Bengs et al. (1993)
2b	C_4H_9	8	17,000	g 72 Col$_h$ 164 Col$_h$' 176 I	
2c	C_4H_9	10	6400	Col$_h$ 133 Col$_h$' 144 I	
2d	C_4H_9	12	5400	Col$_h$ 138 I	
2e	C_8H_{17}	6	7400	Col$_r$ 132 I	
2f	C_8H_{17}	8	14,500	g 54 Col$_r$ 96 I	
2g	C_8H_{17}	10	8800	Col$_r$ 108 I	
2h	C_8H_{17}	12	7600	Col$_r$ 127 I	
2i	$CH_2CH_2CH(CH_3)$ $(CH_2)_3CH(CH_3)_2$	12	13,691	Col$_r$ 56 I	Bisoyi and Kumar (2008)

Source: Raja et al. (1998) and Bisoyi and Kumar (2008)

Further Bisoyi and Kumar (2008) tried to study the effect of inclusion of carbon nanotubes on mesophase behaviour of Rufigallol-based Main chain DPLCs. They found that insertion of small amount of carbon nanotubes does not affect the mesophase structure of the pure compounds and lower the isotropic transition temperature. Greater the amount of Carbon nanotube induce downfall in isotropic transition temperature. These room temperature liquid crystalline nano composite with broad mesophase range and different electronic properties can be important for many applications.

20.1.2 *Benzene-Based Main Chain Discotic Liquid Crystal Polymers*

Kreuder et al. (1985) were made first attempt to synthesize the difunctionalized benzene monomeric units to prepare the benzene-based liquid crystalline main-chain polymers. The polymers with ester and amide linkage were prepared via solution polycondensation of these difunctionalized monomers **4**, **5**, and **6** with various spacers **7** and **8** (Scheme 20.2).

   Synthesis of tetraalkanoyloxy benzene polyesters **9a–f** were achieved by reacting equimolar mixture of dihyroxy tetraalkanoyloxy benzene and flexible spacer alkane-α,ω-dioic acid dichloride in pyridine and toluene (Scheme 20.2). The polymers **9a** and **9b** with short spacers were found to be nonmesomorphic in thermal analysis (Table 20.2). At the same time, the polymer with long spacer **9c**,

Monomers	Reaction condition and reagent	Polymers
4 + 7	pyridine, toluene, r.t., 7 days	
4 + 8	pyridine, toluene, −20°C, 2 h, r.t., 5 days;	
5 + 8	pyridine, toluene, 60°C, 24 h.	
6 + 8	N-methyl-2-pyrrolidone, r.t., 2–4 h, 60°C–70°C, 24 h.	

Scheme 20.2 Synthesis of benzene based DLCPs polyester and polyamides

Table 20.2 Thermal behavior of benzene-methylene-based polymers

Structure	n	Mn	Phase transition	Reference
9a	7	–	g 54 I	Boden et al. (1995)
9b	8	10,400	g 55 I	
9c	10	9800	g 55 M 95 I	
9d	12	12,400	g 54 M 97 I	
9e	14	12,100	Cr 64 M 92 I	
9f	20	6600	g 30 I	

Source: Kreuder et al. (1985)

Table 20.3 Transition temperatures of benzene-based polyesters and polyamides

Structure	R	R'	Phase transition	Reference
10a	C_7H_{15}	H	g 97 M 146 M' 260 I	Boden et al. (1998)
10b	C_9H_{19}	H	g 50 Cr 95 M 138 I	
10c	$C_{11}H_{23}$	H	g 55 Cr 63 M 123 I	
10d	C_7H_{15}	OC_8H_{17}	Cr 50 I	
11a	C_8H_{17}	H	g 150 M 208 M' 246 I	
11b	$C_{12}H_{25}$	H	Cr 25 M 210 I	
11c	$C_{12}H_{25}$	$OC_{12}H_{25}$	Cr 74 I	
11d	$C_{12}H_{25}$	OC_8H_{17}	Cr 67 I	
12a	C_8H_{17}	H	Cr 273 I	
12b	C_8H_{17}	OC_8H_{17}	Cr 39 M 117 I	
12c	C_8H_{17}	$OC_{12}H_{25}$	Cr 51 M 69 I	
12d	$C_{12}H_{25}$	H	Cr 270 I	
12e	$C_{12}H_{25}$	$OC_{12}H_{25}$	Cr 17 M 70 M' 130 I	
12f	$C_{12}H_{25}$	OC_8H_{17}	Cr 61 M 122 I	
12g	$C_{14}H_{29}$	$OC_{14}H_{29}$	Cr 38 M 74 M' 88 M' 106 I	
12h	$C_{16}H_{33}$	$OC_{16}H_{33}$	Cr 86 I	

Source: Ringsdorf et al. (1987)

9d and **9e** were found to be liquid crystalline with the higher isotropization temperatures, as compare to monomeric tetraalkanoyloxy benzene unit. The liquid crystalline nature disappears, if spacer length in polymer **9f** increases to 20 methylene units. Replacing the flexible spacer, alkane-α,ω-dioic acid dichloride **7**, with terphthaloyl dichloride **8** in the same synthesis provides an opportunity to study the benzoate-based polyesters. Thermal analysis of polyesters **10a–d** shows that, all the polyesters **10a**, **10b** and **10c** with four lateral alkyl chains were liquid crystalline (Table 20.3). However, polyester **10d** having six lateral chains did not display any mesomorphism. The value of isotropization temperature highly depends on the lateral alkyl chain length of difunctionalized benzene monomers. The synthesis of corresponding tetraalkoxybenzene derived polybenzoates is shown in Scheme 20.2 (Herrmann-Schönherr et al. 1986; Ringsdorf et al. 1987). It was noticed that polymers with four lateral alkyl chains **11a** and **11b** were liquid crystalline, whereas polymers with six lateral alkyl chains **11c** and **11d** were found to be nonmesomorphic.

Benzene-based discotic polyamides **12a–h** were prepared by reacting tetra substituted 1,4-phenylenediamine **6** with terphthaloyl dichloride **8** in *N*-methyl-2-pyrrolidone as solvent. Polyamides with four lateral alkyl chains **16a** and **16d** were found crystalline in nature, whereas six lateral chains make them liquid crystalline. This reverse behaviour, as compare to polyesters, is most likely because of hydrogen bonding caused by amide linkage. Polyamides **12a** and **12d** with only four lateral substituents per repeating unit are able to form strong intermolecular hydrogen bonding and thus have a tendency to crystallize. Attachment of two more lateral substituents per repeating unit causes weaker intermolecular interactions and hence favours the formation of mesomorphic phase.

20.1.3 Triphenylene-Based Main Chain Discotic Liquid Crystal Polymers

Kreuder and Ringsdorf (1983) first reported the synthesis of triphenylene-based main-chain DLPCs. They prepared the difunctional triphenylenes precursor monomer via partial hydrolysis/alkylation of triphenylene hexaacetate. This method had a big disadvantage of giving mixture of diacetate isomers with two hydroxyl at 2,3-; 2,6-; 2,7-; or 2,11-positions. The separation of these isomers requires extensive column chromatography. These difunctional monomers (mixture 2,6- and 2,7-isomeric) yielded Triphenylene-based main chain DLCPs **13a–j** via melt polycondensation with various α,ω-diacids.

The thermal behaviour of these polymers is presented in Table 20.4. All the polymers except **13e** and **13i–j** were liquid crystalline. These polymer exhibit

Table 20.4 Thermal behavior of mixtures of 2,6-positions and 2,7-positions linked triphenylene main-chain polymers

Structure	R	Spacer	Phase transition	References
13a	C_5H_{11}	$-(CH_2)_{10}-$	g 35 Col 195 I	Boden et al. (1999)
13b	C_5H_{11}	$-CD_2(CH_2)_8CD-$	g 50 Col 220 I	
13c	C_5H_{11}	$-(CH_2)_{14}-$	g 60 Col 150 I	
13d	C_5H_{11}	$-(CH_2)_{14}-$	g 57 Col$_h$ 143 I	Boden et al. (2001)
13e	$C_5H_11$1	$-(CH_2)_{20}-$	g 35 I	Brand et al. (2000)
13f	$CD_2C_4H_9$	$-(CH_2)_{14}-$	g 58 Col$_h$ 140 I	Boden et al. (2001)
13g	$(CH_2)_2CD_2C_4H_9$	$-(CH_2)_{14}-$	g 50 Col$_h$ 180 I	Bryant et al. (1995)
13h	$CH_2C^*H(CH_3)$ C_2H_5	$-(CH_2)_{10}-$	g 140 Col$_h$ 192 I	Cameron et al. (1997)
13i	$CH_2C^*H(CH_3)$ C_2H_5	$-(CH_2)_{14}-$	g 108 I	
13j	$CH_2C^*H(CH_3)$ C_2H_5	$-(CH_2)_{20}-$	g 79 I	

Source: Kreuder and Ringsdorf (1983) and Hüser and Spiess (1988) and Ringsdorf et al. (1989) and Voigt-martin et al. (1994) and Green et al. (1990)

broader mesophase range as compare to monomeric units. Thermal behaviour remains nearly unchanged on deuteriation of the side-chain or aromatic groups. Among polymers **13i** and **13j**, **13i** changes amorphous to liquid crystalline on doping with electron acceptor TNF. It exhibits a nematic columnar phase. The substitution of chiral chain at peripheral positions induces the formation of a helical superstructure in the liquid crystalline polymers **13i–j** (Green et al. 1990).

To prepare the single isomer of difunctionalized triphenylene monomer Wenz's et al. (Wenz 1985) rationalized the synthesis of 2,3-difunctionalized triphenylene derivative. Later on Boden et al. (1995) prepared pure 2,7-dihydroxy-3,6,10,11-tetrahexyloxy-triphenylene and 2,11-dihydroxy-3,6,7,10-tetrahexyloxy-triphenylene respectively. Further polycondensation of 2,3-difunctionalized triphenylene with various α,ω-diols having different spacer length produce polyester **14**. The polycondensation of malonic acid diethyl ester afforded polymer **15** (Voigt-Martin et al. 1992). In polymers **16** triphenylene units having chiral peripheral chains were linked together via ester linkages. Condensation of 2,3-dihydroxy-6,7,10,11-tetrahexyloxytriphenylene)with 1,10-dibromodecane gives polymer **17**. The polyesterification of 2,7-dihydroxy-3,6,10,11-tetrahexyloxy-triphenylene and 2,11-dihydroxy-3,6,7,10-tetrahexyloxy-triphenylene with α,ω-dibromoalkanes furnished polymers **18** and **19a**. Polyesterification of 2,11-dihydroxytetrahexyloxytriphenylene with α,ω-diacids produced polymers **19b–d**.

Thermal studies and GPC studies of these polymer having different lateral alkyl chains and linkages are given in the Table 20.5. The polymers **14** melt at about 93 °C and clear between 100 and 200 °C whereas polymer **15** shows the glass transition at -10 °C and isotropic transition at 31 °C. Discotic nematic phase of polymer **15** transform into more ordered columnar phase, when it was doped with the electron-acceptor TNF. This charge transfer polymer composite exhibit the thermal transition at 135 °C from columnar phase to isotropic phase (Vandevyver et al. 1993). Polymer 16a and 16b were amorphous in nature and exhibit glass transition temperature at 105 °C and 75 °C respectively. Polymer **17** showed a columnar phase to isotropic transition at 115 °C (Fig. 20.2) (Disch et al. 1995). All polymers **19b–d** form an ordered columnar mesophases, between the glass transition and clearing temperatures as per the Table 20.6 (Wan et al. 2003).

To study the difference between structures displayed by lower mass and polymeric amphiphilic discotic liquid crystalline triphenylene derivatives in the bulk

Table 20.5 Thermal behavior of triphenylene main-chain polymers 14–18

Structure	N	Phase transition	Reference
14	12	g 93 Col 163 I	Caseri et al. (1988)
15	9	g -10 N 31 I	Catry et al. (1993)
16a	14	g 105 I	Cook (1995)
16b	20	g 75 I	
17	10	Cr 100 Col 115 I	Disch et al. (1995)
18	11	Cr 98 Col 118 I	

Source: Wenz (1985 and Vandevyver et al. 1993 and Green et al. (1990) and Boden et al. (1995)
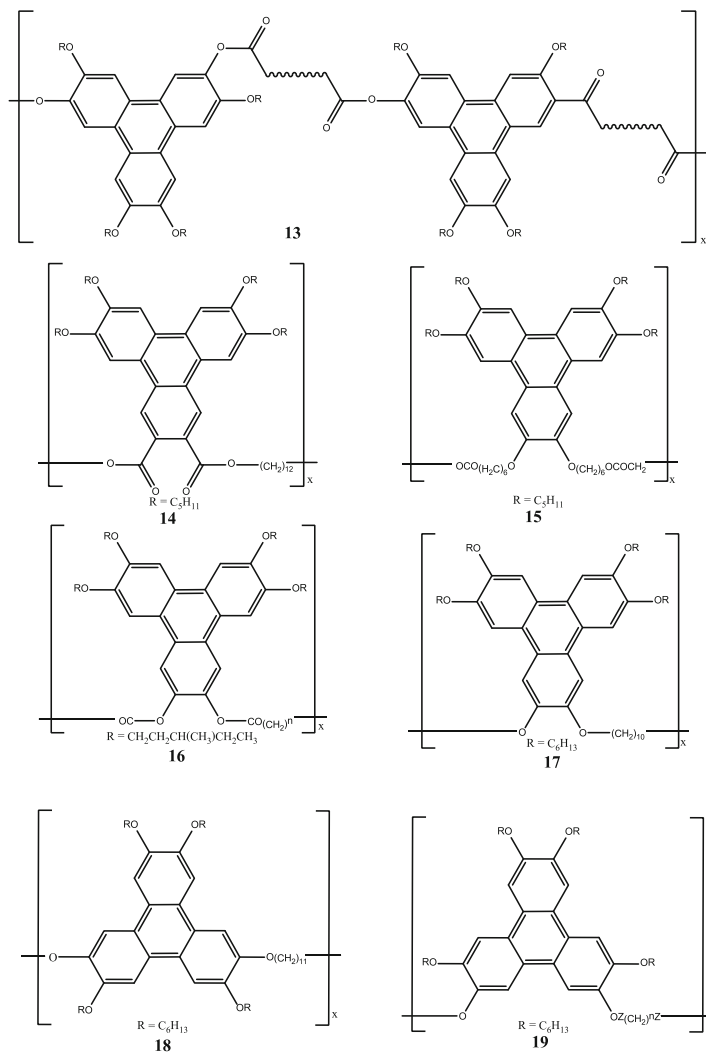
Fig. 20.2 Schematic diagram of Triphenylene based main chain polyethers and polyesters

Table 20.6 Thermal behavior of triphenylene main- chain polymers 19

Structure	Z	n	Phase transition	References
19a	CH_2	9	Cr 93 Col 120 I	Disch et al. (1995)
19b	CO	8	g 56 Colh 211 I	Dulog et al. (1993)
19c	CO	10	g 40 Colh 198 I	
19d	CO	12	g 25 Colh 162 I	

Source: Boden et al. (1995 and Wan et al. 2003)
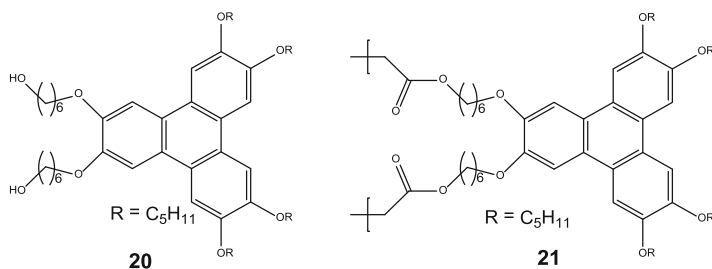
Fig. 20.3 Schematic diagram of Triphenylene based amphiphilic derivatives
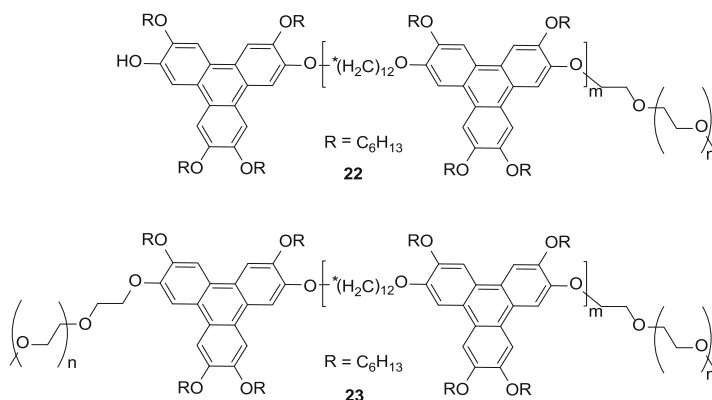
Fig. 20.4 Schematic diagram of TP and PEG based diblock mad triblock polymers

state and Langmuir-Blodgett (LB) films, Ringsdrof and group synthesized the discotic triphenylene amphiphilic derivatives **20**, **21** (Fig. 20.3) (Karthaus et al. 1992). An edge-on arrangement of the discotic molecules within a double-layer packing of columns being parallel to the solid support is formed in the LB films of both compounds. While comparing the monomer **20** and polymer **21** in bulk state of polymer form a less ordered nematic phase as compare to highly order columnar phase shown by monomer.

Block copolymers are known to form a range of microphase-separated structures like lamellae, hexagonal-packed cylinders, cubic-packed spheres, and bicontinuous cubic gyroid morphology. With the advantage to tailor the properties of block copolymers by combining blocks with distinct characteristics Boden et al. (1999) were prepared Discotic main-chain diblock and triblock copolymers containing one triphenylene block and either one or two polyethyleneoxy blocks (Fig. 20.4). Block polymers were found liquid crystalline having columnar phase at room temperature. The copolymer **22** clears at 86 °C and **23** at 66 °C. The triblock copolymer **23** under goes microphase separation, giving a nano structured material consisting of a hexagonal array of poly(ethylene oxide) rods in the matrix of columnar liquid crystal (Boden et al. 2001).

The electrolyte properties of these triblock)copolymers, doped with lithium perchlorate, were reported by Imrie group. The polymer exhibit a phase separated morphology consisting of a columnar hexagonal liquid crystal phase and PEO rich regions. The self-supporting solid film of polymer electrolyte shows a good conductivity above 60 °C, due to the malting of crystalline PEO rich regions at this temperature (Stoeva et al. 2013).

20.1.4   Phthalocyanine-Based Main Chain Discotic Liquid Crystal Polymers

Phthalocyanine is an intensely blue-green-coloured aromatic macrocyclic compound which coordinates with nearly all elements of periodic table to produce intensely colour dyes or pigment. These metal phthalocyanines dyes and pigments are very useful in catalysts for redox reactions, organic field-effect transistors, storage in quantum computing. To explore these potential application, verities of phthalocyanine based polymers were synthesised, however only few of them are liquid crystalline (Scheme 20.3).

Phthalocyanine-Based Main chain discotic liquid crystal polymers were first prepared by Cook (1995) via., condensing a dihydroxy-functionalized phthalocyanine 24 with oxalyl chloride (Scheme 5.14). The phthalocyanine monomer 24 was converted onto bis-acid chloride 25 and coupled with diol 24 at 90 °C in dichloromethane to yield)the polymer 26. DMAP was used as a coupling agent for synthesis of polymer results higher molecular weight polymer 26b (Bryant et al. 1995). Both polymers 26a and 26b exhibit hexagonal columnar mesophase over a broad mesophases. The polymer with higher M_w shows small increase in isotropic transition temperature.

The second class of Phthalocyanine based main chain polymers are also called spinal columnar or shish kebab type polymers, when Phthalocyanine macrocyclics are coaxially stacked over each other and linked by a bridging atom bonded to coordinated atom such as silicon, tin, or germanium atom at the centre of the

26a: M_w = 7,180; Col$_h$158 I

26b: M_w = 157,000; Col$_h$161 I
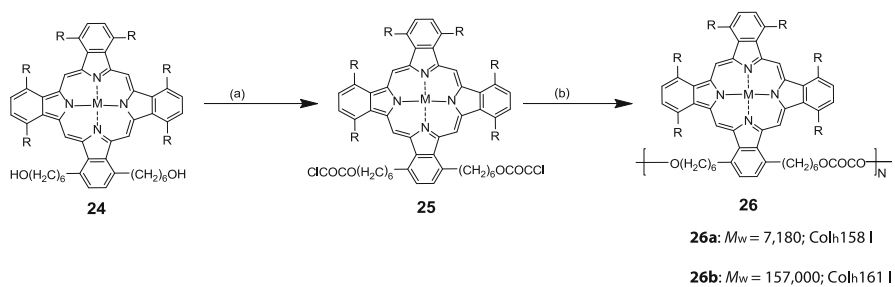
Scheme 20.3   Synthesis of phthalocyanine-based main-chain polymer: (*a*) ClOCCOCl; (*b*) 24, 48 h, 90 °C for 26a or pyridine and 4-dimethylaminopyridine to yield 26b
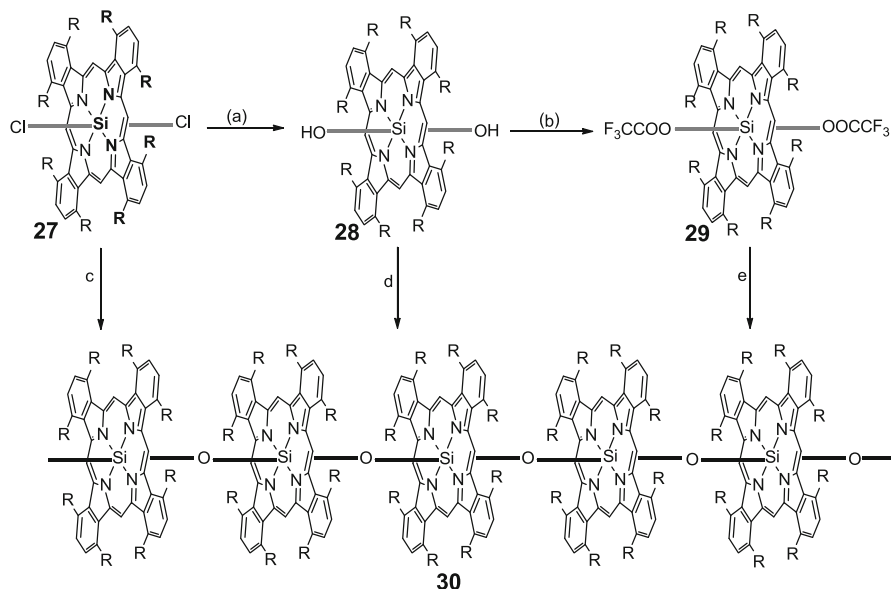
Scheme 20.4 Synthesis of phthalocyanine-based polymer having metal–oxygen–metal bond as a linker: (*a*) ion exchange; (*b*) CF$_3$COOCOCF$_3$, pyridine; (*c*) AgSO$_3$CF$_3$, TlSO$_3$CF$_3$, [Cu(CH$_3$CN)$_4$] SO$_3$CF$_3$; (*d*) 180 °C, 7 h or catalyst (FeCl$_3$, ZnCl$_2$, AlCl$_3$, CdCl$_2$, CaCl$_2$, CsCl); (e) 200 °C

phthalocyanine molecule. Bridging can happen through covalent bonds, covalent–coordinate bonds or coordinate–coordinate bonds. Synthetic routes to synthesize the)polysiloxane spinal based phthalocyanine polymers are shown in Scheme 20.4. Polymerization process involve the heating of dihydroxy-functionalized discotic metallomesogens for bulk condensation at about 200 °C in the presence of catalysts such as, FeCl$_3$, ZnCl$_2$, AlCl$_3$, CdCl$_2$, CaCl$_2$, etc., for approximate 7 h. Catalysts can be avoided by replacing the hydroxyl groups by better leaving groups such as trifluoroacetate. The polymerization can also be carried out at lower temperature (about 100 °C) by taking a dichloro monomer and using halogenophilic condensation agents such AgSO$_3$CF$_3$, TlSO$_3$CF$_3$, [Cu(CH$_3$CN)$_4$]SO$_3$CF$_3$ etc. (Sirlin et al. 1987, 1988a, b; Caseri et al. 1988; Sauer 1993; Sauer and Wegner 1991; Orthmann and Wegner 1986; Schouten et al. 1992; Dulog et al. 1993).

The X-ray diffraction studies shows the formation of columnar mesophases by these polymers. In DSC studies it was found that, the polymer with short lateral side-chain derivatives didn't exhibit any phase transition up to the decomposition temperature. Whereas polymer with medium lateral side-chain show only melting transitions below 100 °C. The long side-chain derivatives shows an isotropic transitions at high temperature under polarizing microscope without decomposing however this transition was absent in DSC thermograms.

Another interesting example of spinal polymers was reported by Nolte and co-workers (Sielcken et al. 1990; van Nostrum et al. 1995; Van Nostrum and Nolte 1996). They prepared the phthalocyaninato polysiloxanes substituted with
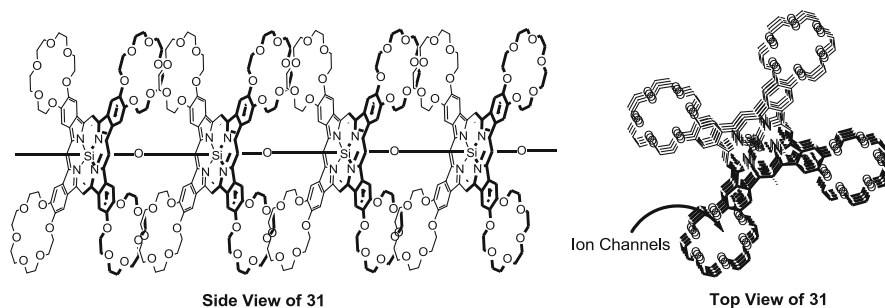
Side View of 31   Ion Channels   Top View of 31

Fig. 20.5 Schematic diagram of columnar or shish kebab type crown ether substituted phthalocyaninato polysiloxanes polymers

crown ether moieties **31** (Fig. 20.5). Crown ether substituted phthalocyanine macrocycles were prepared from 4, 5-dicyanobenzo-crown ether followed by heating its dihydroxysilicon complex in the presence of catalyst for polymerization. The X-ray studies revealed that polymer exhibit hexagonal columnar phase (Orthmann and Wegner 1986), however monomeric dihydroxysilicon didn't show any aggregation due to the steric hindrance of axial hydroxyl groups.

20.1.5   Cyclotetraveratrylene-Based Main Chain Ionic Discotic Liquid Crystal Polymers

Molecules with flexible cores, such as octasubstituted cyclotetravera-trylene (CTTV-n), tetra- and hexasubstituted cyclic poly-amine, and hexasubstituted scyllo-inositol etc. can adopt a quasi-flat conformation, known to form columnar mesophases (Zimmermann et al. 1988; Percec et al. 1991; Mertesdorf and Ringsdorf 1989). However, only hexasubstituted cyclotriveratrylene (CTV-n) flexible, which have a cone like shape and form columnar mesophases was explore as main chain DLCPs (Malthete and Collet 1987; Malthete et al. 1989).

The synthesis of main chain liquid-crystalline polyethers containing hexa-substituted cyclotriveratrylene (CTV-n) disk-like mesogens was reported by Percec et al. (1992). The branched polymers were synthesized by the cocyclotetra-merization of various ratios of a mixture containing 3,4-(di-n-alkyloxy)benzyl alcohol **32** and α,ω-bis[[2-(n-alkyloxy)-5-(hydroxymethyl)phenyl]oxy]alkane **33** in different and using CF_3COOH as the cyclotetramerization catalyst. This unique reaction construct the disklike octaalkyloxy-substituted cyclotetraveratrylene derivatives (CTTV-n) molecules during the polymerization process (Scheme 20.5).

In a columnar mesophase the backbone of a main-chain liquid-crystalline polymer containing CTTV-n mesogens can either connect mesogens from adjacent columns or link two mesogens within the same column. These polymers display hexagonal columnar mesophase. All the polymers had clearing temperature in the
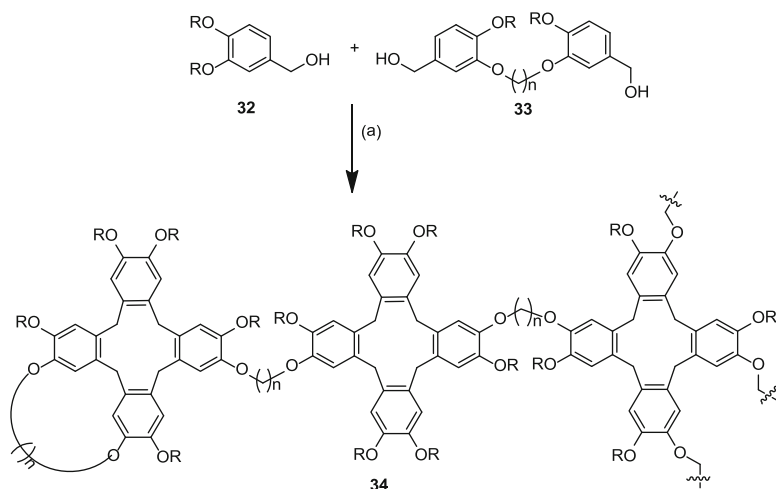
Scheme 20.5 Synthesis of cyclotetraveratrylene-based polymer: (*a*) CF$_3$COOH, CH$_2$Cl$_2$, r.t., 4.5 h

range 102–145 °C. The Clearing temperature depends on **32** to **33** ratio (x/y) used in reaction mixture, keeping the spacer and peripheral alkyl chain length constant. The clearing temperature decreases on decreasing the ratio of **32** to **33**. Hence its shows reciprocally effect by the proportion of the reactant **33** in the reaction mixture.

20.2 Side Chain Discotic Liquid Crystalline Polymers

Side chain DLCPs are the most studied DLCPs, having discotic mesogens as a pendent groups on polymeric back bone. These pendent group can be attached to polymer backbone mainly with two methods, first involve the polymer substitution reaction between already synthesised polymer and discotic mesogens and in second method discotic mesogens are functionalized to polymerizable monomers. Literature of side chain polymers can be divided on the basis of different discotic mesogens.

20.2.1 Alkynylbenzene-Based Side Chain Discotic Liquid-Crystalline Polymers

A natural tendency to form nematic mesophase by alkynylbenzene can be used to suppress the crystallization of a polymer backbone by attaching it to the polymer backbone. It helps to achieve the low-temperature liquid crystalline polymers with a broader mesophase range. A series of radial pentayne based side-chain polyacrylates were synthesised by (Kouwer et al. 2000, 2001a, b, c, 2002a, b,
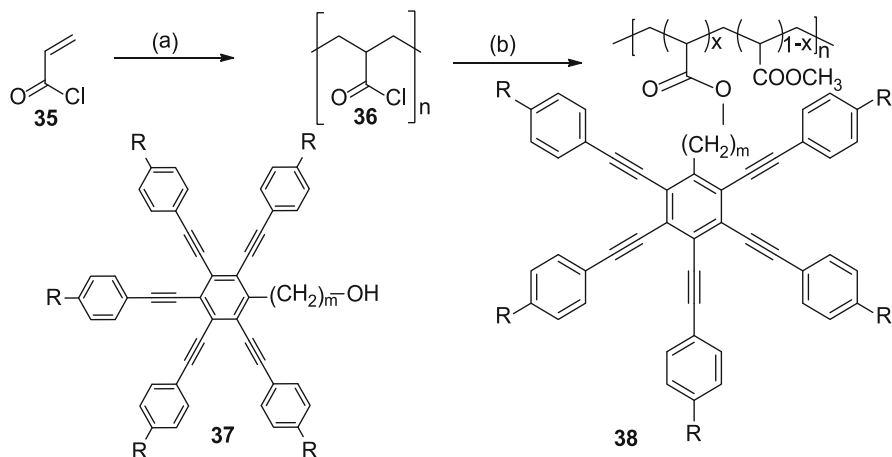
Scheme 20.6 Synthesis of alkynylbenzene-based side-chain polyacrylates: (*a*) AIBN, dioxane; (*b*) **37**, C_5H_5N, DMAP, CH_2Cl_2

Table 20.7 Thermal behavior of pentaalkynylbenzene-based side-chain polymers

Structure	R	x	Phase transition	References
38a	C_7H_{15}	0.50	g −15 I	Green et al. (1990)
38b	OC_6H_{13}	0.60	g 25 N 107 I	
38c	OC_6H_{13}	0.63	g 24 N 113 I	
38d	OCH_3	0.63	g 41 N >200 dec	Herrmann-Schönherr et al. (1986)
38e	OCH_3	0.70	g 50 N >200 dec	
38f	OCH_3	0.83	g 45 N >200 dec	
38g	H	0.72	g 53 I	Hueser et al. (1989)

Source: Kouwer et al. (2002a, b, 2003)

2003; Picken et al. 2004). The synthesis process involve the polymer substitution reaction between hydroxyl-terminated radial pentaalkynylbenzene derivative **37** and polyacryloyl chloride **36**, in the presence of pyridine and catalytic amount of *NAN* dimethylaminopyridine, in dry dichloromethane followed by quenching with excess methanol. Scheme 20.6 shows the synthesis process of these polymers.

In DSC studies polymer **38a** and **38g** were found out to be non-mesomorphic, however, connecting the lateral alkyl chains with oxygen instead of methylene induces a nematic phase in the polymers **38b–f**. Polymers with short methoxy peripheral groups **38d–f** decompose at higher temperature before reaching the isotropic phase, whereas polymer with long alkoxy chains have lower isotropic temperature and show a clear transition from mesophase to isotropic phase. Table 20.7 summarize the thermal transition data of these polymers.

Same group also synthesised side-chain pentaalkynylbenzene co-polyacrylates **39a–j** by modifying the final quenching step. The quenching in this process involve two step, first step involve the partial quenching with an alcohol other than methanol and secondly with excess methanol. A general structure of these

Table 20.8 Thermal behavior of pentaalkynylbenzene-based side-chain copolymers

| Structure	R	x	y	Phase transition	References
39a	CH_3	0	0.90	g 43 N_c 164 N 235 I	Hüser and Spiess (1988)
39b	CH_3	0	0.64	N_c 165 N 233 I	
39c	CH_3	0	0.48	g 92 N_c 158 N 204 I	
39d	CH_3	0	0.31	g 62 N_c 149 N 148 I	
39e	C_5H_{11}	0.31	0.69	g 77 N_c 157 N 209 I	
39f	C_5H_{11}	0.43	0.41	g 70 N_c 169 I	
39g	C_5H_{11}	0.50	0.42	g 51 N_c 157 I	
39h	$C_{12}H_{25}$	0.11	0.61	g 86 N_c 155 N 210 I	
39i	$C_{12}H_{25}$	0.45	0.45	g 50 N_c 154 I	
39j	$C_{12}H_{25}$	0.42	0.33	g 49 N_c 136 I	

Source: Kouwer et al. (2001a)
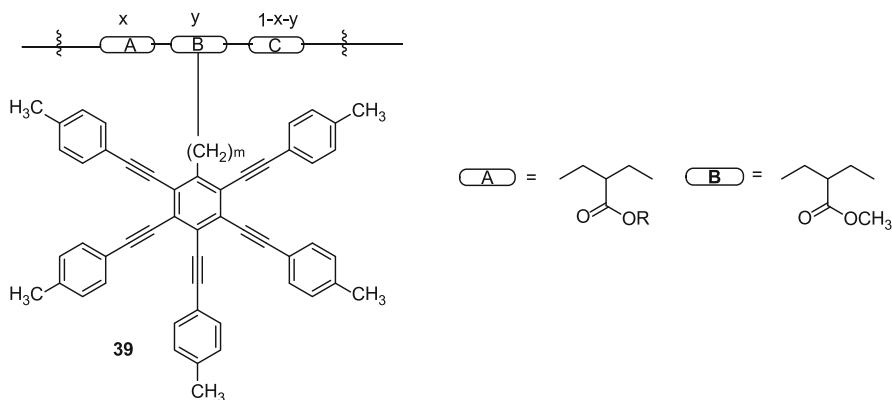
Fig. 20.6 Schematic diagram of Alkynylbenzene-Based side chain discotic liquid-crystalline co-polymers

copolymers is shown by **39** (Table 20.8, Fig. 20.6). All copolymers displayed nematic columnar phase at lower temperatures. The weight fraction of mesogen in copolymer highly affect thermal behavior of these polymers. Thermal behaviour of these polymers suggested that, higher percentage of discotic mesogen in copolymer increases the glass transition as well as clearing temperature and induce the formation of nematic phase at higher temperature.

20.2.2 Hexabenzocoronene-Based Side Chain Ionic Discotic Liquid Crystal Polymers

Pericondensed hexabenzocoronenes (HBC) show diode-like current–voltage signals for single molecules (Stabel et al. 1995) and a rapid charge transport along self-assembled columns with high charge carrier mobility. Again in columnar phase one
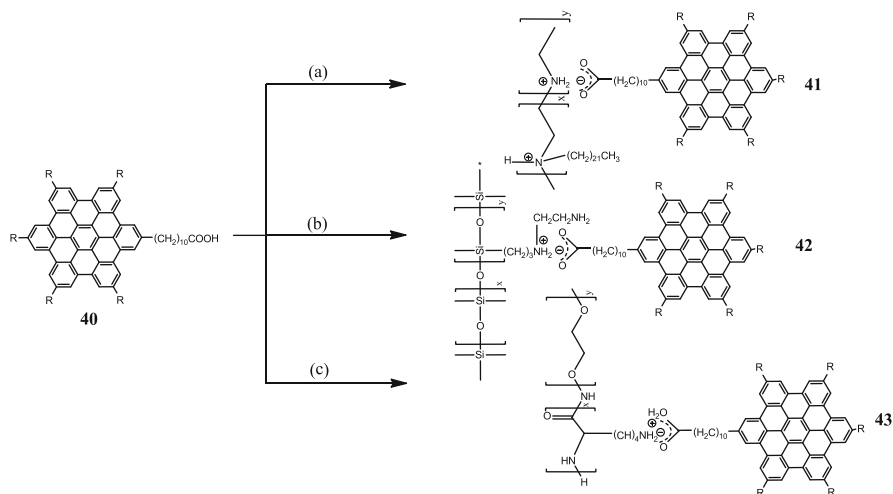
Scheme 20.7 Synthesis of)hexabenzocoronene-based side-chain ionic polymers: (*a*) polyethyleneimine, (*b*) polysiloxane, (*c*) poly(ethylene oxide)-block-poly(L-lysine)

dimensional charge transport makes these molecules promising as nanowires in molecular electronic devices. To explore these advantages Mullen and co-workers prepared HBC-based side-chain ionic polymers. The polymers were prepared via acid–base reaction of HCB carrying carboxylic acid moiety and polymer backbones like polyethyleneimine (Thunemann et al. 1999), polysiloxane (Thunemann et al. 2000), and poly(ethylene oxide)-block-poly(L-lysine) (Thünemann et al. 2002) (Scheme 20.7).

To prepare the **41** carboxylic acid functionalized HBC was complexed with hydrophobically modified polyethyleneimine. The X-ray studies revealed that, the polymer **41** exhibit rectangular mesophase morphology at room temperature and transform into ordered hexagonal columnar phase on heating up to 110 °C. Inter-columnar order was found higher in case of noncomplex HBC derivative **40** as compare to **41**. Whereas intra-columnar long range order in the polyethyleneimine complex of HBC **41** was more than HBC **40**. The polymer **42** having amino-functionalized polysiloxane backbone shows columnar-to-columnar (Col_1-to-Col_2) transition at 90 °C in heating cycle, however in cooling cycle this transition appears at 57 °C. The Col_1 phase possesses short-range intra-columnar order with tilted arrangement of HBC disks with respect to the column axis, whereas Col_2 phase have long range of intracolumnar order. The intracolumnar ordering of complex **42** follows same trend like **41**, when compared with **40**.

Poly(ethylene oxide)-block-poly(L-lysine) (PEO-PLL))was complexed with an amphiphilic hexaperi-hexabenzocoronene (HBC) to produce the **43**. Due to the self-organizing property of poly(L-lysine) blocks polymer, backbone of **43** form a R-helical. This helix was surrounded symmetrically by six discotic columns of HBC. The dense packing of these helixes and columns produces hexagonal

sublattices (formed by the columns) in the frame of a two-dimensional hexagonal lattice (formed by the helices). It shows a columnar-columnar (Col$_1$-to –Col$_2$) phase transition at 54 °C. From above three example, it is clear that Polymer chains is highly responsible for unexpected higher intracolumnar order at the higher temperature phase as compared to the lower temperature mesophase.

20.2.3   *Triphenylene-Based Side-Chain Polymers*

Triphenylene-Based Side-Chain Polymers are probably the most widely studied DLCPs and particularly promising because of their relatively easy availability, self-assembly ability and high performance. These polymers have been extensively investigated for their mesomorphic and physical properties. A mono-functionalized triphenylene (TP) derivative is the basic requirement to prepare these polymers. Ringsdorf and co-workers functionalized mono-functionalized triphenylene (TP) derivatives **44** with 10-undecenyl bromide to produce 3,6,7,10,11-pentakis (pentyloxy)-2-(10-undecenyoxy)-TP **45** . These TPs **45** produces side-chain triphenylene polymers **46** and **47** when reacting with Si–H containing polymers (Scheme 20.8). Both homopolysiloxane **46** and copolysiloxane **47** have broad glass transition and clearing transitions. Thermal transitions of these class of polymer (with polysilican backbone) are given in Table 20.9. Polymer **46** shows the phase behavior, g -19 Col 39 I on thermal annealing at 20 °C for 2 days. In a different report, published by Werth and Spiess in 1993, different thermal behavior g −41 Col 75 I was reported. It shows the dependence of thermal behavior on polymer processing. The clearing temperature of these polymers increases on decreasing the spacer length (Werth and Spiess 1993) as shown in Table 20.9. The deuterated triphenylene-containing polysiloxane **48** shows nearly same phase behavior corresponding to undeuterated polymer **46a** (Hüser and Spiess 1988; Hueser et al. 1989). The polymers with ester linkages **49** exhibit higher clearing temperature as compare to polymer with ether linkages **46–48**.

The mono functionalized Triphenylene unit can undergo free radical polymerization by functionalizing it with acrylate or methacrylate group. Varity of liquid crystalline homopolymer and copolymers were reported with different lateral side chains, spacer and polymer backbones via this route. A generalised structure of these polymers **50–52** are presented in Scheme 20.8 and there thermal transition are summarized in Table 20.10 along with side chains and spacer lengths. The polymer **50a** and **51a** changes its behaviour from amorphous polymers to nematic columnar liquid crystalline polymers on doping with trinitrofluorenone (TNF) (Ringsdorf et al. 1989). Because of the rigid nature of methacrylate-based polymer backbone, only polyacrylates **50b** show liquid crystalline behavior among **50b** and **51b**. However, Imrie and Boden groups have shown that, polymethacrylates triphenylene containing suitable substituent can form columnar phases (Boden et al. 1998). The low glass transition at 2 °C and a mesophase to isotropic phase transition at 45 °C shown by polymer **51c** was attributed to high polydispersity (Stewart et al. 1998).
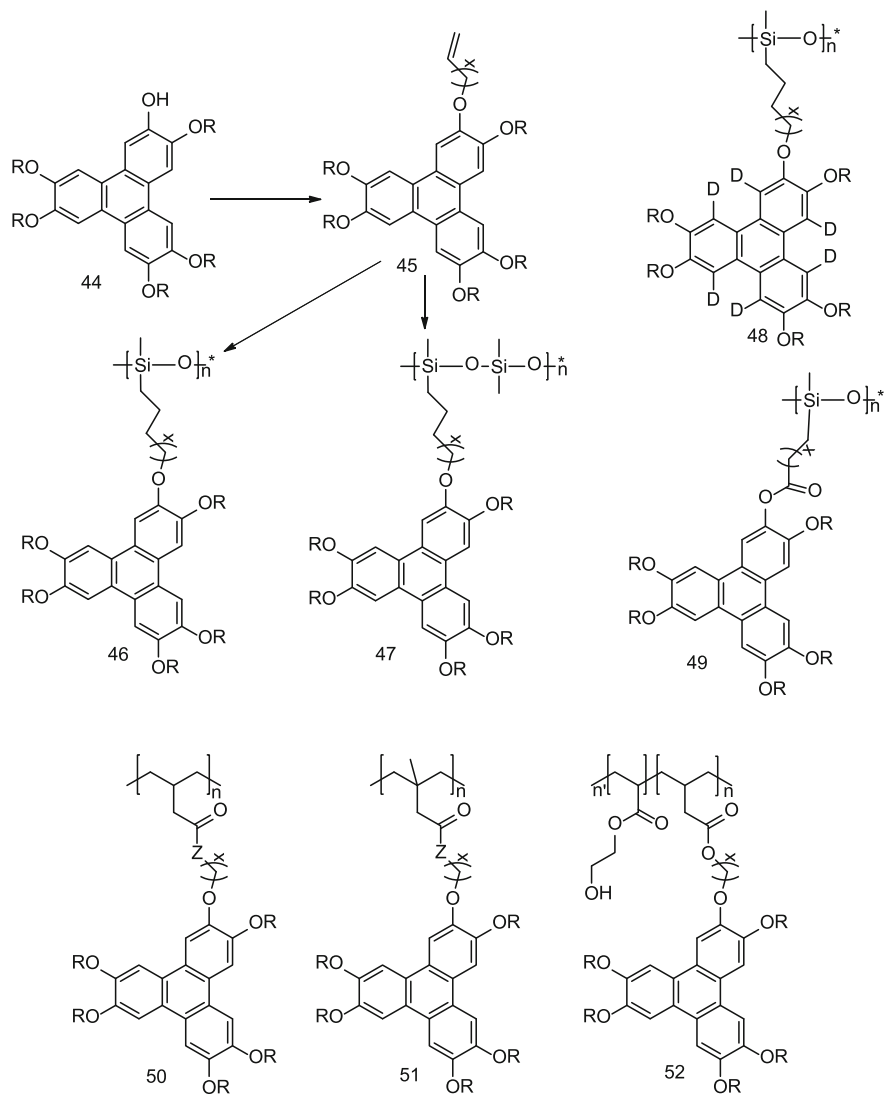
Scheme 20.8 Synthesis of triphenylene-based side-chain polysiloxanes: (**a**) poly(methylsiloxane), toluene, H$_2$PtCl$_6$; (**b**) poly(dimethylsiloxane-*co*-methylsiloxane), toluene, H$_2$PtCl$_6$

These acrylate functionalized Triphenylene monomers were mixed with 2-hydroxyethyl acrylate or methyl acrylate functionalized triphenylene monomer to produce copolymers with a general structure **52**. Copolymer with building block triphenylene and 2-hydroxyethyl acrylate exhibit mesophase to isotropic transitions between 104 and 165 °C depending upon their composition (Talroze et al. 2000).

Table 20.9 Thermal behavior of triphenylene-containing polysiloxanes

Structure	R	x	Phase transition	References
46a	C_5H_{11}	9	g −19 Col 39 I	Boden et al. (1999)
			g −41 Col_h 75 I	Imrie et al. (2004)
46a′	C_5H_{11}	9	g −35 Col 75 I	Karthaus et al. (1992)
46b	C_5H_{11}	3	g −53 Col_h 141 I	Imrie et al. (2004)
46c	C_5H_{11}	6	g −52 Col_h 131 I	
47	C_5H_{11}	9	g −29 Col 36 I	Boden et al. (1999)
48	C_5H_{11}	9	g −35 Col 75 I	Kouwer et al. (2000)
49a	C_5H_{11}	3	g −54 Col_h 171 I	Imrie et al. (2004)
49b	C_5H_{11}	6	g −51 Col_h 186 I	
49c	C_5H_{11}	9	g −37 Col_h 112 I	
49d	C_7H_{15}	9	g −62 Col_h 112 I	
49e	$CH_2CH_2CH(CH_3)_2$	9	Col_h 81 I	

Source: Kreuder and Ringsdorf (1983) and Werth and Spiess (1993) and Hueser et al. (1989) and Hüser and Spiess (1988)

Table 20.10 Thermal behavior of triphenylene-containing polyacrylates and methacrylates

Structure	R	x	Z	Phase transition	References
50a	$(CH_2)_2O$ $(CH_2)_2OCH_3$	0	$(CH_2CH_2O)_3$	g −6 I	Kouwer et al. (2001a)
50b	C_5H_{11}	11	O	g −8 Col_h 39 I	Imrie et al. (2004)
50c	C_6H_{13}	6	O	g 5 Col 84 I	Kouwer et al. (2001b)
50d	C_6H_{13}	0	$(CH_2CH_2O)_2$	Col 117 I	Kouwer et al. (2001b)
51a	C_5H_{11}	6	O	g 30 I	Kouwer et al. (2001c)
51b	C_5H_{11}	11	O	g −16	Imrie et al. (2004)
51c	C_6H_{13}	11	O	g 2 Col 45 I	Kouwer et al. (2001c)

Source: Ringsdorf et al. (1989) and Werth and Spiess (1993) and Boden et al. (1998) and Stewart et al. (1998)

However, copolymer of triphenylene-based acrylate and methyl acrylate was reported non liquid crystalline.

The malonate-terminated triphenylene-based monomer **53** was condensed with a, α,ω-diols to produce triphenylene-based side-chain polyesters **54** and **55** (Fig. 20.7) (Catry et al. 1993). Thermal studies shows that, polymers **54** is nonmesomorphic with a glass transition at −10 °C, whereas polyester **55** show liquid crystalline (LC) behaviour with thermal transitions, g −20 LC 35 I. The isophthalate-terminated triphenylene-based monomer was condensed with polyethylene glycol (PEG 300) by Imrie co-workers to furnish the polymer **56** (Imrie et al. 2004). The polymer exhibits the thermal transition behaviour g -17 lc 47 I.
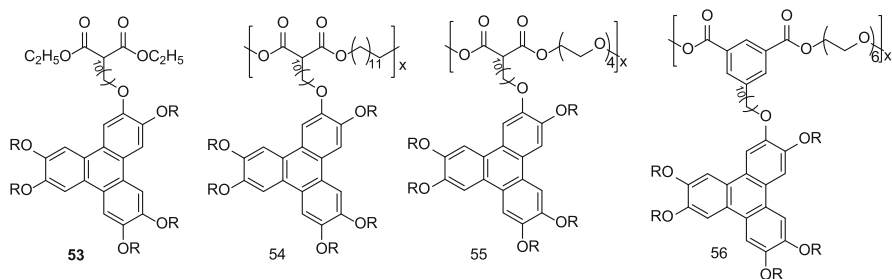
Fig. 20.7 Schematic diagram of malonate-terminated triphenylene-based monomer 53 and polymers

Table 20.11 Thermal behavior of polynorbornene-, polybutadiene-, and polybutane-bearing alkoxytriphenylenes triphenylene-based poly(1-alkyne)s

Structure	R	Phase transition	References
60a	C_5H_{11}	g −4 I	Kouwer et al. (2002a)
60b	$C_{10}H_{21}$	g −3 Colh 36 Colh 42 I	
61a	C_5H_{11}	g −12 I	
61b	$C_{10}H_{21}$	g −17 Colh 37 Colh 45 I	
62a	C_5H_{11}	g −17 I	
62b	$C_{10}H_{21}$	g −18 Colh 34 Colh 43 I	
64a	C_4H_9	Colh 132.9 I	Kouwer et al. (2002b)
64b	C_5H_{11}	g 113.8 Colh 156 I	
64c	C_6H_{13}	g 115.1 Colh 160.3 I	
64d	C_7H_{15}	Colh 154.3 I	
64e	C_8H_{17}	Colh 144.6 I	
64f	C_9H_{19}	g 115.7 Colh 139.1 I	

Source: Weck et al. (1997) and Xing et al. (2008)

Ring-opening metathesis polymerization was also explored by functionalizing Triphenylene terminal with norbornenes **57**, and butadienes **59** to produce polymer **60** and **61** (Scheme 20.8) (Weck et al. 1997). Thermal behavior of these polymers is given in Table 20.11. The polymers **60b** and **61b** with long lateral alkyl chain (decyl) exhibit columnar mesophases, whereas polymer **60a** and **61a** with short lateral alkyl chains (pentyl) found to be non-liquid crystalline. On Further reduction of polybutadiene polymer **62b** turns out to be liquid crystalline (Scheme 20.9).

Metal catalysed polymerization of alkyne-terminated triphenylene derivative **63** using molybdenum-based catalysts, tungsten-based catalysts and rhodium-based catalyst was tried to produce Triphenylene-Based Side-Chain Polymers by Zhao and co-workers (Scheme 20.10) (Xing et al. 2008). However, only rhodium-based catalyst, [Rh(norbornadiene)Cl]₂, in THF/Et₃N yielded the desired polymer **64a–f** in good yield. These polymers were found more thermal stable than unsubstituted poly(1-alkyne)s and exhibit hexagonal columnar mesophase. The hexagonal mesophase of polymers with small and long peripheral chains has homogenous
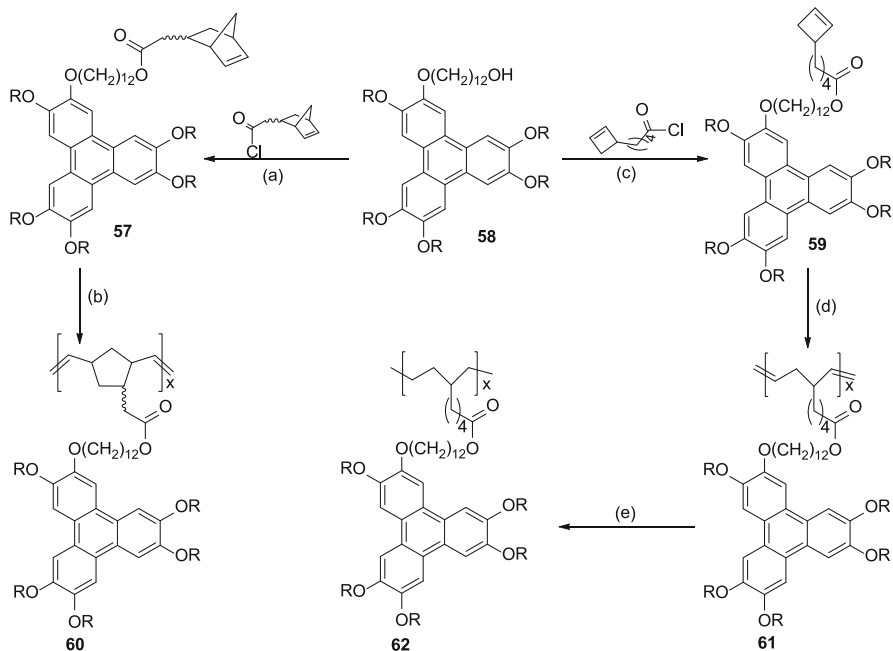
Scheme 20.9 Synthesis of triphenylene-based side-chain polynorbornene and polybutadiene: (*a*) THF, triethylamine, reflux, 16 h; (*b*) Cl$_2$(PCy$_3$)$_2$Ru$=$CPhH, CH$_2$Cl$_2$; (*c*) SOCl$_2$, THF, triethylamine, r.t., 16 h; (*d*) Cl$_2$(PCy$_3$)$_2$Ru$=$CPhH, CH$_2$Cl$_2$; (*e*) [Ir(COD)(Cy$_3$)(py)]PF$_6$, CH2Cl2, 55 °C, 16 h
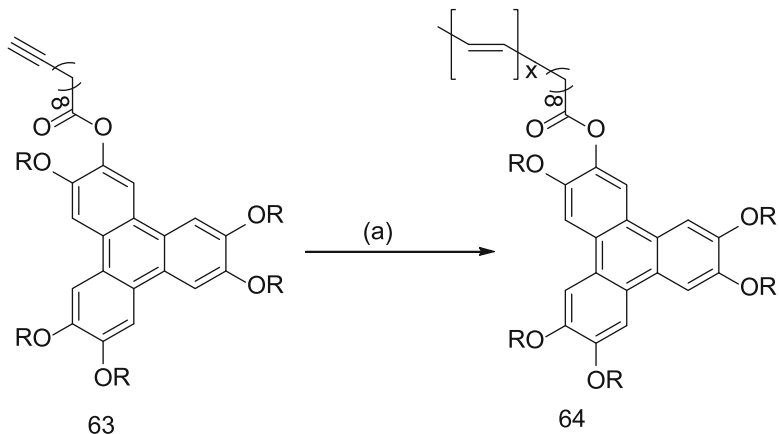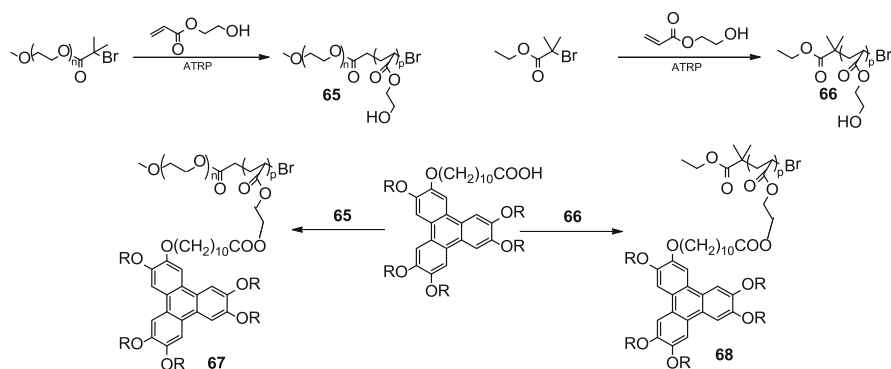

Scheme 20.10 Synthesis of triphenylene-based side-chain polyalkynes: (i) [Rh(norbornadiene) Cl]$_2$, THF:Et$_3$N (3:1 v/v), r.t., 24 h

hexagonal columnar lattice, whereas polymers with medium chain length exhibit hexagonal lattice with mixed structures. Thermal transitions of these polymers with different peripheral lateral alkyl chains are listed in Table 20.11.

To understand the interrelation of microstructures and the discotic mesogenic orders, a series of diblock copolymers **67** and **68** having Triphenylene and PEG blocks have been prepare by Dongzhong Chen et al. using atom transfer radical polymerization (ATRP) (Scheme 20.11) (Wu et al. 2013). The copolymers having different weight fraction of DLC blocks in range 37–90 % were synthesised. The copolymers with lower DLC contents ($f_{w,dlc} = 37$ % and 43 %) were shown to form lamellar structures of variant periods and undergo order-order transition at 45 °C. The different discotic mesophases transition was observed at 25 °C. The copolymer with intermediate DLC contain ($f_{w,dlc} = 62$ %) above 35 °C from nanocylinders of amorphous PEG packed in hexagonal matrix of DLC, which turned into a mixed lamellar structure with PEG region crystallization upon cooling below 35 °C. The copolymers with higher DLC contain ($f_{w,dlc} = 67$–80 %) exhibits HPC structure with the DLC matrix showing Ncol or ND mesophases. For copolymers with 90 % DLC overall ND phase was observed resembling the ordered columnar phase formed by their corresponding DLC homopolymers.

To prepare a novel polymers)polymeric material useful for unidirectional ion transport at nanoscale Pal and Kumar (2008) prepared triphenylene-imidazole-based side-chain ionic liquid crystalline polymer (Scheme 20.12). The triphenylene-bearing imidazolium salt **69** was synthesised by reacting brominated triphenylene **67** with 1-vinylimidazole. The photopolymerization of **69** with a

Scheme 20.11 Synthesis of reactive polymer precursor through ATRP 65 and 66 and the TP-Based Side Chain Discotic LC Homopolymer 68 and Copolymers 67
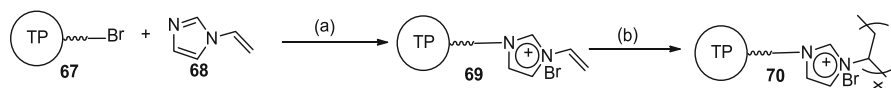
Scheme 20.12 Synthesis of triphenylene-imidazole-based side-chain ionic polymers: (a) toluene, reflux, 8 h; (b) 2,2-dimethoxy-2-phenylacetophenone, 100 °C, r.t., $h\nu$

photoinitiator 2,2-dimethoxy-2-phenylacetophenone yielded polymer **70**. The polymer **70** is a glassy material at room temperature, on heating up to 224 °C transform to rectangular columnar phase.

20.3   Discotic Liquid Crystal Elastomers

The properties of Liquid crystal elastomers having orientation order, responsive molecular shape, and quenched topological constraints made them potential candidate for various industrial applications like sensors, micro-robots, micro-pumps, and actuators. Considering the potential of them, calamitic elastomers has been explored up to a great extant, however very few reports are there on Discotic Elastomers.

Ringsdorf et al. was prepared the first discotic elastomer using an olefin-terminated monofunctionalized triphenylene derivative **71** and two cross-linkers **72** and **73** with different reactive groups (Bengs et al. 1993). Due to the reactivity difference in olefinic group and a methacryloyl group during the first step of crosslinking reaction, vinyl groups almost react completely, whereas methacryloyl group remains unreacted. This weakly cross- linked network can deform to obtain a macroscopic alignment of the liquid crystalline phase. In second step locking of this anisotropic network was done by reciting methacryloyl group. Figure 20.8
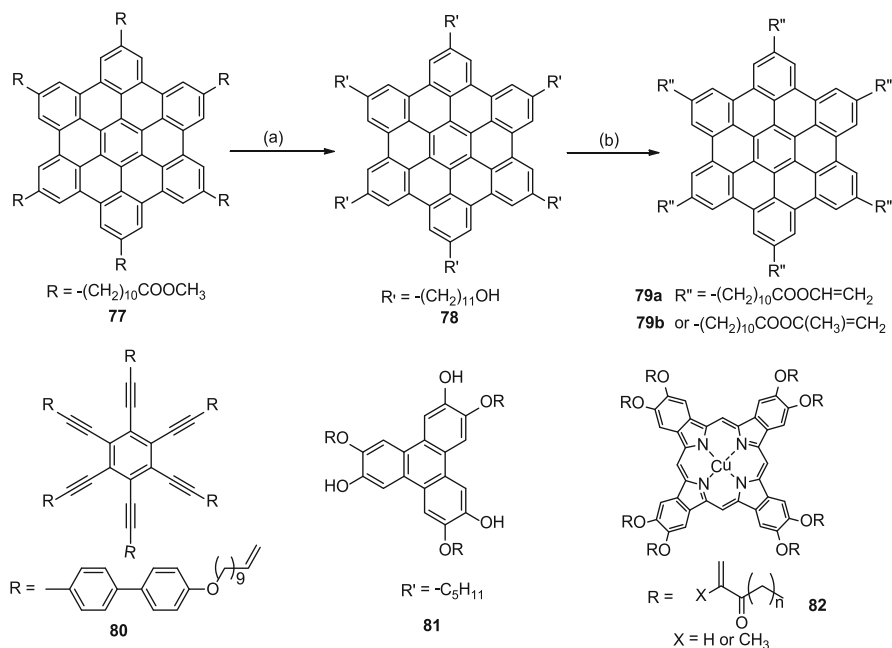

Fig. 20.8 (**a**) LiAlH₄ in THF; (**b**) N,N-dimethylaniline, 2,6-di-tertbutyl-p-crysol in THF, acryloyl chloride or methaaryloyle chloride

represents the schematic diagram of these elastomers. To understand the mechanical strain effect prior to the second cross-linking process polymer **75b** was prepared without applying the mechanical field, whereas **75a** with same methodology. The polymers **76a–e** were synthesised by replacing bifunctional calamitic cross-linker with bifunctional triphenylene-based cross-linker in different loading proportions to avoid the columnar packing disturbance caused by calamitic cross-linker (Disch et al. 1995). Table 20.12 summarized the thermal transitions of these polymers (Scheme 20.13).

Table 20.12 Thermal behavior of triphenylene-based discotic elastomers

Structure	Phase transition	Reference
75a	g −50 Col 28 I	Kouwer et al. (2004)
75b	g −50 Col 28 I	
76a	g −50 Col 106 I	
76b	g −49 Col 94 I	
76c	g −50 Col 94 I	
76d	g −45 Col 78 I	
76e	g −44 Col 76 I	

Source: Bengs et al. (1993) and Disch et al. (1995)
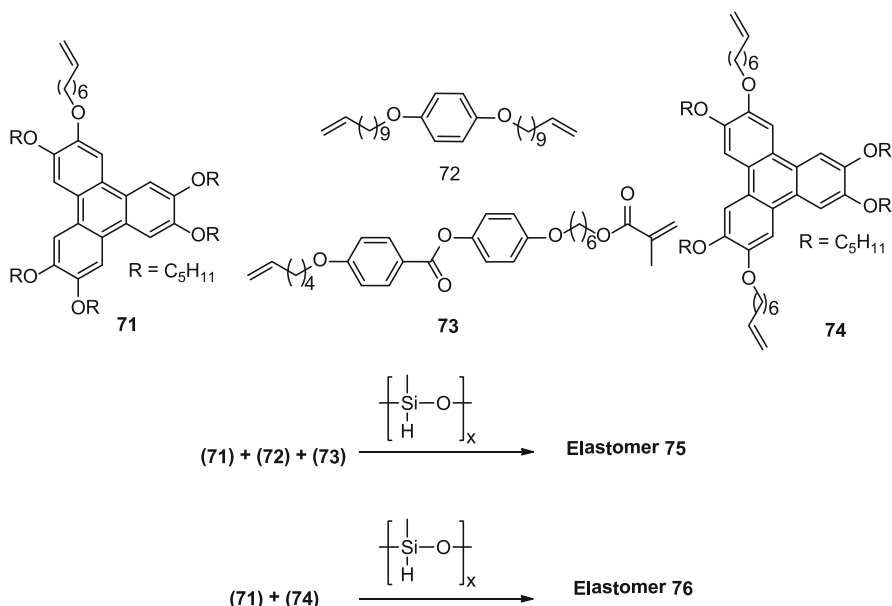
Scheme 20.13 Schematic diagram of triphenylene-based discotic elastomers

20.4 Liquid Crystalline Hyperbranched Polymer

Klaus Mullen et al. were reported synthesis of hexa-*peri*-hexabenzocoronene (HBC) substituted with terminal acryloyl **79a** and methacryloyl **79b** functionalized *n*-alkyl chains (Boden et al. 2000). Hexasubstituted hexa-*peri*hexabenzocoronene derivatives were prepared via cobalt octacarbonyl catalysed cyclotrimerization of suitably substituted diphenylacetylenes, followed by an oxidative cyclodehydrogenation with iron (III) chloride dissolved in nitromethane. Hyperbranched Polymers containing HBC was achieved via thermal polymerization of HBC derivatives containing acryloyl or methacryloyl functions at the terminal position of the alkyl chains in liquid crystalline phase. Columnar superstructure of liquid crystalline phase was preserved during and after polymerization and stable between -100 and $300\,^{\circ}$C.

Suzuki and group synthesised the monomeric hexayne **80** having six terminal double-bond containing biphenyl unit to prepare the Alkynylbenzene-Based Discotic hyperbrached polymers. The monomeric hexayne **80** having six terminal double-bond containing biphenyl units can be photopolymerized to yield the polymer. Hyperbranched Polymer had glass transition temperature at 51 $^{\circ}$C and exhibit liquid crystalline phase above 230 $^{\circ}$C up to decomposition due to high cross-linked network (Suzuki and Koide 2001).

Triphenylene-based hyperbranched polymer were reported by Zhang et al. (2007). Triphenylene derivative 2,6,10-trihydroxy-3,7,11-tripentyloxytriphenylene **81** was reacted with adipoyl chloride in pyridine and THF followed by quenching the terminal phenolic hydroxyl groups by adding butyryl chloride to obtain the triphenylene based hyperbranch polymer. This hyperbranched polymer was reported to be liquid crystalline in temperature range of 165–180 $^{\circ}$C.

To produce the phthalocyanines based hyperbranch polymer van der Pol et al. synthesised Phthalocyanines substituted with eight terminally acryloyl or methacryloyl functionalized alkoxy chains **82** (Van der Pol et al. 1990). Thermal polymerization of **82** produces a highly branched polymer network. While photo polymerization of the acrylate failed to produce any polymer, thermal polymerization of the acrylate as well as methacrylate in the columnar mesophase leads to liquid crystalline hyperbranch polymer. These polymer do not show any phase transition in DSC probably due to the formation of highly cross-linked network. The columnar nature of the mesophase formed by these polymers was revealed by X-ray diffraction studies.

20.5 Discotic Liquid Crystalline Dendritic Polymers

Dendritic polymers are special class of polymer composed of a large number of monomer units that were chemically linked together. Due to their wide range of applications like adhesives and coatings, chemical sensors, drug-delivery systems,
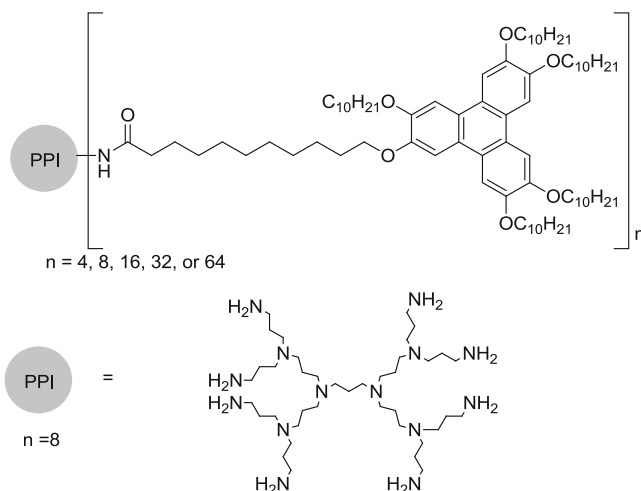
Fig. 20.9 Schematic diagram of Discotic Liquid Crystalline Dendritic polymers

high-performance polymers, catalysts, separation agents etc., their literature is always getting rich.

Dendrimers tend to adopt the spherical structure to minimize the free energy associated with them. However, incorporation of anisotropic mesogenic units at the periphery deviates them from this spherical structure due to the strong interactions between such units. McKenna MD et al. (2004) have reported the attachment of discotic triphenylene moieties to the first five generations of commercially available PPI-$(NH_2)_n$ dendrimers (Fig. 20.9), which produce the highly ordered hexagonal columnar mesophases in the second to fifth generations and rectangular columnar mesophases for the first generation. The mesophase temperature range of the dendrimers is larger and start at low temperature as compare to analogous low molecular weight unit, hexakis-(decyloxy)triphenylene. These compounds were highly ordered as compare to previously reported columnar dendrimers (Cameron et al. 1997; Marcos et al. 2001).

20.6 Metallomesogenic Discotic Liquid Crystalline Polymers

Metallomesogeniuc polymers are relatively new area in the field of DLCPs. The metal present in these polymers can afford new and unexpected physical properties that can be combined with the process ability inherent in the polymer system. Metallomesogenic polymers having discotic units have been synthesised using diketones complex of Cu(II) and Pd(II) by Valdebenito et al. (2000). Synthesis of polymers is given below (Scheme 20.14). All the polymers 84a–b and 85a–b
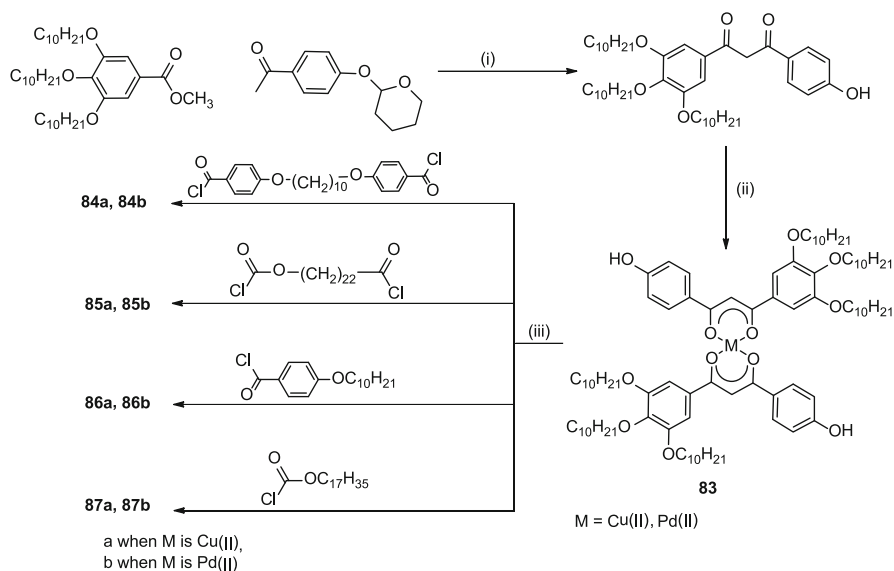
Scheme 20.14 synthesis of Metallomesogenic discotic intermediate (*i*) NaOH in 1,2-dimethoxy ethane; (*ii*) Copper(II)acetate in ethanol or Palladium acetate in ethanol/methanol (1/2); (*iii*) dry 1,1,2,2-terachloroethane

prepared exhibit columnar mesophases. The low molecular weight monomer exhibit a columnar hexagonal mesophases. More flexible polymer 85a-b shows a hexagonal mesophase whereas rigid polymer 1a-b exhibit a columnar rectangular mesophases. Fibers of these polymers have an orientation of the polymeric chain along the stretching direction and the disk-like unit are arranged in columns perpendicular to the fibers axis (Fig. 20.10). Thermal transitions of these polymers are given in the Table 20.13.

20.7   Conclusion

In conclusion, LCPs containing Disc-shape mesogense are relatively new area of research. Varity of DLCPs are synthesised by varying the Disc shape and polymer back bone. The attachment of discotic mesogens on polymer backbone can be achieved via different methods, like polymer substitution reaction, free radical polymerization, ring opening metathesis etc. By changing the disc shape and its position on the polymer back bone physical properties of DLCPs can be tailored. Their thermal transitions were found to be very much related to the peripheral lateral chains and the nature of polymer back bone.

Again, self-assembling nature of discotic mesogens into columnar phase helps in unidirectional charge or ion transfer. These unidirectional charge or ion transfer
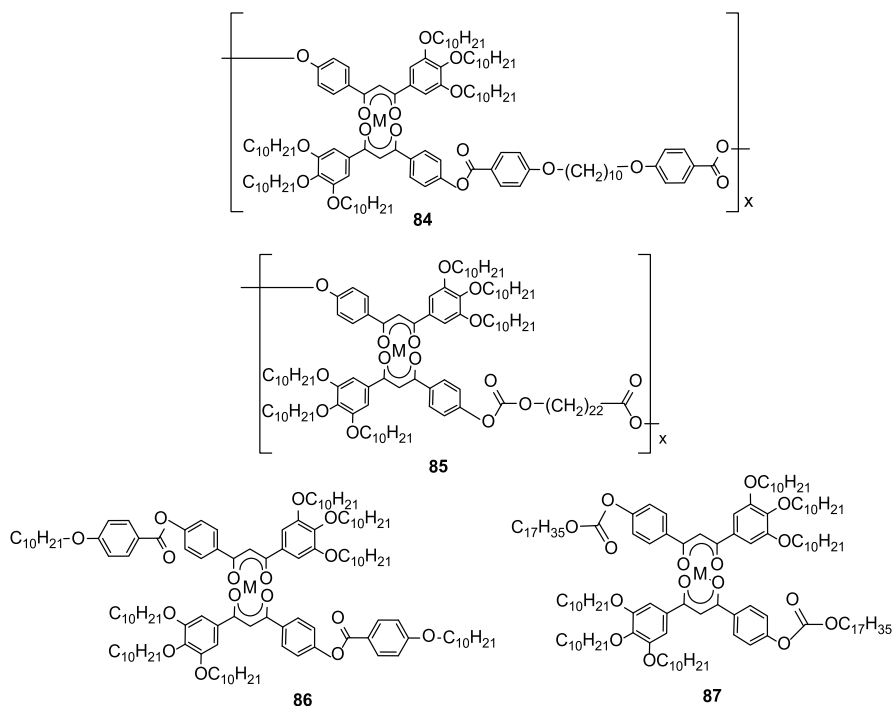
Fig. 20.10 Schematic diagram of Metallomesogenic discotic polymers and low weight analogues

Table 20.13 Thermal transitions of metallomesogenic discotic polymers and low molecular weight analogues

Structure	Phase transitions	Reference
84a	g 88 Col$_r$ 193 I	Kreuder and Ringsdorf (1983)
84b	Col$_r$, dec at T 170 C	
85a	Col$_h$ 135 I	
85b	C 60 Col$_h$ 103 I	
86a	C 55 C′ 78 Col$_h$ 106 I	
	I 105 Col$_h$ 42 C′	
	C′ 76 Colh 107 I	
86b	Col$_h$ 115 I	
	I 115 Col$_h$ 14 C′	
	Cr 72,91 Col$_h$ 115 I	
87a	C 60 Col$_h$ 116 I	
	I 115 Col$_h$ 18 C′	
	C′ 55 Col$_h$ 114 I	
87b	C 53 Col$_h$ 120 I	
	I 116 Col$_h$ 6 C′	
	C′ 40 Col$_h$ 113 I	

Source: Valdebenito et al. (2000)

properties can be potentially used for various applications like, catalysts for redox reactions, organic field-effect transistors, storage in quantum computing, sensors, micro-robotics, micro-pumps, and actuators to solve the energy and health problems.

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