Methods of Controlled Radical Polymerization for the Synthesis of Polymer Brushes

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Abstract—Methods for the synthesis of polymer (molecular) brushes via various controlled-radical-polymerization approaches are considered, and their properties are analyzed. Special attention is paid to atom-transfer radical polymerization, which is most frequently used for these purposes. The potential of the synthesis of molecular brushes with various chemical structures, including amphiphilic brushes, is demonstrated in many examples.

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INTRODUCTION

For the successful use of polymer materials and composites in hi-tech applications, such as biomedical technologies, optoelectronics, etc., it is necessary, on the one hand, to synthesize polymers of increasingly complex architectures and topologies and, on the other hand, to precisely control their characteristics and to find conditions of their stable reproduction. Until recently, macromolecules with complex architectures (block and graft copolymers, polymer stars, polymer brushes, dendrimers, etc.) with the required functional groups at predefined positions of the chain could be synthesized only via living ionic polymerization, which is characterized by the absence of both chain-termination and chain-transfer reactions under certain conditions. However, its use is limited because purification of the reaction mixture from trace amounts of water and ionogenic compounds is a laborious and expensive procedure and the range of monomers that may be involved in these processes is narrow.

Radical polymerization is a well-studied, relatively simple, and widely used method of polymer synthesis. Its drawback is that it is always accompanied by chain-termination and/or chain-transfer reactions, which lead to broadening of the molecular-weight distributions (MWDs) of polymers, the appearance of branches and crosslinks, and uncontrolled modifications of terminal groups. All these circumstances restricted its application for the synthesis of polymers with complex architectures. The discovery of ways to control radical polymerization provided new possibilities for the design of various macromolecular objects with precisely defined molecular-weight characteristics. This development caused a snowballing growth of the number of publications in the field in the past two decades [1].

Among the thousands of papers devoted to the synthesis of polymers via the methods of controlled radical polymerization, a vast number of publications deal with the obtainment of branched (co)polymers of various structures. In the present review, issues related to the use of controlled radical polymerization (CRP) are discussed.

Polymer brushes are an ensemble of polymer chains attached with one end to a flat or spherical surface or to a linear macromolecule (the so-called molecular polymer brushes) [2—5]. The synthesis and studies of polymer brushes are the topic of a large number of publications, the majority of which concern grafting polymerizations onto different surfaces, including inorganic (silica, gold nanoparticles, and magnetite) and polymeric surfaces (polysaccharides, polypeptides, polyimides, etc.). Polymer brushes of this type are considered in detail in numerous original papers, reviews, and monographs [3, 6]. In this review, our attention is focused on molecular polymer brushes.

Molecular polymer brushes are a variety of graft copolymers characterized by a high grafting density of side chains (in the ideal case, one side chain is attached to every monomer unit of the backbone) [4]. If the backbone length is much longer than that of side chains, then, when the latter are grafted densely enough, the macromolecule takes an extended cylinder conformation due to steric repulsions of densely grafted side chains. Therefore, such macromolecules are often named cylindrical molecular polymer brushes [2, 4]. If the lengths of the backbone and side chains are comparable or the grafting density of side chains is not too high, the macromolecule may adopt various conformations, including the spherical conformation [4]. A high grafting density of side chains of

brushes gives rise to a significant increase in the rigidity and strain of the backbone, depending on the grafting density, solvent quality, and side-chain length [7]. A substantial growth of the backbone strain is observed during adsorption of brushes on surfaces, and this phenomenon may even lead to the scission of the backbone [8−10].

Reversible changes in the conformation of a brush in response to an external effect in these systems may be limited by an individual macromolecule, a phenomenon that is observable via AFM [2, 4, 5]. In contrast to linear block copolymers, polymer brushes may form both multimolecular and stable monomolecular cylindrical micelles [4]. The formation of monomolecular micelles that cannot dissociate, because their side chains are attached covalently to the backbone is especially characteristic of polymer brushes with block-copolymer side chains [5, 11−13].

Owing to the possibility to vary the length and structure of side chains in a controlled manner, molecular brushes may acquire the ability to retain microscopic particles on the surface of water [14] and to incorporate large molecular objects or nanoparticles of different types. Therefore, polymer brushes show promise in the field of intramolecular nanoengineering as, for example, nanocontainers for inorganic nanoparticles or nanofibers [15−17] and polymeric carriers for targeted drug delivery [18]. Nanocomposite materials obtainable via this technology are applicable in opto-, acousto-, and spin-electronics in information storage devices and actuators [19, 20] as well as for the development of materials with new properties, e.g., ultrasoft elastomers [21, 22].

GENERAL CONCEPTS OF THE SYNTHESIS OF POLYMER BRUSHES

The synthesis of molecular brushes necessitates the use of methods that allow polymers with predefined architectures, functionalities, and molecular-weight characteristics to be prepared in a controlled manner [2].

There are three main approaches to the synthesis of polymer brushes: "grafting through," "grafting on," and "grafting from" [2, 4].
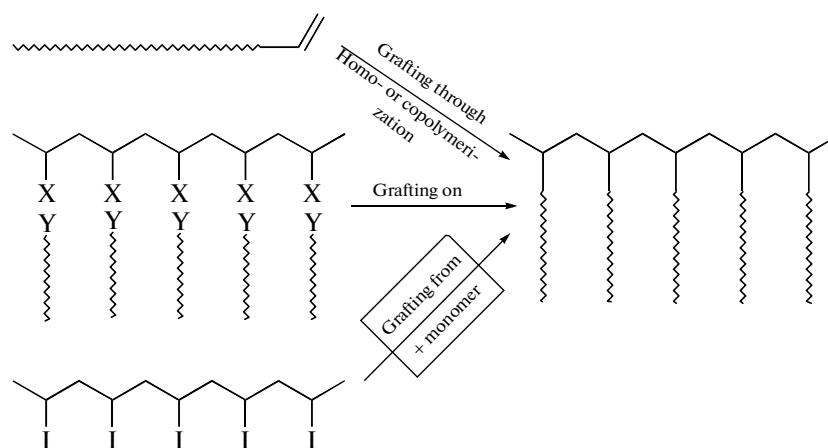
Scheme 1.

The method that was subsequently named "grafting through" was firstly successfully applied for the synthesis of brushes by Y. Tsukahara [23, 24], and in fact, this is the polymerization of macromonomers [2]. Brushes obtained via this method possess the highest possible degree of grafting, namely, one side chain per unit of the backbone. However, low concentrations of vinyl groups and steric hindrances lead to a drastic drop in the rate of chain growth and force researchers to use large excesses of macromonomers in order to increase the degree of polymerization of the backbone. The reaction product contains the unreacted macromonomer as an impurity, a circumstance that creates considerable problems for purification of the product [2, 4].

In the "grafting on" method, the main chain with functional groups X and polymers with terminal functional groups Y that serve as side chains are initially synthesized separately (Scheme 1). The synthesis is performed via one of the living ionic or controlled radical polymerization methods, a circumstance that makes it possible to prepare polymer precursors with a predefined degree of polymerization. It is followed by a polymer-analogous transformation, that is, the reaction between X and Y groups [25−30]. In the ideal case, all groups X of the backbone react with Y groups of side chains. However, with the increasing density of grafting, steric hindrances grow abruptly and thus prevent the reaction between X and Y groups. Moreover, the attachment of side chains becomes entropically unfavorable during the process. Therefore, it is diffi-

cult to attain the grafting of side chains onto each repeat unit of the main chain. The concentration of the polymer forming side chains is usually increased in order to increase the grafting density. As a result, difficulties related to purification from the unreacted component arise.

The appearance and development of the "grafting from" method is mainly due to the progress in atom-transfer controlled radical polymerization. In this case, initiating sites are attached to a linear macromolecule that plays the role of a multicenter macroinitiator obtained by one of the CRP or living-anionic-polymerization methods [22, 31—35] (Scheme 1). To insert initiating groups providing the growth of side chains, the polymer precursor undergoes proper functionalization.

Brushes obtained via the "grafting from" method are the only polymer product of the reaction. A simple analysis of molecular-weight characteristics relative to those in the "grafting through" method and the possibility to attain a high grafting density should also be mentioned as advantages of the method. As its drawbacks, more complicated control over the grafting density and molecular-weight characteristics of side chains, as well as their difficult analysis, which requires detachment of side chains from the backbone, may be noted [36—38].

Different mechanisms of controlled radical polymerization are used to obtain polymer brushes via the "grafting from" method. These mechanisms are considered in more detail below.

USE OF CONTROLLED-RADICAL-POLYMERIZATION METHODS FOR THE SYNTHESIS OF POLYMER BRUSHES

Various CRP methods are actively used for the synthesis of polymer brushes via each of the above-considered approaches, and among them, polymerization via the reverse-inhibition mechanism, atom-transfer radical polymerization, and polymerization via reversible addition—fragmentation chain transfer should be emphasized [1, 39].

These methods are based on the replacement of square-law termination of active radical sites with their reversible transformation into an inactive "dormant" form, thereby making it possible to isolate the polymer product that is able to regenerate active sites of chain growth and may be used in the subsequent synthesis of copolymers with different chain structures (random, alternating, block, graft, and gradient) and the required topology (linear, cyclic, dendrite-like, star-like, polymer brushes) [1, 39, 40].

Each of the CRP methods has its own specific features, advantages, and disadvantages. At the same time, as a whole, they represent the most universal and simple method for the synthesis of polymers with complex architectures and precisely predetermined structures and molecular-weight characteristics.

Controlled Radical Polymerization via the Reversible-Inhibition Mechanism

Historically, the reversible-inhibition mechanism was the first implemented CRP mechanism [41—47]. The reversible activation of dormant chains is achieved in this mechanism with the use of stable radicals. Most frequently, nitroxide radicals [43], together with conventional radical initiators [41], are used for this purpose.

One of the most efficient ways to implement this mechanism is polymerization mediated by alkoxyamines that reversibly generate stable nitroxide radicals [43].
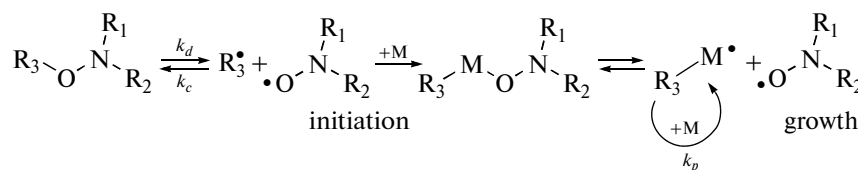
With the use of this mechanism, polymerizations of styrene and its derivatives, acrylates, acrylamides, 1,3-dienes, and acrylonitrile may be accomplished [43]. The reaction is tolerant to amine, carboxyl, and hydroxyl functional groups. However, polymethacrylates cannot be obtained via this method, owing to competitive disproportionation that leads to elimination of hydrogen atoms from α-methyl groups followed by formation of double bonds at the ends of polymer chains [43].
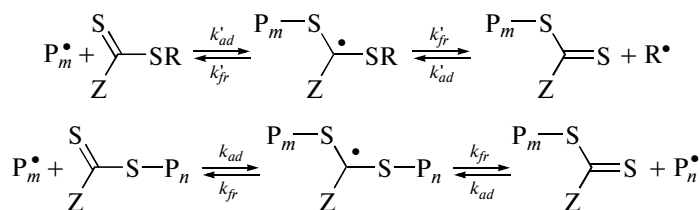
This approach is not often used for the synthesis of branched (co)polymers. Its use in the "grafting from" version is prevented by the presence of radicals in the reaction system that are able to initiate linear polymerization. Thus, there are literature data only for graft polymerizations onto the surfaces of nanoparticles (e.g., magnetite), layers, (e.g., silicon layers), or polymer microspheres [48—50]. For instance, the grafting of polystyrene and poly(2-vinylpyridine) onto the surfaces of 10-nm-dia Fe_2O_3 nanoparticles that were preliminarily functionalized with alkoxyamine groups was described [48]. At the same time, polymerization mediated by stable radicals is widely used for the synthesis of molecular brushes via the "grafting through" method [51].

Controlled Radical Polymerization via Reversible Addition−Fragmentation Chain Transfer

This variant of CRP is one the youngest methods applied to control radical reactions [39, 47, 52−59] that has attracted steadily growing interest from researchers. Formation of a narrowly dispersed polymer is provided by rapid chain transfer between active radical species and a reversible-chain-transfer (RCT) agent and by the participation of macroradicals in the reaction of chain growth:

$$P_m^\bullet + \underset{Z}{\overset{S}{{>}}}-SR \; \underset{k'_{fr}}{\overset{k'_{ad}}{\rightleftharpoons}} \; \underset{Z}{\overset{P_m-S}{{>}}}\!\!\!\!{}^\bullet-SR \; \underset{k'_{ad}}{\overset{k'_{fr}}{\rightleftharpoons}} \; \underset{Z}{\overset{P_m-S}{{>}}}{=}S + R^\bullet$$

$$P_m^\bullet + \underset{Z}{\overset{S}{{>}}}-S{-}P_n \; \underset{k_{fr}}{\overset{k_{ad}}{\rightleftharpoons}} \; \underset{Z}{\overset{P_m-S}{{>}}}\!\!\!\!{}^\bullet-S{-}P_n \; \underset{k_{ad}}{\overset{k_{fr}}{\rightleftharpoons}} \; \underset{Z}{\overset{P_m-S}{{>}}}{=}S + P_n^\bullet$$

A specific feature of RCT polymerization is that the obtained polymers always contain the chain-transfer agent residue (−S−C(=S)−Z). Note that the range of commercially available chain-transfer agents is not too broad. Moreover, this method is not applicable for the CRP of monomers containing primary or secondary amine groups, because they are able to react irreversibly with thiocarbonyl compounds [52].

This variant of CRP is widely employed for the synthesis of polymer products that serve as a backbone or side chains of polymer brushes; however, it is rarer used for the grafting polymerizations of side chains [60]. In this case, for the synthesis of polymer brushes via the "grafting from" method, it is necessary first to modify the backbone and to prepare a multicenter macroinitiator. This modification may be accomplished via "stabilizing" Z groups
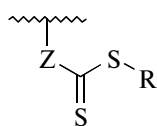
or leaving R groups [60]
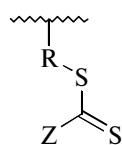
In the former case, macroradicals grow outside the backbone (the Z approach), thereby leading, in fact, to the "grafting on" mechanism with its typical disadvantage related to difficult grafting of side chains onto every repeat unit of the backbone [57, 60−62], while in the latter case, they are grafted on the backbone (the R approach) [60], thereby allowing the "grafting from" method of side-chain growth to be accomplished to the full extent.

Modification of the backbone through attachment of the reversible chain-transfer agent via its R group was applied for the first time by T.P. Davis et al. for the grafting polymerization of styrene [63]. However, the obtained polymer brushes were characterized by multimodal MWDs, which may be associated with the occurrence of intermacromolecular termination reactions [63] and a shift of equilibrium between dormant and growing chains [60]. This problem was solved, and narrowly dispersed molecular brushes were synthesized via the addition of a low-molecular-weight chain-transfer agent that is structurally similar to that attached to the backbone [60]. A disadvantage of this approach is that impurities of an inevitably formed linear polymer should be removed.

Subsequently, the R approach was seldom used for the synthesis of molecular polymer brushes, owing to the indicated difficulties. Only few attempts were made to use it for the synthesis of loosely grafted brushes [64−66] and spherical brushes with poly(vinyl acetate) and polyvinylpyrrolidone chains [67, 68].

Atom-Transfer Controlled Radical Polymerization

The method of atom-transfer controlled radical polymerization is based on the mechanism of reversible transfer of an atom (usually, halogen) or a group of atoms from the dormant form of the active site of chain growth P−X to a transition metal complex Mt^n/L [1, 39, 52, 69−75].

$$P-X + Mt^n/L \; \underset{}{\overset{}{\rightleftharpoons}} \; \underset{\underset{k_p}{+M\;\nearrow}}{P^\bullet} + X-Mt^{n+1}/L$$
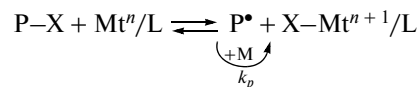
Besides linear (co)polymers, a vast variety of branched polymer structures, including polymer brushes, have been obtained in this way. Presently, this is the most versatile and widely used method for the synthesis of molecular brushes owing to its tolerance to various functional groups of monomers (styrenes, (meth)acrylates, (meth)acrylamides, acrylonitrile, and dienes as well as monomers with labile or highly reactive groups, such as epoxy, amine groups, etc.). Moreover, further modification of side groups results in new functional groups that cannot be introduced via direct polymerization of the corresponding monomers.

In contrast to anionic polymerization, ATRP is insensitive to various admixtures in the reaction system except oxygen, which interacts with the catalyst, thereby poisoning it. At the same time, the rate of the process is little affected by trace amounts of oxygen, owing to the so-called Ingold−Fischer persistent radical effect [72].

Owing to the high practical importance of this type of polymerization, its new modifications have been extensively developed [1, 71] to reduce the sensitivity of initial reagents to oxygen and to refine a less tedious procedure for purification of the polymer product from the catalyst [76−86]. Nowadays, these modifications include methodologies [70] based on one of the approaches listed below:

reverse atom-transfer radical polymerization [72, 76],

simultaneous reverse and normal initiation (SR and NI ATRP) [77, 78],

the use of activators generated via electron transfer (AGET ATRP) [76, 79],

the use of activators regenerated via electron transfer (ARGET ATRP) [76, 79],

the use of initiators for continuous activator regeneration (ICAR ATRP) [83, 84], and

the use of a supplemental activator and reducing agent (SARA ATRP) [85, 86].

In all these methods, a stable form of a transition metal in the highest oxidation state is used to prepare the reaction mixture. A catalytically active complex of transition metal at a lower degree of oxidation is generated either with various reducing agents or via a reversible reaction between a growing macroradical and the complex of the transition metal in the highest oxidation state. In the former case, a reducing agent is additionally introduced into the reaction system, while in the latter case, generation of a growing radical is provided by addition of a conventional initiator of radical polymerization. In addition, some new methods allow the catalyst concentration to be reduced to 10 ppm [80, 81, 87, 88]; as a result, purification of the final polymer is substantially simplified.

Note that the modifications of this method with the use of conventional radical initiators are inapplicable to the synthesis of linear and branched block copolymers under homogeneous conditions because additionally introduced initiators initiate the formation of a linear homopolymer. However, such procedures are successfully used in the methodology of heterophase ATRP; that is, when polymerization is conducted in a miniemulsion [77, 78]. Note that the modifications of ATRP based on the use of electron transfer to regenerate the activator have an important advantage because initiators introduced into the system cannot initiate polymerization by themselves; therefore, they are suitable for the synthesis of linear block copolymers [89, 90] and copolymers with complex architectures, such as polymer brushes [91], and for controlled synthesis in organic media and heterogeneous systems, e.g., in miniemulsions [91−94].

For the synthesis of polymer brushes, the ATRP method is mainly combined with the "grafting from" approach. When the "grafting through" approach was used [95, 96] only low degrees of polymerization of the main chain were attained.

It should be emphasized that, during the "grafting from" synthesis of molecular brushes, square-law-termination reactions of macroradicals lead to either crosslinking (intermolecular termination) or cyclization (intramolecular termination), which may cause the multimodal MWDs of polymerization products or even lead to the formation of crosslinked polymers. For this reason, considerable attention was paid to the optimization of synthetic conditions and minimization of chain-termination reactions to the highest possible extent. As was shown in [33], an increase in the ratio between the amounts of the monomer and initiating groups and the addition of a deactivator (in the form of the Cu^{2+} complex) make it possible to improve the control over the molecular-weight characteristics of brushes and to obtain polymers with unimodal MWDs.

Another disadvantage of ATRP with multicenter macroinitiators is that the efficiency of initiation is lower than that in the synthesis of linear polymers. This phenomenon may be explained by the fact that initiation is not instantaneous; hence, side chains, which have been already formed, may create steric hindrances to the initiation of neighboring groups [36−38]. As shown in [38], a decline in the rate of growth as a result of the addition of 20−30% deactivator with respect to the catalyst allows the efficiency of initiation to be increased to 90%.

A relatively high molecular weight of polymer brushes makes gelation in such systems more probable than CRP, which leads to the formation of linear polymers at close concentrations of the components. Therefore, polymerization is usually performed up to monomer conversions of 20% at most, at a lower temperature, and in a strongly diluted solution [33, 37, 38, 97−99]. A solution suggested in [91] for this problem is based on the use of polymerization in miniemulsions.

Among the specific features of the ATRP method in the synthesis of polymer brushes, the need to carefully purify the product from the catalyst should be mentioned because crosslinking reactions may occur otherwise. This effect is especially significant for brushes with high degrees of polymerization of the backbone (about 400) containing large amounts of functional terminal groups (Br, Cl) of side chains [100].

In the literature, there are many examples of the synthesis of molecular polymer brushes with different chemical structures of the backbone and side chains via the above methods.

TOPICAL DIRECTIONS IN THE DESIGN OF THE MACROMOLECULAR ARCHITECTURES OF POLYMER BRUSHES

The unique architectures of molecular polymer brushes makes it possible to vary their properties within a wide range through changes in the types and lengths of the backbone and side chains as well as in the distribution of side chains along the backbone, a circumstance that offers exciting possibilities for the design of polymers [2−5].

The main chain (macroinitiator) is, in fact, a "spine" on the basis of which the polymer brush structure is formed. Therefore, its structure largely determines the grafting density and the total size and MWD width of the brush obtained on its basis [2]. The number of macroinitiators described in the literature is very high, but they are mostly carbon-chain

polymers. Among them, the following backbone structures may be highlighted.

Polymer Brushes with Carbon-Chain Homopolymer Backbones

Polymethacrylate macroinitiators are usually obtained via ATRP or reversible chain-transfer homopolymerization of a "protected" (rarer, "unprotected") hydroxyethyl methacrylate. The grafting of side chains may be performed via the same methods. As a backbone for grafting under atom-transfer-polymerization conditions, polychloromethylstyrene [101], poly(vinyl chloride) [102], and polyvinylidenefluoride [103] are used also.

Depending on the selected grafting method, the macroinitiator is functionalized with appropriate groups. If ATRP is to be used, 2-Br-isobutyrate groups are often inserted into the macroinitiator. The scheme illustrating the synthesis of such a carbon-chain macroinitiator, which is most often applied for the synthesis of brushes [2, 4, 33−35], is presented below.

2-Trimethylsilyloxyethyl methacrylate
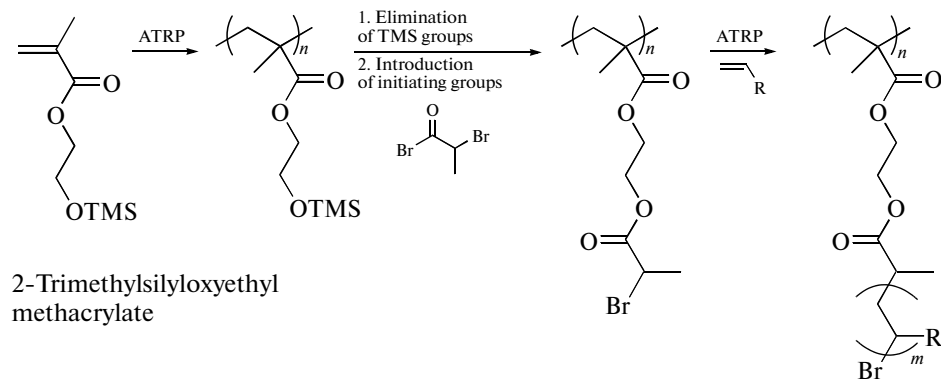
A topical problem that has been intensely developed for the past decade is related to the synthesis of amphiphilic linear and graft copolymers, including amphiphilic polymer brushes. Of most interest are the abilities of such copolymers to self-organize, to undergo reversible changes in conformation, and to undergo changes in solubility during variations in external factors. The different characters of interactions of hydrophilic and hydrophobic blocks included into a single macromolecule with the solvent and each other result in the appearance of complex microscopically ordered states (micelles, bilayers, etc.) in solutions and melts of these macromolecules. With changes in the physical parameters of the systems (temperature, ionic strength, and solvent quality), these interactions may become weaker; as a result, the structures disintegrate and the conformations of macromolecules change. These specific features of

amphiphilic copolymers create a possibility for their applications in such fields as materials science, biomedicine, ecology, for targeted drug delivery, solubilization, catalysis, modification of coatings, and synthesis of artificial nanoparticles.

Most papers cited below deal with the synthesis and study of amphiphilic polymer brushes with hydrophilic or hydrophobic backbones, while side chains are hydrophobic or hydrophilic, respectively.

Of interest is the series of papers [104−109] devoted to the synthesis of brushes with a hydrophilic backbone (poly(acrylic acid) and hydrophobic side chains [poly(methyl methacrylate) [104, 108], poly(n-butyl methacrylate) [105], polystyrene [106, 107], and poly(vinyl acetate) [109]). The scheme of synthesis of brushes with a hydrophilic backbone of poly(acrylic acid) and side chains of poly(n-butyl methacrylate) applied in [104−108] is shown below.
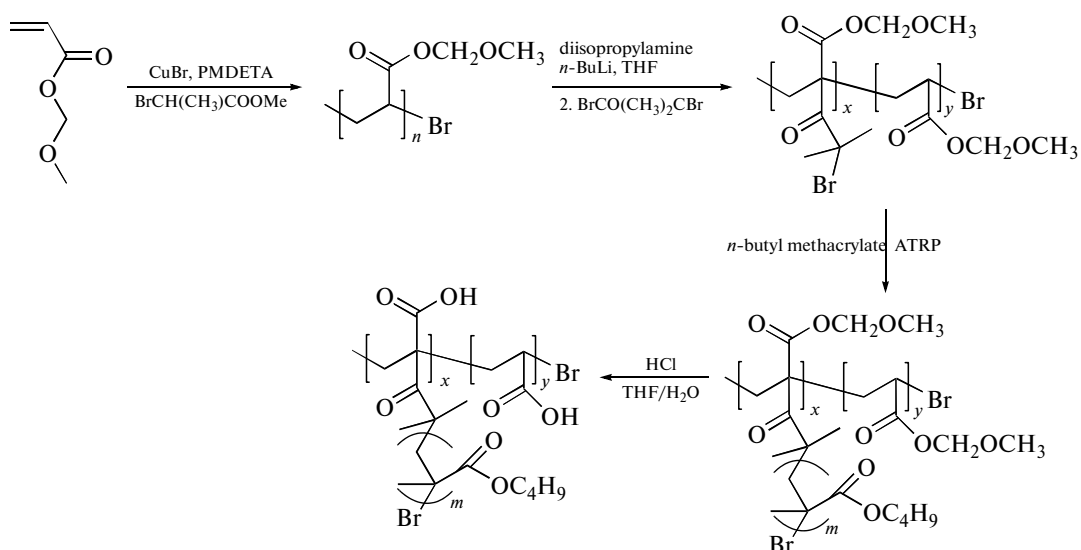
Poly(methoxymethyl acrylate)—a precursor of poly(acrylic acid)—was synthesized for further use as a backbone. This polymer was lithiated at the α-carbon atom of the main polymer chain by lithium isopropylamide in THF and then modified at the α-carbon atom with 2-Br-isobutyroyl (or 2-Br-propionyl) bromide. After grafting of side chains via the ATRP method, the backbone was transformed into poly(acrylic acid) through "soft" hydrolysis by hydrochloric acid.

The use of another well-known precursor of poly(acrylic acid), namely, poly(*tert*-butyl acrylate), as a macroinitiator was described by the same authors in [109]. In this case, the macroinitiator contained xanthate-type side groups that were used to graft poly(vinyl acetate) (PVA) side chains via reversible addition–fragmentation chain-transfer (RAFT) polymerization [109].
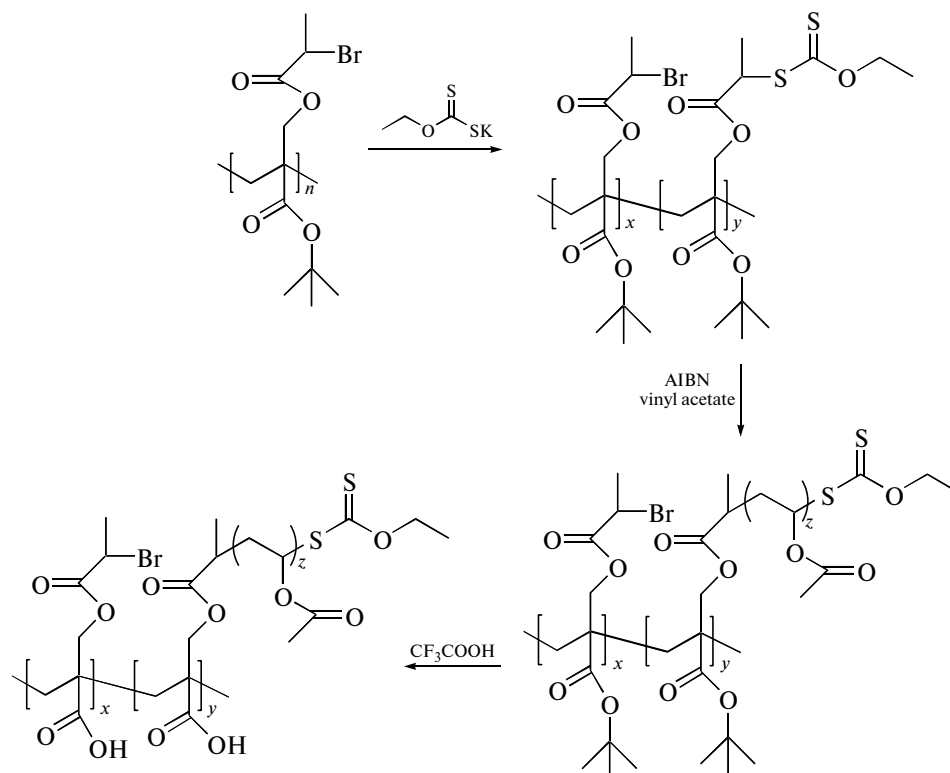
It is interesting that, unlike in [63], in [109], the R approach used to functionalize the main chain of the macroinitiator made it possible to prepare narrowly dispersed PAA-*graft*-PVA polymer brushes ($M_w/M_n = 1.3-1.4$).

Another synthesis of a polymer brush with a hydrophilic backbone was described in [110], where the ATRP method was used to graft polystyrene onto polyepichlorohydrin. A nanocomposite was further formed on the basis of the polymer brush and silver nanoparticles. Such composites show promise for the improvement of electrical, mechanical, and antibacterial properties of polymers [110].
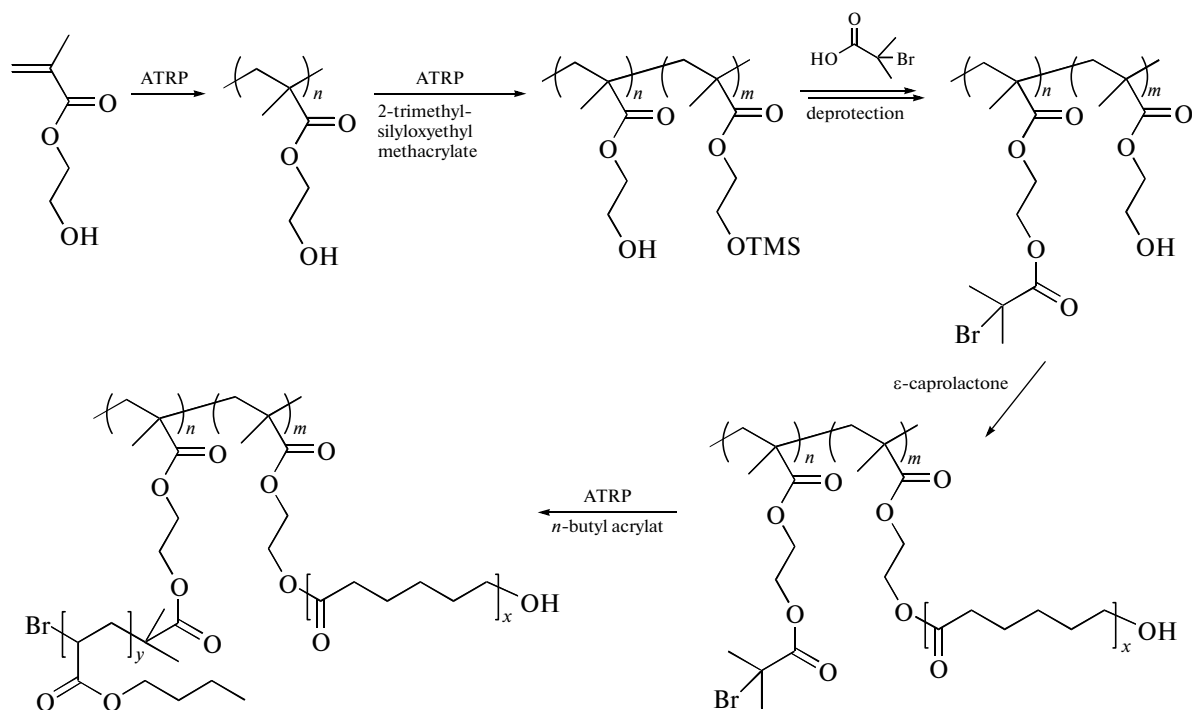
Heterogeneously Grafted Polymer Brushes

These polymer brushes are distinguished by the fact that their macromolecules contain side chains of different natures that are arranged either in blocks or randomly along the backbone.

Macromolecules of the majority of brushes based on block-copolymer macroinitiators contain the block of a polymer brush block and the block of a linear polymer [4, 111]. Another variant, when both blocks are polymer brushes, was implemented via the combi-

nation of "grafting through" and "grafting from" methods. In [112], the block copolymerization of oligo(ethylene glycol methacrylate) with 2-hydroxy-ethyl methacrylate was performed ("grafting through") and followed by modification of monomer units of the latter with halogen-containing initiating groups and grafting of side chains onto them via the ATRP method ("grafting from"). A similar approach was applied in [113] to implement the block copolymerization of octadecyl methacrylate with 2-hydroxy-ethyl methacrylate, and after modification of the monomer units of the latter with 2-Br-isobutyroyl bromide, poly(*n*-butyl methacrylate) chains were grafted onto the block copolymer through a method similar to that described above. These experiments originated the synthesis of a new class of ultrasoft thermoplastic elastomers [22].

An example of using only the "grafting from" method for the synthesis of brushes with block-copolymer main chains is described in [14], where the ring-opening polymerization of ε-caprolactone followed by the ATRP of *n*-butyl acrylate was performed with a block-copolymer macroinitiator containing two types of initiating groups.

In addition, molecular randomly heterogeneously grafted polymer brushes are obtained via the copolymerization of macromonomers or the copolymerization of a macromonomer and a monomer containing the precursor of initiating groups [4] used for further chain growth, in a way that is similar to

that applied for the above synthesis of block copolymers, but yields random copolymers in this case. For instance, heterogeneously grafted copolymers with poly(ethylene glycol) and poly(*n*-butyl methacrylate) side chains were prepared via this approach [114].

Molecular Brushes with Alternating and Gradient Backbones

In order to control the grafting density of polymer brushes, monomer units that are unable to initiate chain growth are introduced into macroinitiators together with units containing initiating groups [115, 116]. In this case, alternating [115] or random [116] copolymers are formed, depending on the relative reactivity of the comonomers. Gradient brushes are obtained either on the basis of comonomers with close reactivities via introduction of one of them additionally during copolymerization [117] or on the basis of macroinitiators prepared through copolymerization of

monomers with substantially different reactivities, e.g., acrylates and methacrylates [118].

Polymer Brushes with Non-Carbon-Chain Backbones

At present, along with the most extensively studied polymer brushes with carbon-chain backbones, a wide range of various polymers are used as backbones. For example, the ring-opening metathesis polymerization (ROMP), which makes it possible to implement the controlled synthesis of polymer brush backbones with double bonds, has becomes increasingly popular. This method was used for the polymerization of a number of functionalized monomers
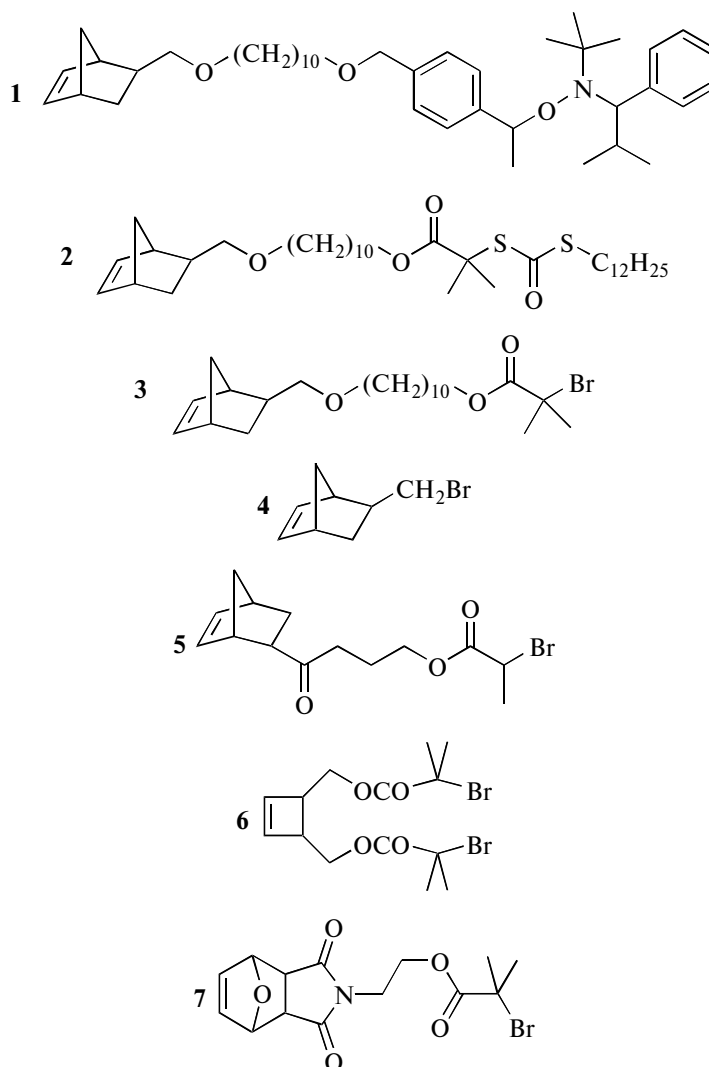
to yield multicenter macroinitiators containing side-chain functional groups, which provide the subsequent CRP "grafting from" via reversible inhibition [119], reversible chain transfer [120], and ATRP [121−124] mechanisms.

"Core−shell" polymer brushes were obtained on the basis of monomer **1** via the above-described method [119]. A hydrophobic core of these brushes is formed by the backbone and adjoining polyisoprene blocks of side chains, while a hydrophilic shell is

formed by side-chain blocks of poly(acrylic acid) prepared via the hydrolysis of poly(*tert*-butyl acrylate) blocks. The subsequent peripheral crosslinking of the hydrophilic shell and the selective destruction of polyisoprene in the hydrophobic core via its ozonolysis and the reduction of ozonolysis products with sodium sulfite made it possible to form hollow nanostructures that can be used as nanocontainers for the controlled delivery and release of drugs.

In [120], the ring-opening metathesis polymerization of monomer **2** was combined with reversible chain-transfer CRP. The macroinitiator was not isolated and purified before the grafting copolymerization of styrene with maleic anhydride; nevertheless,

narrowly dispersed polymer brushes ($M_w/M_n = 1.32$) were obtained.

In [121], the one-pot synthesis of molecular brushes with the use of the Grubbs catalyst to simultaneously implement metathesis polymerization and ATRP was performed.

The "grafting through" approach was accomplished via the ring-opening metathesis polymerization of compound **7** to synthesize polymer brushes with side chains based on (2,2-dimethyl-1,3-dioxolane-4-yl)methyl methacrylate (ATRP) [125] and to synthesize heterogeneously grafted block copolymer brushes on the basis of a macromonomer obtained via reversible chain-transfer polymerization [126].
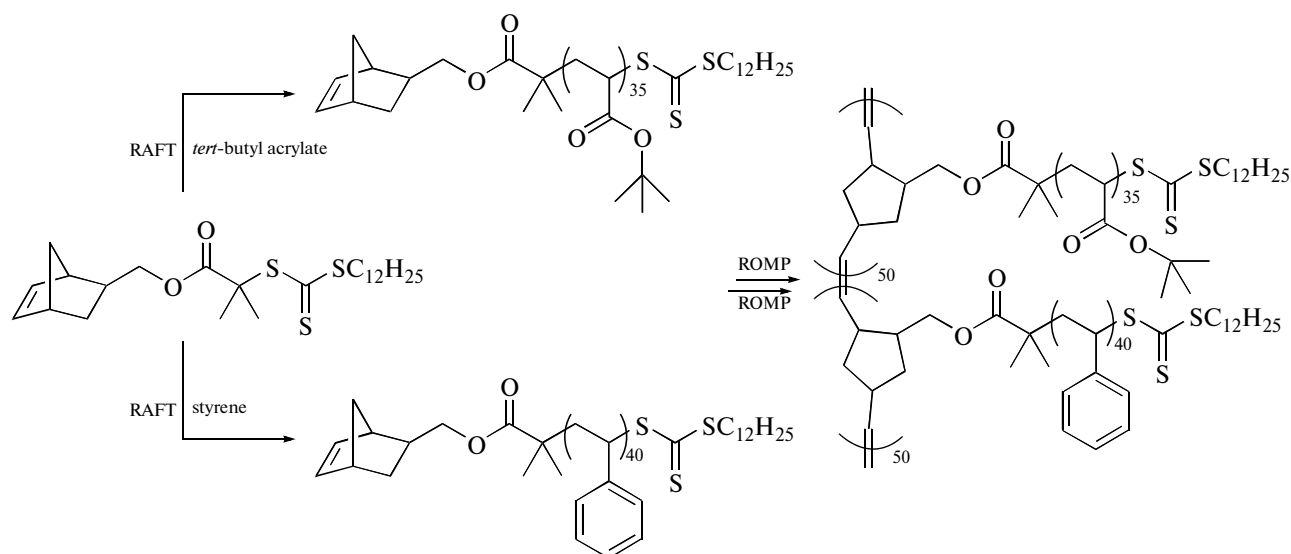
A macroinitiator with only sp^2-carbon atoms in the main chain was synthesized via the catalytic polymerization of substituted Br-containing acetylenes [127]
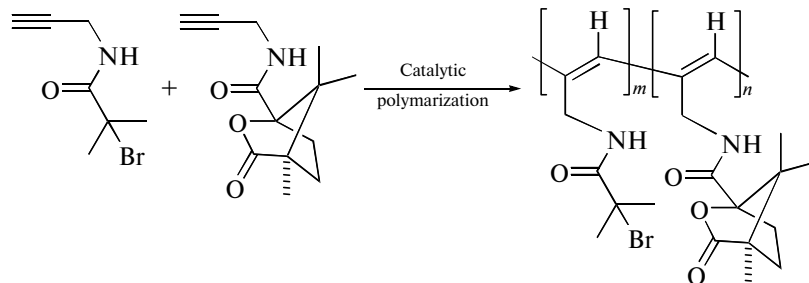
and used for the ATRP grafting of *N,N*-dimethylaminoethyl methacrylate. An interesting feature of the obtained brushes is the helical backbone conformation, which is responsible for their optical activity. These molecular brushes are capable of self-organization under certain conditions; this phenomenon is of interest for the creation of materials useful for targeted drug delivery, chiral catalysis, and sensor development [127].

In addition, polysiloxanes may be used as backbones for building polymer brushes. For instance, a macroinitiator—a polysiloxane with side benzyl chlo-

ride groups that initiate the ATRP grafting of polystyrene, poly(*n*-butyl acrylate), and polychloromethylstyrene—was obtained in [128]. Brushes with polychloromethylstyrene styrene chains were modified with 4-(phenylazo)phenol to yield to a photosensitive material [128].

CRP methods made it possible to combine poorly compatible polymers into a polymer brush, thereby offering a promising approach to modification of well-known polymers for the development of new materials. For example, reversible chain-transfer CRP [129]

and ATRP [130−132] are used for grafting of side chains (polystyrene and poly(methyl methacrylate)) onto cellulose macromolecules. In [132], the synthesis of a multicenter macroinitiator with a degree of functionalization of up to 98% via acylation of cellulose with 2-Br-isobutyroyl bromide in an ionic liquid (1-allyl-3-methylimidazolium chloride) and its use for the ATRP of methyl methacrylate were described.

A new direction in backbone design that has been under development in recent years is the search for synthetic approaches to molecular brushes based on widely used hi-tech thermally stable polycondensation-type polymers, such as aromatic polysulfones, poly(phenylene oxide), and aromatic polyimides [133−139]. Different thermodynamic properties of arylene-containing polycondensation-type main chains and carbon-chain side chains in these polymer brushes are responsible for their clearly pronounced diphilic character. Grafting of side chains imparts new properties to materials based on these polymerization−polycondensation-type polymer brushes. Thus, "click chemistry" grafting of poly(*tert*-butyl acrylate) side chains onto polysulfone (a widely known mem-brane material) followed by their transformation into hydrophilic chains of poly(acrylic acid) made it possible to obtain membranes with more hydrophilic surfaces on the basis of the synthesized copolymer [133].

The grafting of carbon-chain polymers onto arylene-containing polycondensation-type polymers is an efficient way to combine these polymers that makes it possible to avoid the phase separation that is often observed in their blends, to impart good solubility in common organic solvents to the obtained graft copolymers, and to improve their processing behavior. For instance, the obtainment of molecular brushes with a poly(phenylene oxide) backbone was described in [134]. The synthesis was implemented via the ATRP grafting of polystyrene and poly(methyl methacrylate) side chains onto a macroinitiator based on poly(2,6-dimethyl-1,4-phenylene oxide) functionalized by brominating methyl groups.

Another example is the analogous grafting of poly[(meth)acrylates] and polystyrene side chains onto multicenter macroinitiators based on aromatic polyimides [135−140].
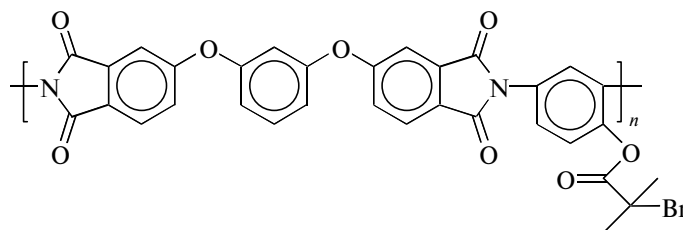
Macromolecules of polyimide brushes are characterized by a high equilibrium rigidity (Kuhn segment length of >40 nm) [141] that is several tens of times higher than the corresponding characteristics of polyimide macroinitiators used for the synthesis of these brushes [140]. In selective solvents of various thermodynamic qualities for the backbone and side chains, such polyimide brushes assume conformations of a more or less elongated ellipsoid of revolution [142, 143] or form a nearly spherical core−shell structure with the collapsed backbone (core) surrounded by side chains protruding into the solution [143], as confirmed by the computer-simulation method [144].

In recent years, polymer brushes with relatively loosely and regularly grafted side chains have aroused considerable interest owing to their structural similarity to natural protein compounds and wide potential to change the conformations of individual macromolecules. A regular grafting of side chains onto polycondensation-type polymers makes it possible to significantly increase the distance between them, because polycondensation-type polymers have substantially longer repeat units. For example, the length of the repeat unit of the backbone of polyimide brushes [136−139] is ~2 nm. This value is an order of magni-tude longer than the length of the monomer unit of polyvinyl main chains of carbon-chain polymer brushes. Grafting of hydrophilic poly(methacrylic acid) side chains onto polyimide through the intermediate stage of poly(*tert*-butyl methacrylate) made it possible to use the resulting molecular brushes as amphiphilic multidentate ligands, which can incorporate drugs in the form of large hydrophobic complexes. It was shown in [138] that such polyimide brushes may serve as solubilizing nanocontainers for the targeted delivery of cyanoporphyrazines and their Yb(III) complexes, which are applied for photodynamic therapy and diagnostics of cancerous diseases, to tumor cells.

DESIGN OF SIDE CHAINS OF POLYMER BRUSHES

The "grafting from" method combined with ATRP makes it possible to efficiently control the structure of side chains of polymer brushes. Side chains may be grafted as homopolymers and random, block, or gradient copolymers. A large number of monomers may be used in the "grafting from" method [2, 4, 5]—including styrene derivatives [31, 33, 34], acrylates

[22, 31, 32, 34, 36, 37, 116], methacrylates [35, 37, 101], and acrylonitrile [145]—as well as specific monomers containing attached sugar [146] or oligo(ethylene oxide) [147] molecules.

Particular attention is given to polymer brushes with side chains that are sensitive to external factors. For this purpose, polyelectrolytes, homopolymers, and copolymers possessing thermosensitivity, photosensitivity, and other properties are introduced into side chains of brushes [5]. The macromolecular conformations and properties of such polymer brushes may be governed through variations in pH, the ionic strength of solvent, and temperature as well as with the use of solvents of various qualities for backbone and side chains. Under certain conditions, such structures are capable of self-organization in solutions, which leads to marked changes in rheological and optical characteristics, which may be controlled through variations in the structures and compositions of copolymers [5].

Polymer Brushes with Polyelectrolyte Side Chains

The presence or absence of charges on the monomer units of side chains of amphiphilic polymer brushes determines their polyelectrolyte properties. Anionic hydrophilic units usually belong to the class of polyunsaturated carboxylic acids, while cationic hydrophilic blocks are mostly protonated tertiary amines or quaternary ammonium groups. Hydrophilic structural elements used in the previous examples for building backbones of polymer brushes may additionally be used as a basis for side chains.

Weak carboxylic acids, such as poly(acrylic acid) and poly(methacrylic acid), are most often used as polyanions in side chains of polymer brushes [4, 31, 32, 148]. It should be noted that the direct ATRP of (meth)acrylic acid is impossible because of catalyst poisoning. Therefore, precursors, for example, poly(*tert*-butyl(meth)acrylate) or poly(methoxymethyl methacrylate), are initially synthesized and then transformed into the corresponding acid via acidic hydrolysis [31, 32, 149].

Polymer brushes with polyacids in side chains can change their conformations, depending on the pH and ionic strength of solvent, to form complexes with transition metals [5] and to incorporate macromolecules, complexes, or nanoparticles [138, 149]. Investigations of such composites are one of the promising and actively developing lines of research. In [149], a composite based on Fe_3O_4 nanoparticles and a multigrafted brush with poly(methacrylic acid) (PMAA) side chains was obtained and its magnetic properties were investigated.
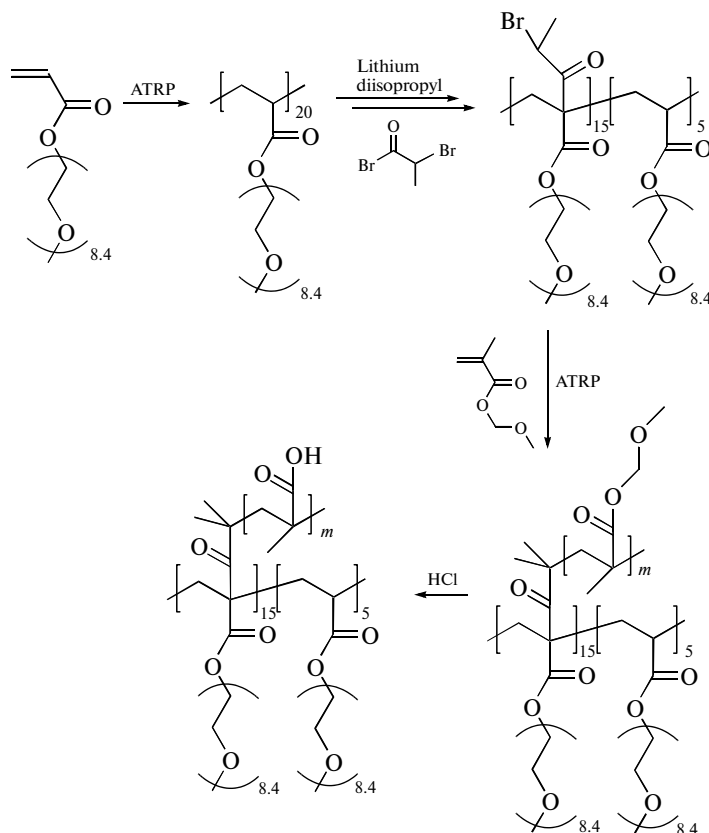
The multigrafted brush was prepared in several stages. First, a graft copolymer with oligomer side chains, poly(oligoethylene oxide acrylate), was synthesized via the ATRP method. Initiating groups were further introduced into the backbone of this polymer via its successive treatment with lithium diisopropyl and 2-Br-propionyl chloride [149]. Poly(methoxymethyl methacrylate) side chains were grafted via the ATRP method and then hydrolyzed to form PMAA.

Composites of these brushes with magnetite show promise as sensors and magnetic labels because their poly(ethylene glycol) side chains are biocompatible. In addition, these composites may be used as catalysts in biotechnologies [149].

Polymer brushes with thermosensitive polymer side chains, such as poly(N-isopropylacrylamide) [150] and poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) [151−155], which are usually obtained via the ATRP method, are the focus of considerable attention from researchers. The latter polymer additionally exhibits clearly pronounced polycationic properties. The collapse of brushes with poly(N-isopropylacrylamide) side chains in an aqueous solution, accompanied by their transition from a cylindrical macromolecular conformation to a dense sphere when the lower critical solution temperature was reached in the range 20−38°C, was observed in [150]. In addition, polymer brushes with PDMAEMA side chains are characterized by the lower critical solution temperature [153]. Their specific feature is that intermolecular aggregation is observed in quite concentrated solutions (5%), while in less concentrated solutions (0.1 and 0.5%), intramolecular aggregation occurs [153].

Brushes with polystyrene backbone and PDMAEMA side chains form micelles in a water−acetone mixture (2 : 3, vol/vol). Depending on temperature, the shape of micelles changes from needle-like to cubic [154].

In [155], PDMAEMA side chains were attached to polythiophene via the "grafting from" method,
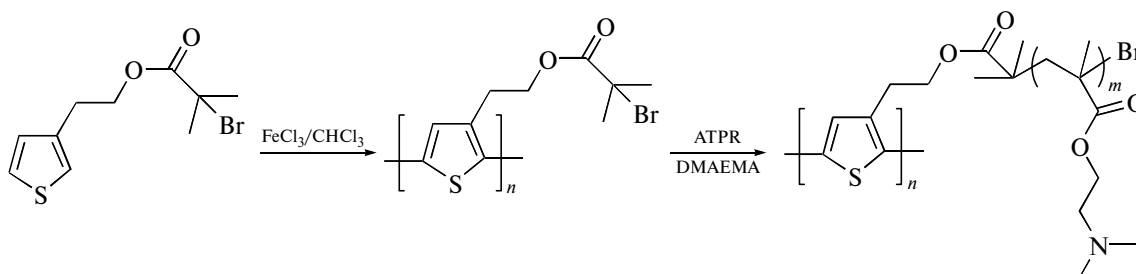
and pH-induced changes of conformations of the brushes were studied via different methods.

Among thermosensitive polymers used in side chains of polymer brushes, poly(ethylene glycol) stands out for its biocompatibility. In review [156], a wide variety of macromonomers (with terminal double bonds) based on poly(ethylene glycol) of various molecular weights are described, methods used to obtain polymer brushes from them via the "grafting through" method are analyzed, and their properties and application prospects are highlighted.

Molecular Brushes with Copolymer Side Chains

The grafting of random, block, and gradient copolymers onto the backbone considerably extends the scope of the structural design of polymer brushes. The synthesis of block copolymers is possible above all owing to the use of CRP, when terminal groups of the resulting polymer survive and can initiate the subsequent polymerization of the monomer.

Using "grafting from" via the ATRP method for polymethacrylate multicenter macroinitiators that was schematically shown above, K. Matyjaszewski et al. prepared a number of thermosensitive polymer brushes with a carbon-chain backbone and side chains containing random and block copolymers of diethylene glycol methacrylate methyl ether and triethylene glycol methacrylate methyl ether [147], as well as binary and ternary copolymers of diethylene glycol methacrylate methyl ether, methacrylic acid, and N,N-dimethylaminoethyl methacrylate [157].

Thermal properties of aqueous solutions of such polymer brushes are strongly dependent on the structure and composition of side chains [147, 157].

In order to obtain photo- and thermosensitive brushes, block and random copolymers comprising units of *trans*-4-methacryloyloxyazobenzene, which are responsible for photosensitivity, and N,N-dimethylaminoethyl methacrylate units, which impart thermosensitve properties to the polymer brushes, were grafted onto carbon-chain backbones of macroinitiators of the same structure via the same method [153].

Polymer brushes with block-copolymer side chains are often called core−shell structures, where the core is the backbone-adjoining block of the side chain, while the shell is the outer block [2]. On the basis of a carbon-chain macroinitiator obtained via the classical scheme, brushes with a flexible poly(n-butyl acrylate) core and a rigid polystyrene shell, as well as the reverse

structures, were synthesized [34]. A.H.E. Müller et al. obtained brushes from the same backbone with either poly(styrene-*block*-poly(*tert*-butyl acrylate) block copolymer side chains and the reverse structure [31] or poly(*n*-butyl acrylate-*block*-poly(*tert*-butyl acrylate) block copolymer side chains and the reverse structure [32]. Afterward, *tert*-butyl groups were hydrolyzed to transform one of the blocks into poly(acrylic acid). Thus, amphiphilic copolymers containing hydrophobic and hydrophilic blocks in side chains were obtained [31, 32] with a variable sequence of their attachment to the backbone.

Molecular brushes with block-copolymer side chains with core−shell (diblock-copolymer) or core−shell−corona (triblock copolymer) structures may be used as nanoreactors for the synthesis of brush-incorporated inorganic nanoparticles (hybrid nanostructures) [2, 158−160]. Inorganic nanostructures may be obtained from them via the removal of brushes, for example, via pyrolysis.

Such approaches to the synthesis of nanostructures based on TiO_2 [161], CdS [162], CdSe [163, 164], Au [15], Fe_3O_4 [165, 166], and Si [159, 167] have been described in the literature. For instance, the method of creating silicon-containing nanostructures via brushes with poly(ε-caprolactone-*block*-PDMAEMA) side chains was studied in [159]. TiO_2 nanoparticles were incorporated into the core−shell−corona of molecular brushes with side chains of the block copolymer of poly(ε-caprolactone), PDMAEMA, and poly(oligoethyleneglycol methacrylate) [160]. In the mentioned papers, poly(ε-caprolactone) was grafted as the first block. This grafting was performed via the polymerization of ε-caprolactone initiated by OH groups of the macroinitiator, that is, poly(hydroxyethyl methacrylate). Ring-opening polymerization used in these cases made it possible to synthesize brushes with a high density of grafting of side chains. Next, blocks were grafted via the ATRP method. Afterward, cores of the formed nanostructures were removed via hydrolysis and nanosized objects with porous structuring were obtained.

CONCLUSIONS

Methods of controlled radical polymerization have been extensively developed and improved for the past 30 years. A vast amount of papers dealing with this kind of polymerization processes have been published. Efforts applied by many research groups have led to the present situation, where controlled radical polymerization has become a powerful tool making it possible to implement the controlled synthesis of polymer complex architectures, as has been demonstrated in this review for the synthesis of molecular brushes as an example.

New atom-transfer-polymerization methodologies that make it possible to reduce both the sensitivity of this method to oxygen and the amount of catalyst are currently being developed. In regards to reversible-chain-transfer polymerization, a broad range of chain-transfer agents have been synthesized, a circumstance that allows polymerizations of nearly all vinyl monomers to be controlled. These methods are successfully used both for the synthesis of multicenter macroinitiators and for the grafting of side chains of molecular brushes. Owing to the tolerance of various functional groups and the possibilities to synthesize block copolymers, different polymeric architectures of molecular brushes have been prepared. Among them, of special interest are amphiphilic structures, which are capable of unique structuring, depending on the external conditions, and providing possibilities for the synthesis of hybrid structures with various nanoparticles. The structuring ability of molecular brushes has opened new vistas for the design of novel materials.

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