Cylindrical molecular brushes: Synthesis, characterization, and properties

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Abstract

Brush-like macromolecules are unique polymer molecules whose conformation and physical properties are controlled by steric repulsion of densely grafted side chains. Molecules can be either flexible or stiff, depending on the grafting density and the length of the side chains. Molecules can switch their conformation in response to alterations in the surrounding environment, e.g. changes of temperature, solvent quality, pH, and ionic strength. Furthermore, one can control molecular conformation and related properties using external stimuli such as light and electro-magnetic fields. Molecular brushes are also very informative model systems for experimental studies of polymer properties. Molecules are readily visualized by atomic force microscopy, opening unique opportunities to observe single polymer molecules as they move, order, and react on surfaces. Brush-like molecular architectures are well-known in biology where they are responsible for various functions including mucociliary clearance of lung airways and mechanical performance of articular cartilage. Polymer chemistry is currently making the first steps in controlling molecular architecture and understanding the distinctive properties of molecular brushers. This article reviews the characteristic physical properties of well-defined molecular brushes and the different strategies employed for their preparation, with particular focus on synthesis via controlled radical polymerization techniques.

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1. Introduction

Among the many amazing biomolecules at work in nature is a group known as proteoglycans [1–3]. Proteoglycans are polyelectrolyte brush-like macromolecules that consist of a protein backbone with carbohydrate side chains. These molecules are found in different places in the human body performing functions from cell signaling and cell surface protection to joint lubrication and lung clearance [4–7]. For example, proteoglycans act as water sponges in cartilage controlling its shock absorption and lubrication properties [8–11]. Another prominent example of biological functions is the mucociliary clearance of lung airways, which is largely controlled by viscoelastic properties of mucus composed of various types of glycoproteins and proteoglycans [12–14]. It is generally believed that the functional properties of proteoglycans are a direct result of their brush-like structure that ensures dense packing of functional groups along the backbone (Fig. 1).

Biological brushes inspired the synthesis of polymers with similar architectures [15]. These synthetic counterparts are known as cylindrical brush polymers or molecular bottle-brushes due to their appearance. The architecture of molecular brushes can vary, being densely or loosely grafted, having flexible or stiff side chains and backbone, being homopolymers or copolymers (Fig. 2). Each of these variables affects their properties, but it is the relatively dense grafting that has the greatest effect on conformations and properties of brush polymers. Steric repulsion between the densely grafted side chains enhances stiffness of the backbone, hinders overlapping and entanglement with neighboring macromolecules, and promotes ordering.

2. Synthesis of molecular brushes

There are three main strategies for preparing molecular brushes (Fig. 3): “grafting through” (the polymerization of macromonomers), “grafting onto” (the addition of
previously prepared side chains to a backbone), and "grafting from" (the polymerization of side chains from a macroinitiator backbone) [19–21]. Each of these strategies controls different structural parameters, including chemical composition, grafting density, degree of polymerization of side chains, and degree of polymerization of the backbone. Controlling many of these parameters has proven challenging because of steric hindrance at the backbone due to dense grafting. Even though each strategy demonstrates distinct advantages with respect to the molecular design, there are also limitations from a synthetic perspective, and it is often advantageous to employ a combination of methods or use a modular approach [22] enabling brushes with structures unobtainable by a single technique.

Within each strategy, various polymerization techniques such as anionic polymerization, ring-opening metathesis...
polymerization, conventional and controlled radical polymerizations (CRPs), various coupling reactions ("click chemistry"), and miniemulsion polymerization have been employed. Not all of these attempts have been successful in creating densely grafted molecules in which every monomeric unit of the backbone contains a side chain while backbones are significantly longer than the side chains. Below we review different synthetic strategies and polymerization techniques to illustrate specific advantages and limitations. Particular attention is paid to syntheses employing CRP techniques, as these have proven particularly useful for the preparation of well-defined, functional molecular brushes.

2.1. Grafting through

The grafting through route involves the polymerization of macromonomers “through” their terminal functionality [23–40]. Perhaps the most attractive feature of this method is that each repeat unit of the backbone contains a covalently bound side chain. Also, because the macromonomers are prepared separately, the side chains can be characterized prior to polymerization. This allows preparation of brushes with well-defined grafting density and side-chain length. However, the grafting-through method suffers from the degree of polymerization of the backbone being dependent on the macromonomer length and type. Additionally, due to the necessarily low concentration of polymerizable end groups and high steric hindrance of the propagating chain end, polymerizations can be slow and not proceed to high conversion [41]. Low conversion may lead to tedious fractionation and dialysis to remove unreacted macromonomer. Nonetheless, there have been several successful reports of the preparation of both homopolymer and copolymer brushes by grafting through polymerizations.

2.1.1. Homopolymerization of macromonomers

The first brushes were successfully synthesized by Tsukahara [25]. However, gelation occurred at high conversion affording only short brushes, so-called oligomacromonomers. Since that time, many new techniques have been developed, each with its own strengths and weaknesses [16–21].

2.1.1.1. Anionic polymerization. There have been several reports on anionic polymerizations of various macromonomers including polysisoprene, polybutadiene, and polystyrene (PS) with terminal styrenic and methacrylic functionalities [42–45]. However, due to significant steric hindrance and difficulty in obtaining macromonomers with high purity, most anionically prepared polymer brushes have been limited to low molecular weight and moderate control over the molecular weight distribution [42,43]. To reduce steric hindrance, a modular approach has been used in which the backbone is polymerized in discrete segments that are subsequently linked together along with the side chains [46–48]. This approach also enabled preparation of multigraft architectures (Fig. 2).

2.1.1.2. Ring-opening metathesis polymerization. As mentioned above, polymerization of most vinyl macromonomers is sterically hindered. Ring-opening metathesis polymerization (ROMP) [49,50] was proposed as an attractive alternative, which offers two advantages. As shown in Fig. 4, norbornenyl macromonomers result in larger spacing between side chains, providing a kinetically favorable environment for propagation reactions [51]. In addition, ring strain in the norbornenyl functionality enhances the thermodynamic driving force for polymerization. Gnanou and coworkers prepared norbornenyl-terminal PS [52] and poly(ethylene oxide) (PEO) [53] and subsequently employed ROMP to prepare molecular brushes. Other norbornenyl-containing macromonomers have been homopolymerized by ROMP including those with chains of polyphosphazene [54], poly(ε-caprolactone) (PCL) [55], and polylactide [56], each of these resulting in high molecular weight and conversion. The versatility of this method for the preparation of molecular brushes was further demonstrated by Wooley et al. [51] who employed ROMP and tandem polymerizations via ROMP along with either atom transfer radical polymerization (ATRP) [57], NMP [58], or reversible addition–fragmentation chain transfer (RAFT) [59] to prepare a range of well-defined and, in some cases, core–shell molecular brushes.

2.1.1.3. Radical polymerization. The majority of grafting through polymerizations has involved free radical polymerization of homomacromonomers [25,28,60–62]. In addition, block macromonomers were successfully polymerized to obtain core–shell structures that can be used to grow nanowires illustrating the broad possibilities for applications of copolymer brushes [47,63,64]. Grafting through was also used to polymerize macromonomers with two or more chains (Fig. 5) [65]. The bulky nature of the doubly substituted macromonomer significantly enhanced rigidity of the backbone; however, it also lowered the monomer conversion.

While conventional radical polymerization allows using a wide range of monomers and reaction conditions, the relatively poor control over molecular weight and chain end functionality precludes its application to prepare well-defined structures. Steric repulsion between bulky macromonomers impacts the rate constants of propagation and bimolecular termination [25,26]. In order

Fig. 4. Ring strain and the decreased density of side chains make ring-opening metathesis polymerization (ROMP) of a norbornenyl macromonomer an attractive for the preparation of molecular brushes.
to facilitate better control over molecular weight and allow the preparation of more advanced architectures, various methods of controlled/living radical polymerization (CRP) have been developed [42,66–77]. Since the rate of CRP processes does not depend on the termination rate but is defined by an activation/deactivation equilibrium, the overall polymerization rates of bulky macromonomers are very slow and often limited to low polymerization degrees [78]. However, grafting through polymerization of less sterically hindered poly(ethylene glycol) methyl ether methacrylate (PEGMA) by ATRP was successful to provide a brush with a degree of polymerization of the backbone of DP = 425 at 90% monomer conversion [77]. When the polymerization was allowed to progress beyond this point, cross-linking occurred leading to materials with super-soft elastomeric properties.

2.1.2. Copolymerization by grafting through

Copolymerization of two different macromonomers allows synthesis of heterograft copolymers wherein side chains of different chemical structure are randomly distributed along the backbone (Fig. 2). The relative reactivity of the two macromonomers determines the distribution of the side chains along the backbone. In addition to the polymerizable moiety, the identity of the side chain and the presence of additives can influence reactivity [79–82]. Copolymerization of PS with maleate-terminated PEG resulted in brushes with comonomer distributions that approached alternation [79]. In addition to polar effects resulting from the electron-donating PS and the electron-deficient PEG macromonomers, monomer reactivities were influenced by phase separation during the copolymerization. Heterograft brush copolymers are expected to demonstrate interesting solution [83–87], bulk [88,89,] and surface [90] properties due to the interspersed nature of the side chains. For example, brushes with PEG and PS side chains undergo phase separation in solution to form large filament-type aggregates [85,86,89]. An interesting bulk behavior was observed for brushes with statistical and gradient distributions of crystallizable side chains. X-ray studies indicated that inefficient packing of the helical PEG and hexagonal octadecyl crystallizable segments resulted in an amorphous fraction of octadecyl side chains instead of the typical semicrystalline morphology [91]. Heterograft copolymers of a poly(dimethylsiloxane) (PDMS) macromonomer with PEGMA (Fig. 6) [92] demonstrated phase separation of the amorphous PDMS grafts and the crystallizable PEGMA grafts, which resulted in super-soft elastomeric behavior [93]. On surfaces, copolymer brushes with poly(methyl methacrylate) (PMMA) and poly(2-vinylpyridine) (P2VP) side chains were manipulated to change their conformation from worm-like to curved structures [90].

2.2. Grafting onto

The “grafting onto” strategy of molecular brush synthesis involves the reaction of end-functional polymers with a polymer backbone precursor containing complimentary functionality on each monomer unit (Fig. 3). This synthetic strategy is largely based on the supramolecular assembly approach exploiting secondary interactions such as hydrogen bonding [94] coordination [95] and ionic interaction [96]. The attractive feature of the “grafting onto” approach is that both the backbone and side chains are prepared independently, i.e. they can be synthesized by mechanisms appropriate to the respective monomer structures and subsequently characterized.
prior to coupling. The modular approach enables complex architectures such as star-like comb PSS [97] and heteropolymer brushes with different kinds of side chains along the backbone [98,99]. However, due to steric repulsion between bulky side chains, limited grafting density is often observed. Typically, an excess of side chains is employed in order to drive the grafting reaction to high conversion; however, purification becomes problematic when trying to remove the unreacted side chains. The requirement of reactive linking groups imposes limitations on the selection of functional groups that can be incorporated into the side chain and backbone polymer structures. These factors have limited the grafting onto approach to only the most efficient, high yielding types of reactions such as nucleophilic substitution and click-type coupling reactions.

2.2.1. Side-chain attachment by nucleophilic substitution

Usually, grafting-to reactions involve the preparation of well-defined side chains by living anionic polymerization and their subsequent reaction with a backbone of monomer units that are susceptible to nucleophilic attack. Examples of such functional groups include esters, anhydrides, benzyl halides, nitriles, chlorosilanes, and epoxides [100,101]. Deffieux et al. clearly demonstrated the reaction of polystyryllithium or polyisoprenyllithium with poly(chloroethyl vinyl ether) (synthesized by cationic polymerization) results in the successful preparation of high-molecular-weight molecular brushes and arboraceous polymers [102–114]. This general strategy proved capable of leading to high grafting densities characteristic of molecular brushes. In other reports, significant contribution from side reactions was observed because of the highly reactive nature of polyanion end groups. For instance, reacting polystyryllithium with poly(chloromethyl styrene) is a fairly efficient means to prepare graft copolymers (Fig. 7), but unless specific precautions are taken, the grafting density rarely exceeds 60% [100,115].

Different approaches have been suggested to improve the yield of the coupling reactions by reducing the contribution of side reactions. By using potassium rather than lithium counterions, near-quantitative conversion was observed during the preparation of four-arm star polymers from 1,2,4,5-tetrachloromethylbenzene [116]; however, extension of this approach to the synthesis of brushes from poly(chloromethyl styrene) resulted in significantly lower yields (~80%) [117]. Capping the living polymer with a single 1,1-diphenylethylene unit prior to reaction with the backbone proved to be a viable means of significantly increasing the reaction yield (>95%) between the PS anions and the chloromethyl groups, but the reaction was conducted with polystyrene-stat-poly(chloromethyl styrene), so true molecular brushes were not prepared [118].

2.2.2. Side-chain attachment by click chemistry

By employing highly efficient copper(I)-catalyzed azide–alkyne coupling reactions [119,120] commonly classified as a form of “click chemistry” [121] post-polymerization modification reactions have been observed to proceed to high conversion [122–126]. These highly efficient reactions opened opportunities for preparation of dendronized polymers with high grafting density [74]. Frechet and Hawker successfully coupled azide-functionalized dendrons to linear backbones of poly(vinyl acetylene) (Fig. 8) and poly(p-hydroxy styrene) (after being functionalized to contain acetylene groups) [122,123]. For the case of the reaction of poly(vinyl acetylene) with benzyl ether dendritic azides, the coupling reaction was quantitative for generations 1 and 2 and greater than 98% conversion was observed for generation 3. Poly(hydroxyethyl methacrylate) was modified with 4-pentynoic acid in order to incorporate alkyne functionality along the backbone. Subsequent reaction with azido-terminated polymers enabled synthesis of well-defined brushes in an efficient manner [127]. Efficiency of grafting onto strongly depends on the size of side chains. For short “thin” PEO side chains efficiency of initiation reached ~90% but was much smaller for longer PEO chains and also for “thicker” PS or poly(butyl acrylate) side chains.

![Fig. 7. Molecular brushes by grafting living polystyrene anions to polychloromethyl styrene [104,115,105,102].](image-url)
2.3. Grafting from

“Grafting from” synthesis of molecular brushes starts with the preparation of a backbone polymer (macroinitiator) with a predetermined number of initiation sites that is subsequently used to initiate polymerization of the side chains (Fig. 3). The macroinitiator can be prepared directly or by first preparing a precursor that is subsequently functionalized to include initiating moieties. The gradual growth of the side chains alleviates concerns over steric issues that are often limiting conditions in the “grafting through” and “grafting to” strategies. In grafting from via CRP techniques, a low instantaneous concentration of radical species necessarily limits termination events. This is especially important during molecular brush synthesis since intramolecular termination can lead to pendant macrocycles, and more importantly, intermolecular coupling can lead to macroscopic gelation. As such, the grafting from approach enables preparation of long-backbone molecular brushes with a high grafting density and a narrow molecular weight distribution. However, compared to the grafting through approach, grafting from allows less control of side-chain length and grafting density. Both parameters depend on the initiation efficiency, as reported for the ATRP of BA and MMA from a poly(2-2-bromopropionyloxymethyl methacrylate) (PBPEM) macroinitiator backbone [128,129].

The “grafting from” approach was applied to anionic polymerization [42] and to ATRP [67,130–132]. The controlled synthesis of brush copolymers via ATRP has been described for several acrylate monomers (methyl, n-butyl, t-butyl) [24,133], methacrylates (methyl, butyl, dimethylaminoethyl, various macromonomers) [77,134,135], acrylamide [134], acrylonitrile [136], and styrene [137]. Other examples of ATRP-made brushes include core–shell molecules with block-copolymer side chains [138], AB and ABA block brushes [139], star-like brushes [140], and cylindrical brushes with gradient grafting density [133]. Recently, a combination of dendritic polymers and molecular brushes has been reported where polymer chains were subsequently grown on the dendritic core using atom transfer polymerization techniques [141]. Furthermore, polymerization of a precursor monomer by grafting from a surface is a means to prepare immobilized molecular brushes [142].

2.3.1. Tailoring the macroinitiator structure

The macroinitiator is essentially the template from which the brush structure will be derived. As such, the structure of the macroinitiator largely determines the grafting density, the overall size, and the polydispersity index of the resulting molecular brushes. In addition, it is beneficial to have the ability to tailor its composition in order to prepare increasingly advanced molecular architectures.

2.3.1.1. Homopolymers. Macroinitiators can be obtained via polymerization of a monomer containing an ATRP-initiator group using conventional free radical polymerization [137], stable free radical polymerization [143] RAFT polymerization [144], or anionic polymerization [138,145]. The majority of reports, however, employed
ATRP of a monomer carrying a precursor that was subsequently transformed to an ATRP-initiating group either directly [24] or after deprotection [137] (Fig. 9). Due to the relative ease by which ATRP initiators can be prepared, a wide range of macroinitiators derived from synthetic and natural polymer scaffolds can be envisioned.

2.3.1.2. Block copolymers. In addition to homopolymers, preparation of molecular brushes with block-copolymer backbones has been reported [145–147]. Most of the examples are brush–coil block copolymers in which one block is a cylindrical brush, while the other is composed of a linear polymer. In order to prepare block copolymers, in which both blocks contain side chains (brush–brush block copolymers), the combination of grafting through and grafting from is employed. Block copolymerization of PEGMA macromonomer with 2-hydroxyethyl methacrylate (HEMA) resulted in a polymer that could be functionalized with halogenated initiating sites [84]. Similarly, polymerization of octadecyl methacrylate (ODMA) followed by blocking with HEMA-TMS was reported [139]. Both AB and ABA block copolymers were prepared, subsequently functionalized and employed as macroinitiators for the polymerization of n-butyl acrylate (BA) (Fig. 10). Due to the propensity of the PODMA segments to aggregate due to crystallization, self-assembly of the AB and ABA block-copolymer brushes was observed by AFM (Section 4). This type of material gives rise to a new class of supersoft thermoplastic elastomers [148].

2.3.1.3. Heterograft copolymers. Brushes with intermixed side chains of more than one identity can be obtained by

![Fig. 9](image_url) **Fig. 9.** Outline for backbone precursor preparation and derivatization to a macroinitiator (two routes) and subsequent side-chain growth by ATRP.

![Fig. 10](image_url) **Fig. 10.** Synthesis of PODMA-block-(PBPEM-graft-PBA) by a combination of grafting through and from. The macroinitiator was prepared by ATRP of ODMA followed by HEMA-TMS. The PHEMA-TMS block was transformed to contain macroinitiator groups, and the PBA side chains were grown by ATRP [139].
either copolymerization of a macromonomer or by copolymerization of a macromonomer with a monomer containing an initiator precursor functionality. Heterograft brush copolymers with PEG and poly(n-butyl acrylate) (PBA) chains were prepared in this manner [149]. Due to the near random distribution of side chains, the crystallization of the PEG segments was suppressed, and the brushes were homogeneous in the bulk. A similar method was used to prepare heterograft brushes with PEG and PHEMA side chains. Heterograft copolymers demonstrated microphase separation resulting in Janus-type structures [84,149].

2.3.2. Tailoring the side-chain composition

In order to systematically vary the spacing between the grafting sites, non-initiating side groups were incorporated into a backbone by copolymerization of a protected monomer, 2-(trimethylsilyloxy)ethyl methacrylate methyl methacrylate (HEMA-TMS), with methyl methacrylate (MMA) [150]. The reactivity ratios of MMA and HEMA-TMS are close to unity, which generally leads to random copolymers being formed; however, a forced gradient in backbone composition was prepared by continuous feeding of HEMA-TMS during the course of the polymerization [151]. A backbone gradient can also be obtained spontaneously by copolymerization of monomers with significantly different reactivity ratios, i.e. acrylates and methacrylates [152]. After polymerization of side chains, preparation of brushes with gradient grafting densities was verified by atomic force microscopy (AFM), which confirmed the asymmetric structure [153].

2.3.1.5. End-functionalized brushes. Synthesis of cylindrical brush molecules with a functional group at the end of the backbone provides construction blocks for more complex architectures such as observed with proteoglycan aggregates (Fig. 1). Recently, cylindrical polyelectrolyte brushes with poly(styrenesulfonate) side chains and a positively charged head group were synthesized by a combination of anionic polymerization to obtain an end-functionalized macroinitiator followed by ATRP to yield the side chains [15]. Preliminary experiments have been conducted to demonstrate formation of brush complexes with negatively charged latex particles.

2.3.2. Tailoring the side-chain composition

The “grafting from” approach allows efficient control of the chemical composition of the side chains. In addition to homopolymer brushes, one can prepare brush-like macromolecules with both random and block-copolymer side chains.

2.3.2.1. Homopolymer side chains. A wide variety of monomers have been successfully homopolymerized from macroinitiator backbones by ATRP including styrenics [25,27,49], acrylates [24,128,133,138,150,152], methacrylates [134,135,154,155,77,129], acrylonitrile [136] and acrylamides [134,156]. Other methods of CRP have been employed as well. For instance, poly(vinyl alcohol) was functionalized with xanthate moieties that facilitated macromolecular design via interchange of xanthate (MADIX)/RAFT polymerization of vinyl acetate [157]. The resulting poly(vinyl acetate) side chains were hydrolyzed to yield poly(vinyl alcohol) brushes.

2.3.2.2. Copolymer side chains. Core–shell molecular brushes have been prepared by sequential monomer addition to form block-copolymer side chains. Brushes with soft PBA cores and hard PS shells as well as the inverted structures were prepared by ATRP [133]. Similarly, one prepared PS–block-PtBA, PtBA–block-PS, and PtBA–block-PtBA (PtBA—poly(t-butyl acrylate)) side chains [24,138]; after hydrolysis of the t-butyl groups, acrylic acid units were obtained. Due to the responsive nature of the PAA blocks, conformational transitions were observed as a function of solvent quality [24]. Compared to conventional multimolecular micelles, these core–shell structures formed unimolecular cylindrical micelles that were not susceptible to dissociation on dilution. Brushes with block-copolymer side chains that coordinate metal ions can act as templates for the preparation of novel nanocomposites (Fig. 11) [158]. Unusual organization of block-copolymer brushes on surfaces is discussed in Section 4.2.

2.4. Summary of synthetic approaches

A variety of synthetic techniques have been employed to obtain controlled-structure molecular brushes. As opposed to typical linear polymers of relatively modest molecular weights, special consideration must be given to the highly congested environment. A primary concern is obtaining grafting densities sufficiently high to bring about the properties typically associated with molecular brushes. Many of the expected applications of these materials arise from their unique, highly dense macromolecular architectures.

The enhanced synthetic capability to prepare brushes with increased complexity and functionality has been accompanied by significant advancements in their characterization. Large sizes and well-defined shapes of molecular brushes enabled accurate molecular characterization through visualization of single molecules. Molecular scale observations of conformation and motion of brush-like macromolecules has received considerable attention both experimentally and theoretically. The following sections will highlight advances made in
fundamental characterization of the solution, surface, and bulk properties of molecular brushes.

3. Molecular weight and size distribution

In polymer chemistry a combination of techniques, such as GPC, light scattering, and viscometry, is employed to characterize molecular weight distribution and molecular conformation. However, the conventional techniques are often limited when applied to complex macromolecules that involve branching and heterogeneous composition [159]. In recent years, visualization of individual molecules by scanning probe microscopes has become a powerful characterization tool [160,161]. In addition to verifying synthetic strategies, molecular visualization enables accurate measurements of molecular weight, size, and conformation. The unique advantage of molecular visualization is that one obtains molecular dimensions in direct space affording more opportunities for statistical analysis. This allows manual fractionation of the visualized molecules by size, branching topology, and chemical composition, and also provides the ability to sort out the irrelevant species.

The molecular weight distribution of brush-like molecules was determined using a combination of the Langmuir–Blodgett (LB) technique and AFM [162]. The LB technique provided mass density information (mass/area), while visualization of monolayers by AFM enabled accurate measurements of the number of molecules per unit area (number/area). From the ratio of the mass density to the molecular density, the number average molecular weight was determined as

\[ M_n = \text{mass/number} \]

As shown in Fig. 12, the obtained results were in good agreement with gel-permeation chromatography (GPC) using a multi-angle laser light scattering (MALLS) detector. This approach can be applied to various molecular and colloidal species. In particular, the visualization-based approach is useful for large objects (> 10^7 Da) that are difficult to measure by light scattering and GPC.

In another study, a series of star-like brushes were prepared (Fig. 13a) with the number of arms varied from two to four, while the lengths of the side chains were kept approximately constant [140]. Molecular visualization by AFM (Fig. 13b) enabled accurate characterization of individual arms (Fig. 13d), separately from the entire molecule (Fig. 13d). In agreement with the Schulz–Flory theory for condensation polymerization, the polydispersity of the total length was significantly lower compared to that of the arm length, confirming

\[ \text{PDI}_{\text{star}} = \frac{\text{PDI}_{\text{arm}}}{f^2(f-1)\left(\frac{f}{C_0}\right)^f} \]

as derived for random coupling of \( f \) arms. The variation in polydispersity had an effect on molecular ordering [163].

4. Molecular conformation and ordering

The conformation of cylindrical brush polymers is a result of competing forces between the backbone and side chains. The densely grafted side chains repeal each other, but their ability to move apart is hindered by the backbone, which locally confines the side chains to a cylindrical volume. As a result, cylindrical brushes may exhibit different conformations on different length scales [164]. The backbone is flexible on the scale of the distance between neighboring side chains, while on length scales longer than the side-chain length, the molecules behave like semiflexible cylinders. This contrasts to flexible comb-like polymers that exhibit Gaussian chain behavior for both backbone and side chains [165]. Therefore, a combination of different techniques is required to measure both local and global dimensions of molecular brushes and to separately analyze the conformation of the backbone and side chains.

4.1. Molecular brushes in solution

4.1.1. Dilute solutions

In solution molecular brushes adopt a conformation of a worm-like object, which is characterized by length per monomer \( (l_m) \), brush diameter \( (D) \), and persistence length \( (l_p) \). The molecular dimensions depend on the degree of polymerization of the side chains and the grafting density of the backbone. However, the effect of the molecular structure on these parameters is not completely understood, and recent literature on the subject is contradictory.
Several theories have been proposed relating $l_p$ to side-chain length. If $l_p$ increases more quickly than the brush diameter, lyotropic ordering of cylindrical brush polymers in solution is expected [166,167]. Birshtein and Zhulina suggested that the ratio of persistence length to brush diameter ($D$) is approximately constant, meaning that both $l_p$ and $D$ increase at a similar rate with the length of the side chains [168]. Computer simulations of brushes with flexible side chains are in agreement with this suggestion, though they also predict that the ratio between the backbone persistent length and the brush diameter levels off with the side-chain length [164,169]. Lyotropic ordering would not be possible in such a system, though it is expected for brushes with stiff [170,171] side chains and bulky [172,173] side groups. It has also been theoretically predicted that the $l_p/D$ ratio increases with the length of the side chains as $l_p/D \sim N^{0.8}$, where $N$ is degree of polymerization of the side chains [174]. If this relation is physically true, lyotropic ordering is asymptotically approached because the persistence length increases with $D$ faster than the brush diameter.

Experimental results have also proven inconclusive, although they have led to new insights into brush conformation. Some light and neutron scattering measurements showed that both $l_m$ and $l_p$ increased with increasing side-chain length and solvent quality [23,175,176]. Other scattering experiments showed that neither $l_p$ nor $l_m$ depend on the side-chain length [87]. Recent experiments [177] have confirmed previous studies [178] that $l_p$ increases with increasing side-chain length in different solvents and that the backbone was fully extended with $l_m \approx 0.25$ nm independent on the side-chain length. Both the stiffness increase and the full extension of the backbone are consistent with theoretical estimations of an extension force on the order of several kT per monomeric unit imposed by densely grafted side chains. There is also disagreement in measurements of the brush lateral dimensions such as hard-core diameter and cross-sectional radius of gyration [87,177], which makes evaluation of the $l_p/D$ ratio as a criterion for lyotropic ordering even more ambiguous. The disagreement between the experiments can be in part due to the variation of stiffness and the backbone extension on different length scales, experimental difficulties in separation of scattering signals from the backbone and side chains, and unknown form factors. Another source of experimental errors could be due to the narrow range of the studied brushes with contour lengths ($L \approx 100$ nm) too close to the persistence length ($l_p \approx 50$ nm) [87]. As was pointed above, a combination of scattering techniques and model macromolecules are required independently to characterize the conformation of the backbone and side chains on different length scales. In addition to scattering measurements, AFM can be used as a complementary technique to determine the persistence length of PNIPAM brushes by measuring tensile forces upon stretching of tethered molecules in an aqueous solution [179].

The structural mobility of monomeric units of molecular bottle-brushes was studied by a systematic evaluation of NMR relaxation dynamics. The spin–spin relaxation time ($T_2$) was determined by Carr–Purcell–Meiboom–Gill (CPMG) NMR spectroscopic measurements.
T2 for protons that reside on the exterior and interior of the bottle-brush macromolecules varied with the grafting density and side-chain length in bottle-brush copolymers. Poly((2-(2-bromopropionyloxy) ethyl methacrylate-stat-methyl methacrylate)-graft-butyl acrylate) (poly(BPEM-stat-MMA)-graft-PBA) was studied as a model brush copolymer. The T2 values for protons of MMA units in the brush backbone significantly decreased with increasing side-chain length and grafting density of PBA. The mobility and relaxation times T2 for the side-chain PBA protons decreased with grafting density. However, after initial increase, the relaxation times eventually decreased with PBA side-chain length [180].

4.1.1.1. Molecules in semidilute solutions and melts. At higher concentrations, macromolecules interpenetrate. Excluded volume interactions become screened on length scales larger than the so-called correlation length, which is the distance at which neighboring chains start to interact. This results in coiling of molecular brushes and reduction of their overall dimensions such as the radius of gyration and end-to-end distance. However, on length scales smaller than the correlation length, the molecular dimensions remain unperturbed by the neighboring chains. This adds additional length scale to molecular brushes, which significantly complicates data interpretation of scattering measurements. Preliminary experiments indicate that cylindrical brushes become more flexible with increasing concentration above the overlap concentration [181]. The observed decrease in the persistence length might occur if the correlation length became smaller than the persistence length. More experiments need to be conducted to verify the origin of the increased flexibility.

Like many semiflexible cylindrical objects, brush-like macromolecules may orient spontaneously when the concentration is increased beyond a threshold concentration. Theoretical studies both for rigid [166] and soft [182,183] rods predict a transition above a critical ratio \( l_p/D \) of about 10. The solution then becomes a uniaxial nematic liquid crystal and forms a hexagonal phase at still higher concentrations while nevertheless displaying liquid-like disorder in the remaining third dimension. Sometimes there is no transition to a nematic system. Rather the system directly goes from the isotropic to the hexagonal state. Even though the measured \( l_p \) and \( D \) values of cylindrical brushes have been proven to be inconclusive, SAXS measurements revealed the emergence of higher-order peaks at concentration above 16 vol.% suggesting formation of a hexagonal phase [184]. At even higher concentrations, the higher-order peaks disappeared, suggesting an isotropic phase, which corresponds to a melt of side chains. These experiments confirmed the previous observations of ordering of brush-like macromolecules in solution [33] however the phase separation leading to a coexistence of isotropic and hexagonal phases has not been systematically corroborated by microscopic techniques [33,34,185].

4.1.1.2. Conformational transitions. One of the unique properties of the molecular bottle-brushes is that the flexible backbone can locally coil while steric repulsion between the side chains maintains cylindrical shape. In solution, the length and flexibility of the molecular cylinders is controlled by the solvent quality, temperature, pH, and ionic strength. The ability to trigger these conformational changes using various stimuli will greatly enhance the significance and practical value of these molecules. They could serve as miniature cushions, pistons, and electrical contacts in ultra-small pumps or locomotives. In addition to the possible micro-mechanical applications, the large number of chain-end functionalities makes them interesting candidates for potential applications as sensors, drug delivery vessels, reaction activators, and other novel applications.

Although fundamental understanding of brush polymer conformation is still incomplete, the first steps have been made in learning how to manipulate brush conformation. The extended nature of molecular brushes in solution can be tuned by incorporation of stimuli-responsive polymer segments. Not only have cylindrical brush polymers been shown to change contour length, they have also been shown to make a transition from rod-like to globular conformation. A brush of poly-N-isopropylacrylamide (PNIPAM), a polymer having a lower critical solubility temperature (LCST), was shown to collapse from an \( R_g \) of 61 nm at 20°C to 25 nm at 32°C (Fig. 14) [156]. It is interesting that after collapsing, the brush molecules did not aggregate and remained in solution as single molecules. Heteroarm copolymer brush with both PS and poly(ethylene oxide) (PEO) side chains also remained unimolecular in benzene, a solvent good for PS, but poor for PEO [86]. Similar stability during conformational changes has also been observed on surfaces and ascribed to steric repulsion of dense corona of side chains [186].

In a similar way, temperature-sensitive molecular brushes with side chains consisting of two copolymers, 2-(dimethylamino)ethyl methacrylate (DMAEMA) with methyl methacrylate, and 4-N-dimethylacrylamide with butyl acrylate were prepared by grafting-from via ATRP [134]. Poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) and poly(2-(2-bromopropionyloxy)ethyl methacrylate)

![Fig. 14. Molar mass \( M_w \) (○, right axis), radius of gyration \( R_g \) (○, left axis), and hydrodynamic radius \( R_h \) (△, left axis) of PNIPAM brushes as a function of the temperature T [156]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.](image-url)
were used as macroinitiators. Dynamic light scattering studies were performed for aqueous solutions of molecular brushes below and above LCST, and an unusual concentration-dependent LCST was observed. Due to the compact structure of molecular brushes, intramolecular collapse occurred when the average distance between molecules was much larger than the hydrodynamic dimensions of the individual macromolecules. However, when the concentration of the solution of molecular brushes was increased to the level in which the separation distance was comparable with the brush hydrodynamic dimensions, intermolecular aggregation occurred, as typically observed for solutions of linear polymers [134].

Molecular brushes with photo-tunable LCST transitions (Fig. 15) were also prepared by both statistical and block copolymerization of PDMAEMA side chains with 4-methacryloyloxyazobenzene (MOAB) [135]. Upon irradiation with UV light, the azobenzene groups of the MOAB units undergo a trans to cis isomerization that is accompanied by an increase in hydrophilicity. The increased solubility of the MOAB units in response to photo-stimulation resulted in brushes with temperature- and light-responsive behavior.

4.2. Molecular brushes on surfaces

Unlike molecular brushes in solution, one obtained better understanding of the conformation of molecular brushes on surfaces. The achieved progress was due to molecular visualization which gave access to both the local dimensions, such as contour length, brush width, backbone curvature, and persistence length, and the overall dimensions, such as radius of gyration ($R_g$) and end-to-end distance ($R_0$).

4.2.1. Homopolymer brushes

The length of molecular brushes on surfaces was shown to be nearly equal to the length of a fully extended polymer backbone [187]. The strong extension was ascribed to steric repulsion between the adsorbed side chains. From the curvature distribution and bond-correlation analysis of molecular images, an apparent persistence length is obtained. The persistence length was shown to strongly depend on the length of side chains as $l_p \sim n^{\alpha}$ with $\alpha = 2.7$, which is consistent with theoretical calculations that predict $2 < \alpha < 3$ [188]. Through variation of the side-chain length and the adhesion forces, the persistence length can be tuned over a range of 10–5000 nm. This is 0.2–100 times larger than the persistence length of DNA (~50 nm) and approaches that of F-actin (~10 μm).

From scaling analysis $\sqrt{\frac{R_g^2}{a^2}} \sim L^2$ of the overall molecular dimensions ($R_g$ or $R_0$) as a function of molecular length ($L$), the characteristic dimensionality ($\frac{\pi}{d}$) is obtained. The latter was shown to depend on the surrounding environment [189]. Under good solvent conditions (Fig. 16), the dimensionality was shown to be 1.36, characteristic of a self-avoiding walk of two-dimensional chains with excluded area [190]. This corroborates experiments on conventional linear chains [191]. On smaller length scales, the dimensionality decreased to $d \geq 1$, as expected for a rod-like object. Under theta-solvent conditions, e.g. upon embedding brushes in a melt of linear chains of the same chemical structure, brushes undergo conformational transformations from swollen coils in a melt of short chains ($d = 4/3$) to a compact coil in a melt of longer chains ($d = 2$).

4.2.2. Block-copolymer brushes

Molecular brushes with block-copolymer side chains add a new dimension to organization of polymer molecules on surfaces. The conformation of block-copolymer brushes depends on the interaction between the individual blocks, underlying substrate, and the surrounding environment (Fig. 17). If both blocks are equally attracted by the substrate, the conformation shown in Fig. 17a is expected. However, if one of block is more highly attracted to the substrate while the other block tends to segregate on the surface, then the side chains may fold back resulting in conformations depicted in Fig. 17b, c. Here, the conformation also depends on which of the two blocks is nearest the backbone. Fig. 19d shows the morphology of a brush molecule with PBA-b-PS side chains on mica [133]. Due to the polar acrylic group, the inner PBA block exhibited strong affinity for the substrate, while the PS block was significantly less attracted to the substrate and segregated at the surface, i.e. preferring the morphology in Fig. 17b. A different morphology was shown by brush molecules with PCL-b-PBA side chains (Fig. 17e) [192]. In this case, the strongly adhering PBA block was at the corona of the brush and partially penetrated between the PCL blocks and the substrate (Fig. 17c). In addition, PCL-b-PBA brushes demonstrated an unusual herring-bone morphology due to crystallization of the PCL blocks.

4.2.3. Conformational transitions

A drop of fluid adsorbed to a surface adopts a variety of equilibrium shapes depending on the interaction of the
fluid with the substrate (Fig. 18a). Unlike simple fluids, the shape of an adsorbed macromolecule is constrained by its covalently bonded architecture. Adsorption of molecular brushes to a flat substrate breaks their cylindrical symmetry resulting in partitioning of the side chains (Fig. 18b). In addition, interaction with the substrate can induce ordering of adsorbed macromolecules with particular conformations.

The conformation of adsorbed brush molecules is determined by the number of side chains adsorbed to the surface and also on the distribution of the adsorbed side chains with respect to the backbone. Depending on the fraction of adsorbed side chains and their distribution with respect to the backbone, the adsorbed molecules can adopt ribbon-like, curved, cylindrical, or globular conformations (Fig. 19). If the fraction of adsorbed side chains ($\varphi = \text{number of adsorbed side chains/total number of side chains}$) is large, then the brush will assume an extended ribbon-like conformation depicted in Fig. 19a. This conformation is energetically favored as it allows a large number of surface contacts. When the side chains are no longer strongly adsorbed to the surface, where $\varphi < 1$, brush molecules may switch to other conformations depending on the surrounding environment. In a poor solvent (e.g., air), desorbed side chains attract each other and cause coiling of the backbone into a globular

![Fig. 16.](image1) Brush molecules change from (a) flexible to (b) rod-like conformation with increasing degree of polymerization of side chains $n$. (c) Persistence length $l_p$ is determined as a distance along the chain at which the fractal dimension changes from $d = 1$ to 1.33. (d) The persistence length increase with the side-chain length as $l_p \sim n^{2.7}$ [187].

![Fig. 17.](image2) (a–c) Schematics of different morphologies that can be observed upon adsorption of brush molecules with block-copolymer side chains. AFM height micrographs of brushes with PBA-b-PS (d) and PCL-b-PBA (e) side chains on a mica substrate. The observed morphology in (d) was interpreted as (b) [133], while the morphology in (e) resembles schematics in (a) [194]. The herring-bone structures in (e) are assigned to crystallization of the PCL blocks at the backbone. Adapted with permission from Refs. [133,192]. Copyright 2001, 2006 American Chemical Society.
conformation (Fig. 19d). Another cylindrical conformation with $\phi_a \ll 1$ is stabilized by steric repulsion of desorbed side chains in a good solvent (Fig. 19c).

### 4.2.4. Rod-globular transition

There is great potential for the application of pressure-responsive macromolecules that change their conformation in response to variations in two-dimensional film pressure. The latter can be controlled by lateral compression and by changing the surface energy of the substrate. Lateral compression of adsorbed cylindrical brushes led to a first-order phase transition from a rod-like conformation to a more compact globular conformation [193]. Similar conformational transformations were observed upon decreasing the surface energy of the substrate [194]. The observed conformational changes are seen in the series of AFM images of PBA brushes in Fig. 20. Two types of transformations were observed. First, the average contour length of the brush molecules decreased. Second, as the interaction energy dropped below a certain limit, the rod-like molecules underwent a transition to a globular conformation. The transition resulted from the competition of the energetically favorable interaction of side chains with the substrate and the entropically unfavorable extension of adsorbed side chains. Partial desorption of PBA side chains decreased tension along the backbone and led to its contraction. When the fraction of adsorbed side chains was reduced below a critical value, a discrete transition occurred from an extended conformation to a globular one. Because the conformation of individual brush molecules on surfaces can be observed by AFM, they can be used to probe the surface energy of a substrate.

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**Fig. 18.** Adsorption of simple liquids and molecular brushes. (a) A drop of simple fluid easily adopts a variety of shapes (shown here is the pancake). (b) The conformation of adsorbed molecular bottlebrush is confined by its interconnectivity and cylindrical symmetry of the branches.

**Fig. 19.** AFM height micrographs along with schematics demonstrate four distinct conformations observed for molecular brushes adsorbed on different surfaces. The conformational transformations occur due to variations in the fraction of adsorbed side chains ($\phi_a$) and due to uneven distribution of the side chains with respect to the backbone. Depending on the interaction with substrate and with the surrounding medium the following conformations were observed: (a) spontaneous curvature ($\phi_a = \phi_b$), (b) ribbons ($\phi_a \geq 1$, $\phi_b = \phi_c = 0.5$), (c) cylindrical ($\phi_a < 1$, $\phi_b = 0.5$, repulsion between desorbed side chains), and (d) globular ($\phi_a < 1$, $\phi_b = 0.5$, attraction between desorbed). As such, the brushes with their responsive conformational changes make ideal molecular actuators that induce bending, contraction, compacting, and coiling.
Recently, environment-controlled AFM was used to in-situ monitor conformational changes of single brush molecules [195]. As shown in Fig. 21, the molecules transformed reversibly from an extended wormlike conformation to a compact globular conformation when the relative vapor pressure of water and ethanol was changed in the surrounding atmosphere. Adsorption of water and ethanol changed the surface properties of the mica substrate and thus the attraction of the side chains to the substrate. Coexistence of collapsed and extended strands within the same molecule indicated a first-order transition in agreement with previous studies of dense monolayers [193].

Along with the side-chain length, the grafting density of side chains is another parameter that governs the rod-globule transition [153]. According to theoretical predictions, denser brushes should readily show this transition, while loose brushes preserve their extended conformation when compressed. This prediction was verified by studying brushes with a gradient of grafting density. Upon increasing the film pressure, the rod–globule transition occurred at the end where the brush was densely grafted.
leaving a molecule with a globular “head” and an exten-
ded “tail”—a so-called tadpole conformation (Fig. 22).
Observing anisotropic behavior of gradient brushes de-
monstrates the ability to design brushes with inherent asymmetry and raises the possibility of controlling the conformation of brushes in such a way as to direct the motion of individual molecules.

4.2.5. Spontaneous curvature

Due to the transition from cylindrical to planar symmetry, the conformation of adsorbed brush molecules is also dependent upon the distribution of the side chains with respect to the backbone given by fractions of the side chains adsorbed on the right ($\phi_R$) and left ($\phi_L$) sides of the backbone. In Fig. 18b the brush molecules exist in a straight conformation because the distribution of side chains is $\phi_R = \phi_L = 0.5$. In contrast, the brush in Fig. 18a illustrates the distribution of side chains as $\phi_R \neq \phi_L$. The uneven distribution of the side chains induces spontaneous curvature in the backbone and may result in a helical conformation [196]. It has been experimentally shown that the random coil (locally straight) conformation is not stable and undergoes a transition to characteristic C- or S-like conformations that have a defined-curvature (Fig. 23). A similar kind of instability was predicted for bilayer planar brushes, wherein polymer chains were allowed to change their position relative to the substrate plane [197]. Spontaneous curvature can also occur in heteropolymer brushes. Schmidt et al. used macromonomer polymerization to statistically copolymerize poly(2-vinyl pyridine) and poly(methyl methacrylate) macromonomers to form a brush that changed from wormlike to horseshoe and meander-like structures in selective solvents [90]. Theoretical interpretations were proposed to explain the origin of the spontaneous curvature.

4.2.6. Ordering in thin films

Thin films possessing long-range structural order on sub-100 nm length scales are vital for many technological applications such as magnetic recording [198] and optoelectronic [199] devices, molecular separation media [200], and liquid crystal displays [201]. Ordered structures can be prepared using lithographic techniques [202,203] and external fields [204]. Ordering can also occur spontaneously upon adsorption of designed macromolecules [205–215] and colloidal particles [216–218]. Large
macromolecules and colloidal particles are attractive building blocks for surface patterning due to native sub-100 nm size and well-defined shape.

4.2.7. Star-like brushes
A series of PBA star-like brush molecules with 2, 3, and 4 arms were synthesized by ATRP [140]. Visualization of these architecturally intriguing molecules by AFM allowed for the analysis of individual arms as well as the whole molecules. The polydispersity of the samples was found to decrease with branching functionality, while the polydispersity of the individual arms was the same for every sample. The lowered polydispersity had an immediate effect on the ordering behavior [163]. As shown in Fig. 24, the four-arm star molecules (PDI = 1.04) under compression were observed to collapse into disk-like formations and undergo ordering with an orientational correlation length of ten intermolecular distances. For a linear brush of similar composition (PDI = 1.15), the correlation length was only two intermolecular distances.

4.2.8. Flow-induced epitaxial ordering
One of the disadvantages of large macromolecules is that their ordering on surfaces is kinetically hindered, typically resulting in a short-range order. Recently, significant enhancement of molecular alignment has been observed during spreading of brush-like macromolecules on the surface of highly oriented-pyrolytic-graphite (HOPG) [219]. Unlike conventional flow-induced orientation of anisotropic objects such as rod-like particles, liquid crystal molecules, and semi-flexible polymer chains [220–222], the observed molecular orientation is not coupled with the direction of flow (Fig. 25). This suggests that the role of flow is merely to enhance diffusion and thus facilitate epitaxial ordering [223–229] of the large macromolecules, while the direction of orientation was independent of the flow direction, being solely determined by the underlying crystallographic lattice of the HOPG surface.

5. Physical properties
5.1. Solution properties
Originally, side chains were introduced to comb-like and brush-like polymers to improve solubility and achieve self-organization of rigid conjugated polymers such as polyaniline [230–233]. In addition, significant interest emerged in adding side-chain mesogens to induce liquid crystalline ordering of flexible linear chains. For flexible side chains, theory predicts that stiffening of the backbone is not sufficient to cause ordering of cylindrical brushes. However, several experimental studies reported hexagonal ordering of cylindrical brushes upon increasing solution concentration (Section 4.1). In recent years, synthetic chemistry delivered even more advanced brush-like architectures including various copolymer structures such as block-copolymer brushes, heterograft brushes, and random copolymer brushes (Fig. 2). For example, a copolymer with a linear PS block and a brush block with PtBA side chains was prepared by anionic polymerization of the backbone and subsequent ATRP for the side chains [145]. After hydrolysis of the t-butyl groups, the resulting PAA side chains rendered the brush block hydrophilic. Due to their amphiphilic and anisotropic nature, the brush–coil block copolymers demonstrated unusual association in selective solvents. In aqueous solution, the copolymers aggregated to form micelles with sizes of $R_g = 54$ nm and aggregation numbers of approximately 4–5, as determined by static light scattering and AFM (Fig. 26). Interestingly, when the
opposite block-copolymer structure was formed, i.e. PAA linear block and brush block with PS side chains, micelles with a broad distribution of sizes, some of which were greater than 300 nm, were observed by transmission electron microscopy (TEM) [146]. The latter brush–coil block copolymers were prepared by grafting through of methacryloyl–PS macromonomers via coordination polymerization with a metalloocene catalyst followed by polymerization of tBA and subsequent hydrolysis to PAA. The living nature of the first polymerization to prepare the polymacromonomer block could not be confirmed, which might explain the broad distribution of micellar sizes observed in solution.

5.2. Bulk properties

The high density and proportion of relatively short side chains present in molecular brushes has an important effect on their resulting bulk properties. Due to the radial distribution and extended nature of the backbone, chain packing can be significantly hindered, leading to morphologies different than expected for simple linear polymers with the same identity as the side chains.

5.2.1. Viscoelastic properties

Viscoelastic properties of brush-like macromolecules are vital for biological functions, such as shock-absorption and lubrication by articular cartilage and mucociliary clearance of lung airways. Based on molecular brushes, one can also design new materials with unusual mechanical properties. A large fraction of densely grafted side chains effectuates in dilution of backbones and therefore lowers the concentration of entanglement strands. The self-disentangled molecular brushes demonstrate interesting viscoelastic behavior which depends on the side-chain length and the backbone length. For brushes with long backbones, master curves for dynamic storage modulus may reveal two rubbery plateaus at about 10^5 and 10^4 Pa [167,148]. The first plateau is ascribed to relaxation of side chains, while the second plateau results from relaxation of an entire brush molecule. Analysis of the brush structure and mechanical properties of PEGMA brushes indicated the specific architecture of the copolymers had completely suppressed crystallization of the PEG, leading to amorphous, homogeneous materials [77]. When the brushes were transformed to a cross-linked network structure by heat treatment (or by spontaneous cross-linking during polymerization), high local mobility and sufficient macroscopic mechanical stability were achieved simultaneously, giving rise to a class of materials termed super-soft elastomers, with a rubbery plateau of the shear modulus (G') of less than 10^5 Pa (Fig. 27). Other materials with moduli in this range (e.g., hydrogels) depend on small molecule solvation of network structures in order to retain a morphology that facilitates the soft elastomeric properties. For the polymeric brushes, these unusual mechanical properties were observed for the first time in the bulk phase and were the result of the molecular network of the backbone being diluted by short side chains that were below the entanglement limit. Because the side chains do not entangle and are covalently attached to the matrix, stability against evaporation or deformation is possible, and the networks resisted collapsing. Due to high molecular mobility of the PEG side chains, these brushes have been considered as solvent-free cation conducting materials for use in lithium battery applications [93].

5.3. Thin film properties

5.3.1. Adsorption-induced association and dissociation

On surfaces, extension of the backbone due to steric repulsion of the adsorbed side chains results in a rod-like conformation. This gives a nanometer-sized building block with well-defined shape and multiple chemical functionalities. Depending on the strength of adsorption and the molecular architecture, brush molecules may undergo both association and dissociation upon their adsorption to surfaces. Fig. 28 demonstrates physical association of brush-linear block copolymers on a solid substrate due to crystallization of octadecyl tail segments [139]. The molecules spontaneously associate to form multimers such as chains and branches.
In a different series of experiments, molecular visualization was successfully used to monitor the reverse process, i.e. scission of covalent C–C bonds of the polymer backbone brush-like macromolecules upon adsorption onto a substrate [187]. Fig. 29a shows a series of AFM images obtained for different incubation times of a brush molecule with particularly long side chains on a water/propanol substrate. As the time spent on the substrate increases, the molecules are become progressively shorter while the number of species per unit area correspondingly increases, indicating to scission of the backbone (Fig. 29b). By measuring the length decrease as a function of time, the scission process was shown to be a first-order reaction with a rate constant of $k = 2.3 \times 10^{-5}\text{s}^{-1}$ (Fig. 29c). The macromolecular destruction occurs because side-chain-induced stretching of the polymer backbone in order to maximize the number of contacts with the substrate. This phenomenon opens intriguing opportunities for molecular-scale studies of dissociation kinetics and for the design of macromolecules that induce tension and fracture on surfaces in a specific way.

5.3.2. Spreading

Wetting properties of thin polymer films impact coatings, lubrications, and microfluidics. The spreading behavior of thick films can be rigorously described by continuum hydrodynamic theories (with a thickness on the order of 10 nm) [234–241], however, their use for thin films, particularly monolayers, is ambiguous [242–252]. This necessitates experimental data for motion of fluids on the molecular scale. A breakthrough in molecular visualization of spreading was achieved by using brush-like macromolecules [253]. Through molecular visualization, both the displacement of the contact line and the movement of individual molecules within the film were simultaneously measured (Fig. 30a). While, the film length was shown to follow the classical dependence $L = \sqrt{Dt}$, the individual molecules moved in a random-walk fashion in the frame of the flowing film (Fig. 30b). The time dependence of the mean square intermolecular distance $\langle r^2(t) \rangle = 4D_{\text{mol}}t$ gives the diffusion coefficient $D_{\text{mol}} = 1.3\text{nm}^2/\text{s}$. The origin of the molecular diffusion within the flowing monolayer is still subject to debate, though the diffusion is clearly enhanced by the flow, as evidenced by linear increase of the diffusion coefficient with flow velocity (Fig. 30c).

The unique properties of brush-like macromolecules on surfaces arise from their ability to change conformation in response to variations of the surface energy of the substrate and lateral compression. Here, molecular visualization of compressible molecules becomes especially powerful tool, as it allows sensing the pressure gradient that drives the flow on the sub-100 nm scale [254]. The conformation of the molecules changes along the length of the film in terms of the curvature, height, and length of the molecules (Fig. 31a). After appropriate calibration, these molecular sensors were used to measure the local pressure within precursor films of polymer drops spreading on a solid substrate (Fig. 31b). From the pressure gradient, the friction coefficient of the molecules with the substrate can be devised. The unique aspect of this method is that, for the first time, it has become possible to decouple and to measure independently the driving and frictional forces that control spreading rate. This method is an alternative technique to diffusion measurements for determining molecular friction on surfaces.

The spreading-induced conformational transformations were shown to have even more dramatic effect on the spreading behavior. Recently, a new type of flow fingering instability in polymer monolayers was observed [255]. Through use of AFM, the development of the instability was monitored over a broad range of length scales from the millimeter-long precursor film all the way down to the movements of individual molecules within the film (Fig. 28). Tracing the evolution of the instability pattern on the molecular scale enabled understanding of the underlying physical mechanism. The instability was shown to be triggered by conformational changes of flowing macromolecules, which lead to an instantaneous jump both in the monolayer thickness and in flow velocity across the phase boundary. This instability demonstrates the unique property of branched macromolecules abruptly switching their conformation, resulting in an

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**Fig. 28.** Association of poly(n-butylacrylate) brushes due to crystallization of linear poly(octadecylmethacrylate) chains on both ends of the brush backbone [139]. Adapted with permission from Ref. [139]. Copyright 2003 American Chemical Society.
abrupt change in the spreading velocity at the interface between two conformationally different phases.

6. Summary and outlook

The relatively recent emergence of polymerization techniques capable of accurately controlling polymer molecular weights and chain architectures has significantly facilitated the preparation of well-defined molecular brushes. As opposed to typical linear polymers of relatively modest molecular weights, special consideration must be given to the highly congested environment to obtain grafting densities sufficiently high to bring about the properties typically associated with molecular brushes. Indeed, many of the expected applications of these materials arise from their unique, highly dense macromolecular architectures. While a variety of techniques have proven useful for the synthesis of densely grafted copolymers, CRP methods have proven particularly promising for the versatile preparation of highly functional molecular brushes by a grafting from approach.

The high molecular weight and extended conformations of molecular brushes facilitates investigation by methods typically not applicable to single molecules, and as a result, molecular brushes have received considerable attention both experimentally and theoretically. Visualization of individual molecules on surfaces by microscopy allows the calculation of size, molecular weight, and molecular weight distribution, while also simplifying...
confirmation of macromolecular architecture (stars, rod-coil brushes, etc.). Observations of individual brushes under more concentrated conditions allows the characterization of, for instance, monolayer spreading and chain scission in an unprecedented, directly visualized manner. In solution, NMR and light scattering investigations have indicated that congestion in the vicinity of the brush backbone is significant enough to affect relaxation dynamics and responsive aggregation behavior.

While several applications for molecular brushes have been suggested, further investigation of synthesis and surface, bulk, and solution behavior are being conducted in order for their potential to be more fully realized. For instance, grafting from via radical polymerization typically requires low polymerization rates and limited monomer conversion to avoid macroscopic gelation arising from intermolecular termination in multifunctional systems. Recent progress in heterogeneous ATRP methods [256–261] demonstrates this undesirable network formation can be limited while maintaining appreciable rates and relatively high degrees of monomer conversion [262]. These types of synthetic advances, coupled with increased understanding of structure-property relationships, are required in order to more fully capitalize on the inherent biomimetic nature of molecular brushes.

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References


Tongue CW, Christensen C, Meidal M. Peptidotriazoles on solid phase: [1,2,3]-triazoles by regiospecific copper(I)-catalyzed


