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Monomolecular Films of Arborescent Graft Polystyrenes

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ABSTRACT: Scanning force microscopy has been employed to visualize the molecular organization of arborescent graft polystyrenes with different branching densities as monolayer films cast on mica. The apolar polymers were depicted as distinct hexagonally packed globuli whose size was consistent with molecular dimensions obtained from viscosity and dynamic light scattering measurements. Distortions of the long-range order were observed and attributed to the inherent polydispersity of the polymers. The layer thickness, i.e., the particle diameter in the *z*-direction, depended on the branching density and indicated formation of a prolate shape in the vicinity of the flat substrate after evaporation of the solvent. Molecules with a high branching density ($M_b \sim 500$ g/mol, average molecular weight between grafting points) recovered a spherical geometry after annealing above the glass transition temperature. In the case of a lower branching density, e.g., $M_b = 2000$ g/mol, the "pancake" structure remained stable upon annealing. The data demonstrate that arborescent graft polymers represent a peculiar type of colloidal particles which consist of one molecule possessing a topologically defined surface.

Introduction

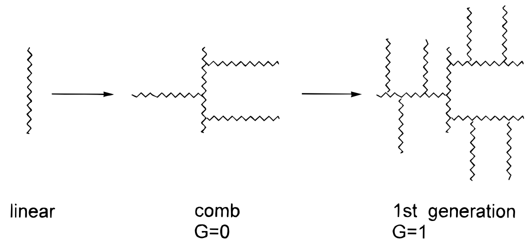
In recent years new macromolecular architectures have been developed with a well-defined topology such as star polymers,[1] dendrimers,[2,3] hyperbranched polymers,[4−6] arborescent graft,[7] or comb-burst[8] polymers, and polymacromers.[9,10] In particular, the concept of dendritic chain growth had a large impact because it allows the preparation of macromolecules with rigorously controlled molecular weights, number of branches, and terminal groups.[11−13]

Instead of using small molecules as building blocks like in the case of dendrimers, polymer units have also been used to build regularly branched structures. Cascade-branched or arborescent graft polymers were obtained by employing the "graft on graft" strategy illustrated in Scheme 1.

Starting with a linear polymer, the branching functionality was progressively increased by repeated functionalization and anionic grafting steps.[7] The concept of arborescent graft polymers allows the preparation of cascade molecules with molecular weights ranging from 5×10^4 to more than 5×10^8 and radii of gyration ranging from 8 to 100 nm.[14,15] The hydrodynamic behavior of arborescent graft polystyrenes in a semidilute solution approached that of a hard sphere as the branching density increased.[7,14]

The topologically defined surface and the colloidal size of cascade-branched polymers justify denoting them as *molecular particles* in which, however, molecular flexibility and surface overlapping should be taken into account. Thus, cascade polymers exhibit some peculiar features: (1) Interactions between molecules depend on interfacial forces which are determined by the chemical nature of the molecular surface, the deformation of the particles, and surface overlapping resulting in a steric repulsion due to a penalty in entropy. (2) The molecular surface is not smooth and rigid but spatially diffuse and dynamically rough. (3) Dynamics of the densely branched molecules cannot be solely effected by segmental motions, e.g., reptation of the branches, but requires displacement of the particles as a whole.

Scheme 1



From this point of view and the fact that size, shape, rigidity, and molecular surface, and hence interactions and dynamic properties, can be tailored quite accurately, molecular particles open new challenges in designing materials. An aspect of particular interest is the formation of thin regular films. Assemblies of colloidal particles can be used to prepare a nanoscopic pattern over the entire surface of a planar substrate.[16,17] So far this has been studied mostly with polymer latices which were deposited from aqueous suspensions.[18−23] Formation of an ordered densely packed monolayer of latex particles was observed under appropriate conditions of particle charge, density of particles, and electrolyte concentration.[20] Although polymerization in microemulsions allows the synthesis of ultrafine latex particles within a size range from 5 to 50 nm with a narrow size distribution,[24] the deposition of an ordered monolayer is known to be increasingly difficult as the diameter of the particles decreases.[18] Vigorous Brownian motion and capillary effects create a state of disorder in the system that is difficult to control. So far, the smallest arrays of latex spheres prepared had a periodicity of 42 nm.[23]

This work is directed toward the formation of ultrathin films from arborescent graft polystyrenes. These well-defined "molecular particles" are nonpolar. Film formation should be controlled by dispersion forces, molecular interpenetration, and rigidity of the branched structure. Recently, we showed that starburst carbosilane−carbosiloxane dendrimers formed regular mono-

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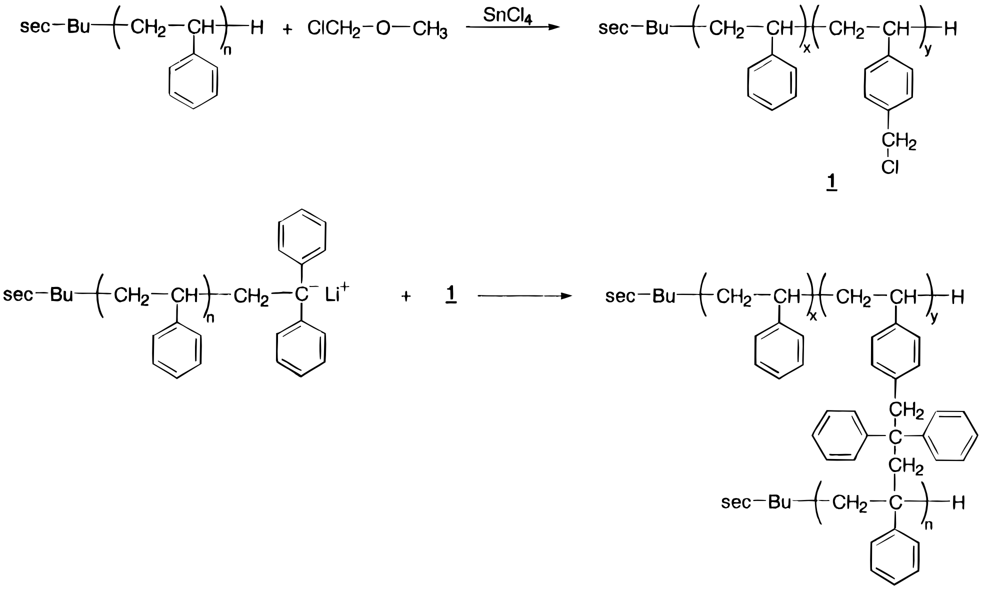
Scheme 2



and multilayers on flat surfaces of either glass, mica, or pyrolytic graphite.[25,26] Whereas in that case the thickness of the layers was determined by the radius of the molecules, introduction of specific terminal groups was shown to cause orientation and deformation of dendritic molecules at the surface.[27−30] Because of their larger size, arborescent graft polymers are expected to form an even more easily ordered surface pattern with a periodicity below 100 nm.

Experimental Section

Arborescent graft polystyrenes have been prepared as described before and were characterized by means of light scattering, size-exclusion chromatography, and viscosity.[7,14,15] The products were fractionated to remove residual ungrafted linear polymers.[15]

Samples for scanning force microscopy (SFM) measurements were prepared by spincasting at 2000 rpm. Dilute solutions in toluene were cast at ambient conditions on a mica surface. Layered crystals of muscovite mica were freshly cleaved before the casting procedure. Depending on the molecular weight, the concentrations were varied in a range of 0.1−0.5 wt % to approach complete coverage by a molecular monolayer.

SFM micrographs were measured with a Nanoscope III (Digital Instruments, Santa Barbara, CA) operated in the tapping mode[31] at a resonance frequency of ~360 kHz. The measurements were performed at ambient conditions using Si probes with a spring constant of ~50 N/m. Tips with an apex radius below 10 nm were selected by using the well-defined stepped structure of a $SrTiO_3$ single crystal wafer consisting of alternating (103) and (101) planes.[32,33]

Results and Discussion

Arborescent graft polystyrenes, AGP, have been synthesized by grafting poly(styryllithium) chains of narrow molecular weight distribution onto partially chloromethylated polystyrene (Scheme 2).

This procedure was carried out repeatedly on the same core, yielding a cascade structure as depicted in Figure 1. The average number of grafts per primary chain was chosen to be about 10, thus ensuring a steep increase in molecular weight with each generation. Molecular mass should be given by $M = M_{\mathrm{br}} + \sum_n^{G+1} M_{\mathrm{br}}$, where $n = 10$ is the number of active sites per branching unit, $G = 0, 1, 2, ...$ is the generation number, and M_{br} is the molecular mass of the branch unit.

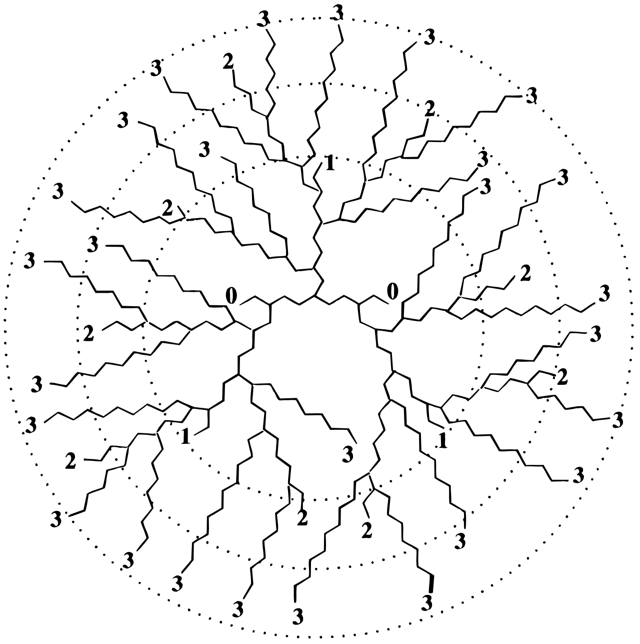


Figure 1. Schematic illustration of the cascade growth of arborescent graft polymers as a result of successive grafting reactions. The dotted circles and numbers correspond to the grafting steps up to generation $G = 2$.

The absolute molecular weights from light scattering, apparent polydispersities from SEC analysis, and average number of branching points per molecule are listed in Table 1. Sample denotation refers to the once-grafted polystyrene as generation 0 and the comb-polystyrene which was further grafted as the first generation. For example, S05-3 is a third-generation arborescent graft polystyrene built from primary chains with a molecular weight of 5 × 10^3 by four successive grafting steps. Even though the grafting efficiency was optimized, graft polymers obtained from the reactions were contaminated by a small amount of ungrafted linear polystyrene. This was particularly the case for higher generations when grafting on the overcrowded arborescent structure became more difficult.[7,15] Linear polystyrene could, however, be removed easily by fractionation in toluene/methanol mixtures.

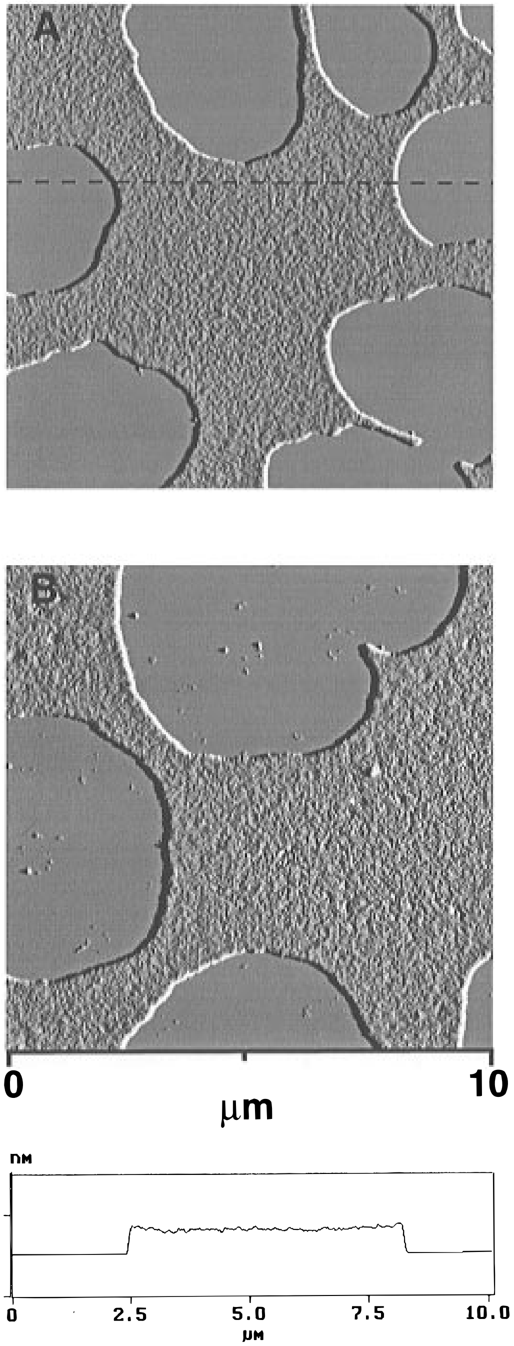


Figure 2. SFM micrographs of thin films prepared by adsorption of fractionated (A) and nonfractionated (B) arborescent graft polystyrene S05-3 on the surface of mica from a 0.5 wt % solution in toluene. The tiny depositions in the dewetted areas of mica are attributed to a small fraction of ungrafted linear polystyrene contaminant. The cross-sectional profile recorded along the reference line in A indicates a monomolecular thickness of the films.

Arborescent graft polystyrenes of different generations and different grafting densities were cast to prepare ultrathin films and studied by scanning force microscopy. Figure 2 shows two SFM micrographs for fractionated and nonfractionated polystyrene S05-3. In both images the substrate is only partly covered by a thin film of the polymer. The incomplete coverage results from dewetting of the substrate during evaporation of the solvent, preventing thinning of the solution layer below a certain equilibrium thickness.[34,35] Dewetting was almost perfect in the case of the fractionated sample, whereas the nonfractionated sample yielded small depositions or islands in the dewetted areas. The latter may be attributed to the small fraction of ungrafted linear polystyrene. According to SEC data, this

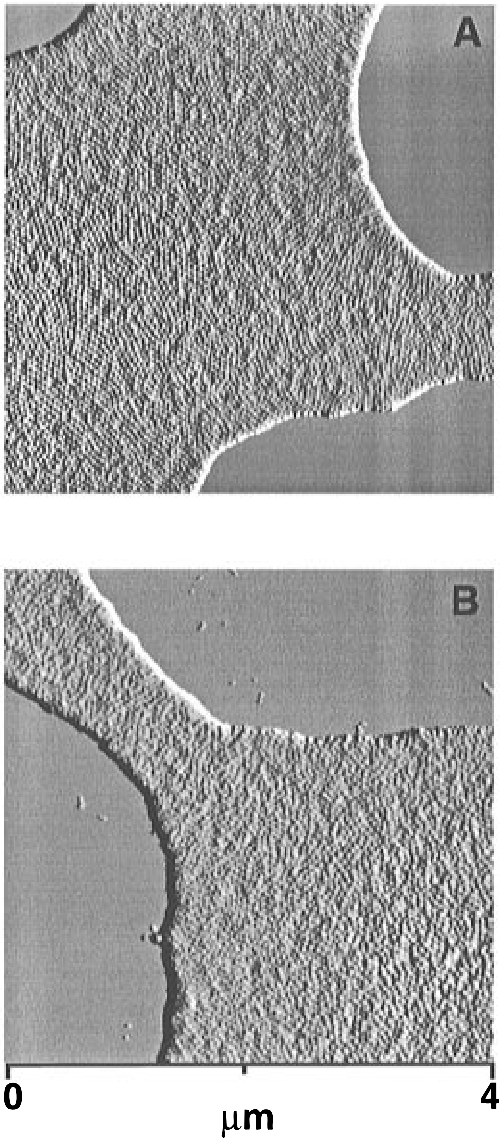


Figure 3. SFM micrographs depict the fine structure of the films in Figure 2 as a monolayer of densely packed globular molecules. In contrast to the irregular packing of AGP molecules (B), the fractionated sample (A) demonstrated almost perfect hexagonal ordering.

Table 1. Nomenclature and Molecular Weights of Arborescent Graft Polystyrenes

sample	M_w(br)[a]	M_w(AGP)[b]	M_w/M_n[a]	f_w[c]
S05 (linear)		4.6×10^3	1.1	1
S05-0 (comb)	7.7×10^3	1.2×10^5	1.13	15
S05-1 (1st gen)	4.7×10^3	1.0×10^6	1.16	190
S05-2 (2nd gen)	5.4×10^3	5.1×10^6	1.28	760
S05-3 (3nd gen)	4.4×10^3	2.9×10^7	1.24	5430
S05-3 (3nd gen)[d]	4.4×10^3	3.0×10^7	1.13	5650
S20		2.3×10^4	1.05	1
S20-0	21.9×10^3	3.9×10^5	1.13	17
S20-1	20.7×10^3	6.8×10^6	1.16	310
S20-2	19.7×10^3	5.5×10^7		2440
S30		28×10^3	1.05	1
S30-0	28×10^3	5.7×10^5	1.12	18
S30-1	27×10^3	9.0×10^6	1.22	310
S30-2	27×10^3	1×10^8		3400
S30-3	28×10^3	5×10^8		14300

[a] By SEC analysis relative to narrow molecular weight polystyrene standards. [b] Determined from light scattering.[16] [c] Branching functionality $f_w = [M_w(G) - M_w(G - 1)]/M_w(\mathrm{br})$. M_w(br) = molecular weight of branches. [d] After fractionation.

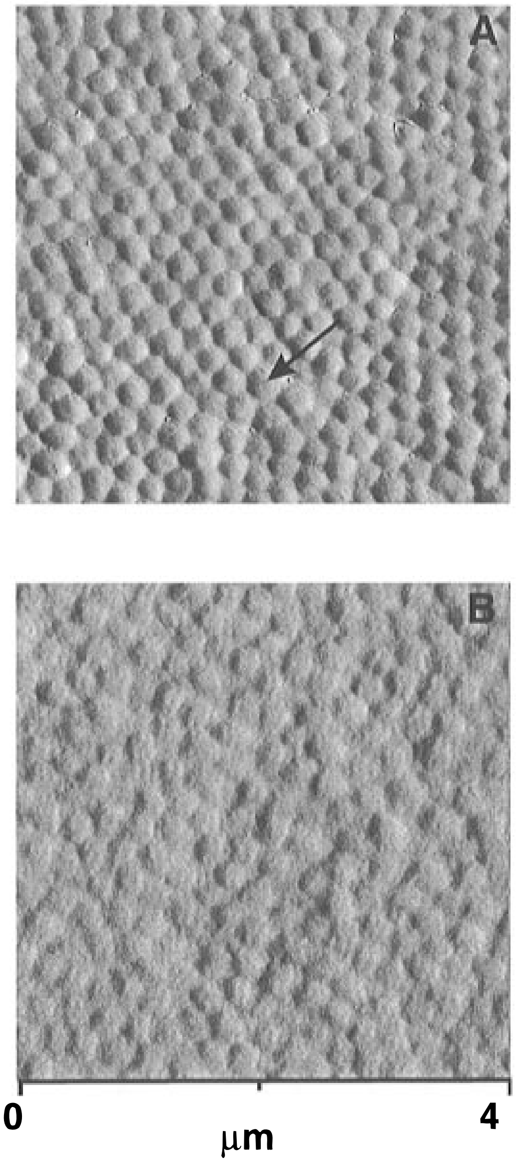


Figure 4. Higher magnification SFM images of monomolecular films of the fractionated (A) and nonfractionated (B) S05-3 polymers. In both cases, each sphere corresponds to one AGP molecule having a diameter of 50 nm and a height of about 35 nm. Due to the inherent polydispersity of the polymers, one of the most typical defects observed was a relatively large molecule surrounded by seven neighbors. One such defect is indicated by the arrow in A.

fraction constitutes approximately 1.3 wt % of the original S05-3 product.

The *z*-profile along the line in Figure 2A demonstrates for the covered areas a uniform film thickness of 35 nm, which is in good agreement with the expected diameter of the globular molecules (see below). The molecules were resolved when the AGP films were scanned with a higher resolution. SFM micrographs in Figure 3 show that the thin films in Figure 2 actually represent a monolayer of densely packed small balls.

Close examination of the micrographs in Figure 3 reveals a difference in the ordering of the globular molecules for the same two samples. In contrast to the irregular packing of AGP molecules in Figure 3b, the fractionated sample displays much more hexagonal ordering. Typical defects like dislocations and point defects resulting in clearly developed domain boundaries can be identified.

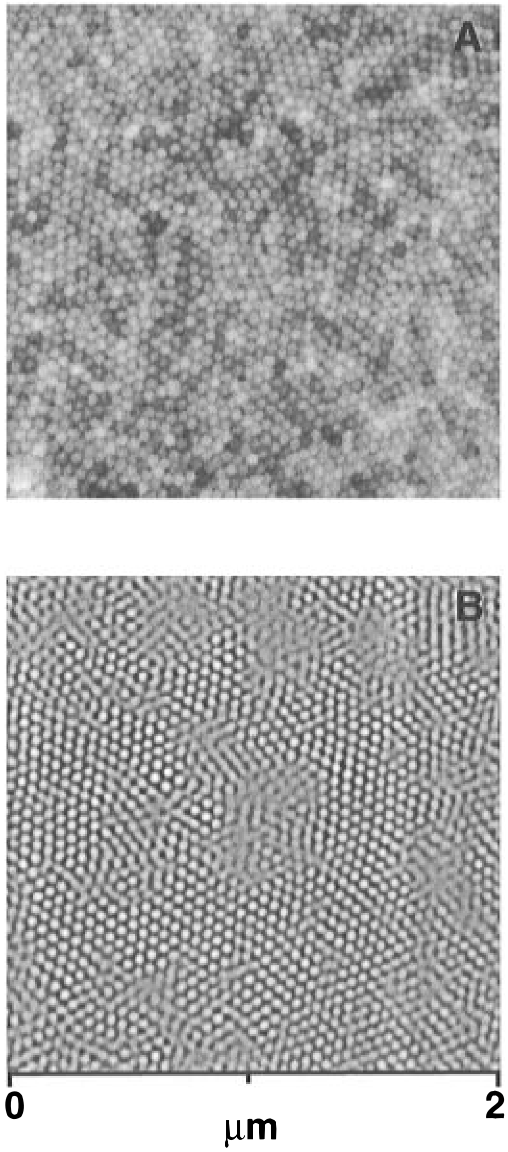


Figure 5. Structure of the monolayer of S05-3 arborescent graft polystyrenes cast on mica as prepared (A) and Fourier filtered (B). The filtering procedure clearly identified the domain structure of the film. The diffuse patterns in B correspond to local defects like grain boundaries and larger molecules which can be seen in the original structure in A.

Figure 4 depicts images of the fractionated and the nonfractionated samples at a higher magnification. In both cases, the molecules have a diameter of about 50 nm. The irregular structure in Figure 4B can be explained by the contamination of the nonfractionated sample with linear polystyrene. The local distortions of the hexagonal ordering in Figure 4A are attributed to the inherent polydispersity of the polymers. A typically observed defect is a relatively large molecule surrounded by seven neighbors. One such defect is indicated by the arrow in Figure 4A.

Long-range order in the S05-3 films was evaluated using two-dimensional Fourier transformation of the SFM images. The original micrograph in Figure 5A was transformed into Fourier space, and the most intense peaks were selected for the reverse transformation. The resulting image in Figure 5B demonstrated ordered domains with a width of about six molecular diameters. Diffuse patterns in the filtered image correspond to the local defects mentioned above.

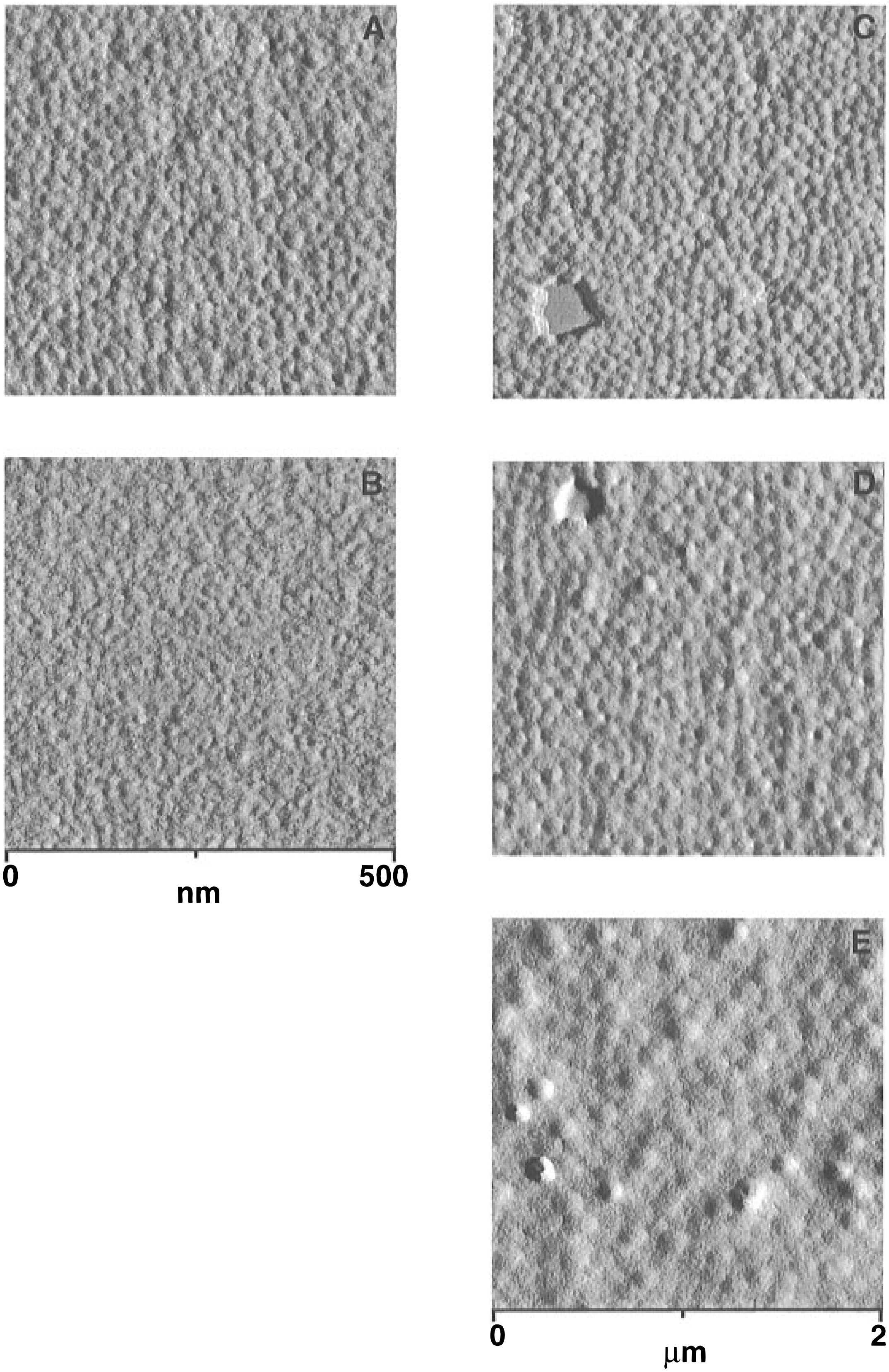


Figure 6. SFM micrographs demonstrating that different types of arborescent graft polystyrenes can form a monolayer of densely packed globular molecules by casting them on mica from toluene solutions: (A) S05-1, (B) S05-2, (C) S20-2, (D) S30-2, (E) S30-3.

Visualization of the individual molecules by SFM offers the opportunity to compare the molecular dimensions shown in the pictures with the molecular characterization results in dilute solution. Taking the molecular weight of S05-3 from Table 1, a hypothetical hard-core diameter of 46 nm is calculated for a collapsed spherical molecule with a bulk density $\rho = 1.05$ g/cm^3 for polystyrene. This value is in very good agreement with the data obtained by SFM measurements, yielding an ellipsoidal shape with a height of 35 nm and a lateral diameter of 50 nm. The ellipsoidal shape can be explained by the interaction of the molecules with the substrate and can be regarded as an indication of the rigidity of the highly branched molecular structure.

Table 2. Molecular Dimensions Determined from SFM Measurements on Thin Films, Viscosity, and Dynamic Light Scattering Data in Toluene

sample	film thickness[a], nm	particle diameter, nm	hard-core diameter,[b] nm	hydrodynamic diameter[c] D_η, nm	hydrodynamic diameter[c] D_h, nm
S05-1	5	19	15	22.8	22.8
S05-2[d]	25	21	26	49.6	55.4
S05-3	35	50	46	91.4	84
S05-3[e]	44	41	46	91.4	84
S20-2	14	96	57		136
S30-2	26	110	72	157.6	161.6
S30-3	80	170	120	248	284

[a] Values from SFM were obtained with an accuracy of ±1 nm.
[b] Calculated for a sphere with a weight of M_w(AGP) and density $\rho = 1.05$ g/cm3 for polystyrene.
[c] From solution viscosity and dynamic light scattering.[9,16,17]
[d] The sample S05-2 did not show any regular pattern. The disk diameter was estimated as a characteristic size of the surface roughness.
[e] After annealing at 150 °C for 2 h.

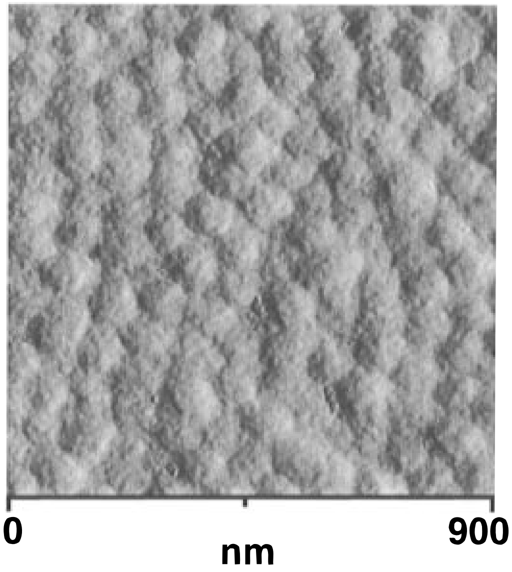


Figure 7. SFM micrograph showing molecular packing of the S20-2 arborescent graft polystyrene. Because of the lower branching density, the AGP molecules of S20-2 were strongly flattened by the adsorption forces. The resulting diameter and height of the S20-2 molecules are about 90 and 14 nm, respectively. The micrograph should be compared with that of S05-3 in Figure 4 whose molecular weight is comparable to S20-2.

Thin films of five other arborescent polystyrenes listed in Table 1 were examined as well. Figure 6 gives an overview of SFM micrographs of the other arborescent polystyrenes, which all formed densely packed monomolecular layers. The molecular dimensions depicted by SFM can be correlated with the molecular weight and the grafting density. The top-view SFM micrographs revealed dense packing of globular polymers, with the only exception observed for polymer S05-2. The film of this polymer did not show any fine structure but only irregular corrugations on the surface. The height and the diameter of the particles as well as an averaged value for the corrugations of the S05-2 film are summarized in Table 2 and are compared with the molecular dimensions as determined in dilute solution, i.e., the hydrodynamic radius from dynamic light scattering and intrinsic viscosity data. The comparison of the film thickness and particle diameter data in Table 2 demonstrates a clear correlation with molecular weight and branching density and the expected deformability of the arborescent graft polymers.

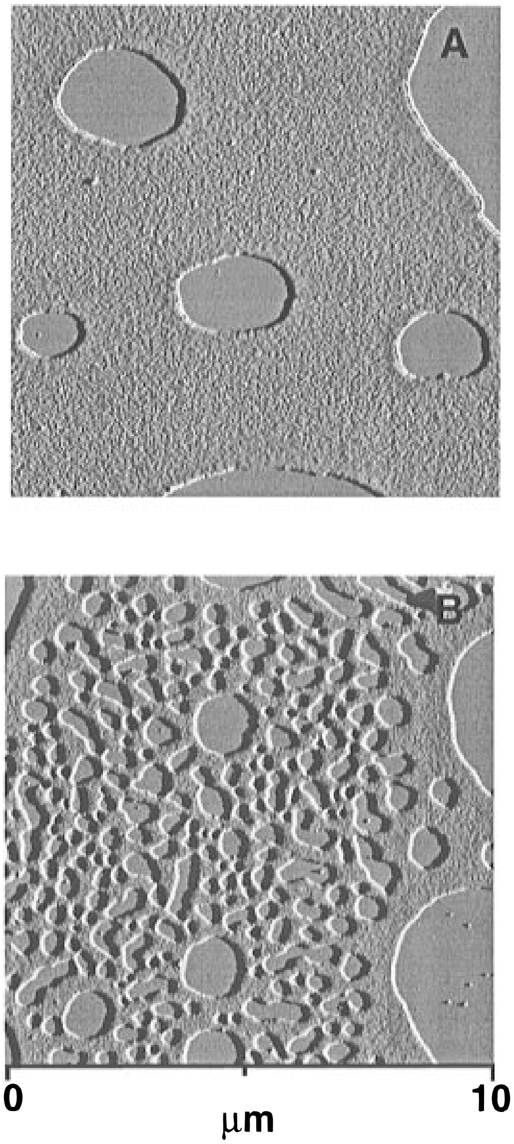


Figure 8. SFM micrograph of a S05-3 monolayer before (A) and after (B) annealing at 150 °C for 1 h. As the globular molecules recovered their spherical geometry upon heating, the thickness of the solution-cast film increased from 35 to 44 nm, resulting in the ruptured structure observed in B.

Sample S05-3 was the only polymer which approached a spherical geometry. The other polymers showed a relatively large discrepancy between the height and diameter. They formed a pancakelike structure where molecules approach the shape of a disk rather than a sphere. An example of such a structure is depicted in Figure 7 for S20-2. The micrograph of polymer S20-2 is on about the same scale as S05-3 in Figure 4. The molecular weights of both polymers are comparable; however, the SFM diameter of S20-2 is about 90 nm, 2 times larger than S05-3. At the same time, the height of the monolayer of S20-2 is less than half of the value determined for the S05-3 film.

Besides 90 nm disks, one can see in Figure 7 a fine structure about 10 nm in diameter. The 10 nm features might be real or a scanning artifact. In the first case, it would indicate some cauliflowered morphology of the collapsed molecules like it has been discussed for polymer brushes of a certain grafting density.[36]

Variations in the branching density, e.g., between S05-3 and S20-2, also resulted in a remarkably different effect upon annealing of the thin films at 150 °C, above

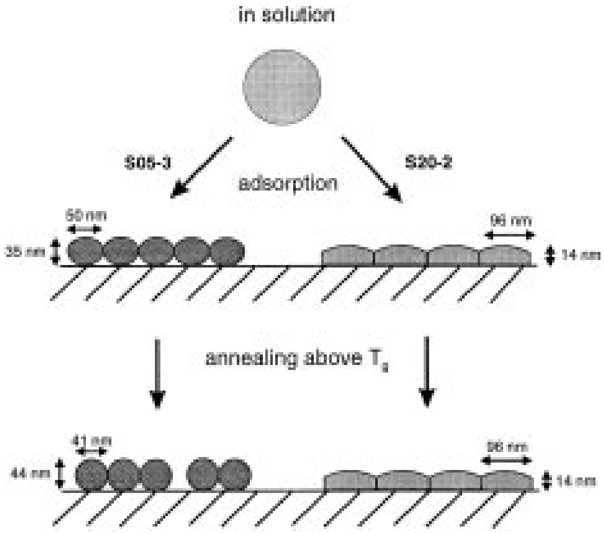


Figure 9. Schematic representation of the film structure of two arborescent graft polystyrenes S05-3 (left) and S20-2 (right) which were cast from solution in toluene on mica and subsequently annealed above the glass transition temperature of polystyrene. The molecules of S20-2 (M_w(br) = 20 000, M_w(AGP) = 5.5 × 10^7) with a branching density 4 times lower than S05-3 (M_w(br) = 5000, M_w(AGP) = 2.8 × 10^7) were strongly flattened by the adsorption forces and did not recover their spherical geometry upon heating, in contrast to what was observed for S05-3.

the glass transition temperature, $T_g = 105 \pm 2$ °C.[15] While S20-2 did not display any changes in the film structure, the film of S05-3 ruptured, resulting in many small holes as shown in Figure 8B. Molecular dimensions were also modified by the annealing procedure. The diameter of the spheres contracted, while the thickness of the films, and hence the height of the spheres, became larger. Thus, the molecular dimensions of S05-3 recovered to a perfect spherical geometry (Figure 9), probably driven by the entropic elasticity of the cascade branched structure.

Conclusions

Solution casting of arborescent graft polystyrenes with different molecular weights and branching densities resulted in monomolecular films of uniform thickness. The densely packed globular molecules did not coalesce but remained distinct upon aggregation. The morphology observed by SFM is consistent with the hard-sphere behavior of the polymers in solution demonstrated in light scattering experiments.[14,15] The size of the molecular particles was in good agreement with the hard core diameter calculated for the density of polystyrene $\rho = 1.05$ g/cm^3.

The thickness of the molecular monolayers was shown to depend on molecular weight and the branching density of the cascade polymers. The highly branched arborescent polystyrene S05-3 with an average molecular weight between grafting points $M_b \sim 500$ g/mol retained its spherical shape in the film. Sample S20-2 molecules with a lower branching density, $M_b \sim 2000$ g/mol, were strongly flattened by adsorption forces, resulting in a pancake molecular shape which remained stable upon annealing.

The most regular packing was achieved for the more rigid polymer S05-3. Besides distortion of the hexagonal ordering of the globular molecules because of intrinsic polydispersity of the molecular size, molecular packing was significantly affected by small amounts of nongrafted linear polystyrene contaminant.

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