Microphase Separation of Diblock Copolymers Consisting of Polystyrene and Acid-Functionalized Poly(propylene imine) Dendrimers

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ABSTRACT: Diblock copolymers consisting of polystyrene and acid-functionalized poly(propylene imine) dendrimers have been found to self-assemble spontaneously into regular microdomains. The hybride dendrimer−linear chain block copolymers yield highly asymmetric molecules which display an aggregation behavior at the strong segregation limit that differs from the well-known all-linear block copolymers. The morphological features are used to determine the relationship between the architecture of the blocks and the arrangement of the molecules in the bulk. Microlattice formation of these materials was examined by using small-angle X-ray scattering and transmission electron microscopy techniques. By increasing the dendrimer generation, the structures changed from hexagonally packed cylinders with polystyrene as matrix to lamellar phases of different packing density. Good agreement between TEM and SAXS results was obtained, and the microlattice morphology was found to be highly dependent on the dendrimer generation.

Introduction

The rapid development of synthetic chemistry allows us to access new molecular structures that can be designed to explore the role of polymer topology on the physical and chemical properties of macromolecules in general[1] and block copolymers in particular.[2] In the past few years an increasing interest emerged in complex copolymer architectures, like triblocks,[3] stars,[4] dendrimers,[5] rings,[6] and hydra-[7] and superamphiphiles[8] of well-controlled structures and dimensions; thereby it is possible to acquire a better understanding about the relation between the chemical structure and the morphology of block copolymers. Bates et al. pointed to the complexity of the phase behavior of block copolymers.[9] They found new microstructures that were not described before and explained this behavior in terms of compositional and conformational symmetry. The composition of the polymer and differences in the conformational and volume-filling characteristics of each block are important parameters. Nonlinear *miktoarm* star polymers have been synthesized to investigate the influence of chain architecture on polymer properties.[10] Comparison with linear block copolymers showed that the macromolecular architecture not only strongly affects the morphology of the domain borders but also can introduce new morphologies as well. Ring polymers have been used to study relaxation and diffusion mechanisms.[6a] Star polymers with multiple arms have been applied also as model for polymeric micelles. Their viscoelastic behavior was compared with linear analogous polymers.[4a] A series of macrocycles with different M_w, like macrocyclic poly(2-vinylpyridine), have been synthesized, and their hydrodynamic size and stiffness have been compared with their linear precursors in the melt.[11] Gnanou et al. studied the possibilities offered by *living* ring-opening metathesis polymerization of macromonomers to engineer novel macromolecular architectures.[12] By this method amphiphilic branched structures with novel topologies have been prepared. The synthesis and morphological studies of well-defined block ionomers, carried out by different researchers,[13] have provided important information about the aggregation mechanisms of ionic groups to form domains.

The first example of carboxylate- and dicarboxyethyl-terminated polystyrene synthesized by Eisenberg et al. can be regarded as the zeroth- and first-generation dendritic superamphiphile, respectively.[14] The aggregation behavior of these ionic copolymers in organic solvents was extensively investigated. Diblock copolymers with one dendritic block and one linear block have been prepared by several groups. Newkome et al. studied the aggregation of hydrophilic arborols bonded at both ends to a long hydrocarbon chain.[15] The preparation of polymeric surfactants with hydrophobic terminal residues on a lysine dendrimer attached to a PEO tail (hydra-amphiphiles) and their surfactant properties have been described as well.[7] Fréchet et al. have reported dendritic−linear diblocks and triblocks with hydrophobic and hydrophilic termini.[16] The thermal behavior of these copolymers was investigated with DSC, and it was found that when the dendrimer block was the majority block, phase mixing took place, while in the case of the linear PEO block having the highest mass, microphase separation was found. More recently, the group of Hammond reported the synthesis of an amphiphilic dendritic block copolymer with PEO as the linear block and PAMAM as the dendritic block.[17] Thermal characterization indicated that these diblock copolymers exhibit some degree of microphase separation as well, though no bulk morphologies were described. The authors suggested that the differences found on the melting temperature of the PEO block was due to changes of crystallite sizes due to variations on the block copolymer sizes or geometries or to an increased extent of mixing for larger dendrimer blocks.

We have reported the synthesis and characterization of amphiphilic block copolymers from the combination

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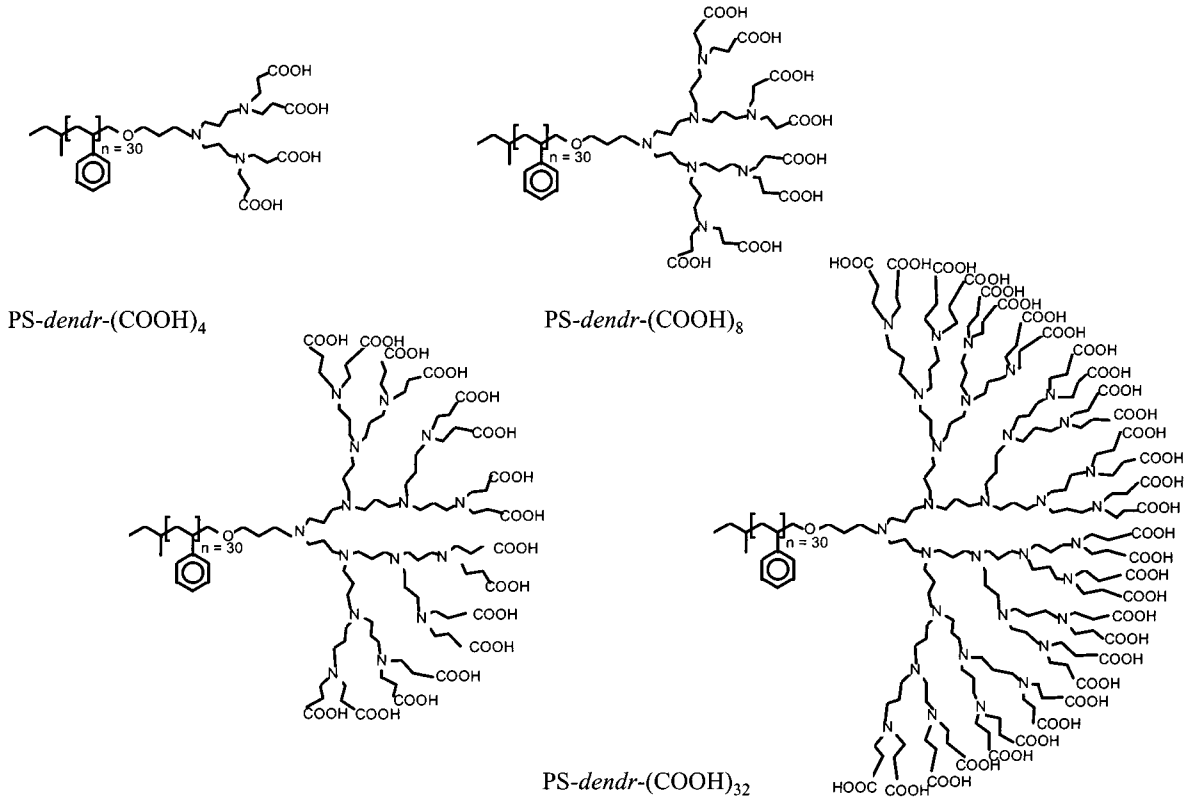

Figure 1. Schematic representation of PS-*dendr*-(COOH)$_n$ dendrimers. The tail of the superamphiphile consists of an atactic polystyrene chain of $M_n = 3.2 \times 10^3$ g/mol. The all-trans conformation has a length of approximately 8 nm and the random-coil conformation a radius of approximately 1 nm (theoretical calculations).

of a hydrophobic linear polymer (polystyrene) and the hydrophilic poly(propylene imine) dendrimers.[8,18] A remarkable generation-dependent aggregation behavior in aqueous solution was observed for these new amphiphilic polymers that qualitatively followed Israelachvili's theory on the relationship between molecular shape and aggregation form.[19] In an analogous way, the configuration of this new type of polymers is expected to influence significantly the microlattice formation in the solid phase as well.

In this paper, we report on the microphase separation of polystyrene−dendrimer block copolymers in the solid state. Morphological studies in the solid phase have been performed for the first time in this type of dendritic−linear block copolymers. These results have yielded a better understanding of the influence of macromolecular architecture on the structure of microlattices of block copolymers.

Experimental Methods

Preparation of Samples. The synthesis of the four block copolymers was published before.[8,18] Solid films of PS-*dendr*-(COOH)$_n$, with $n = 4$, 8, 16, and 32 for SAXS and TEM measurements, were prepared by dissolving ca. 25 mg of polymer in 1 mL of toluene. The solutions were allowed to dry at atmospheric pressure and later at vacuum to remove all the solvent. The resulting solid films were stored under vacuum to prevent absorption of water. The samples were not further pressed or heated.

SAXS Measurements. Small-angle X-ray scattering measurements were performed using Cu Kα radiation ($\lambda = 1.54$ Å), a Riguka Denki small-angle goniometer, and a small-angle flat focus camera using a point focus collimator. The accessible range of scattering vectors $q = (2\pi/\lambda) \sin \theta$ is $0.005 < q/\text{Å}^{-1} < 0.1$, where θ is the scattering angle. The experimental data are plotted in Figure 2. The lines in Figure 2 are obtained by an adjacent average calculation considering each time five points for smoothing the curves.

Electron Microscopy. Transmission electron microscopy was carried out using a JEOL 2000-FX operated at 80 kV. Thin samples for TEM with an approximate thickness of approximately 100 nm were cut at −122 °C. Staining was performed by exposure of the films into RuO_4 vapor.

XRD Measurements. Cast bilayers for X-ray diffraction measurements were prepared from aqueous dispersions of block copolymer PS-*dendr*-(COOH)$_8$ (this polymer has been found to form vesicles in water).[18] Aliquots of the colloidal dispersions (2 mL) were left to dry on Si wafers in a desiccator over sodium hydroxide. These Si single-crystal wafers, cut along the (501) plane, were used for low-angle X-ray measurements. The specimen chamber was maintained at 20 °C and flushed with air of variable relative humidity between 0 and 90% during the XRD measurements. The patterns were digitally recorded. Peak positions were obtained using peak-fitting JANDEL software. Small-angle X-ray diffraction measurements were performed using a Huber D8211 goniometer. This high-accuracy diffractometer is equipped with a Cu LFF XRD Philips tube, variable divergence and antiscatter slits, and an energy dispersive Si/Li Kevex detector, which enable a high peak-to-background ratio.

Results

In this study, we used four generations of dendritic block copolymers PS-*dendr*-(COOH)$_n$, with $n = 4$, 8, 16, and 32 (Figure 1). The synthesis of PS-*dendr*-(COOH)$_n$ block copolymers is based on the use of a well-defined monodisperse atactic polystyrene chain, obtained by anionic polymerization, as a core molecule for building the poly(propylene imine) dendrimer using the standard sequence.[20] This has been reported elsewhere.[18] Characterization was carried out with IR, ^{1}H NMR, ^{13}C NMR, and MS techniques. On the basis of the analytical characterization in nonaqueous solutions and the solid

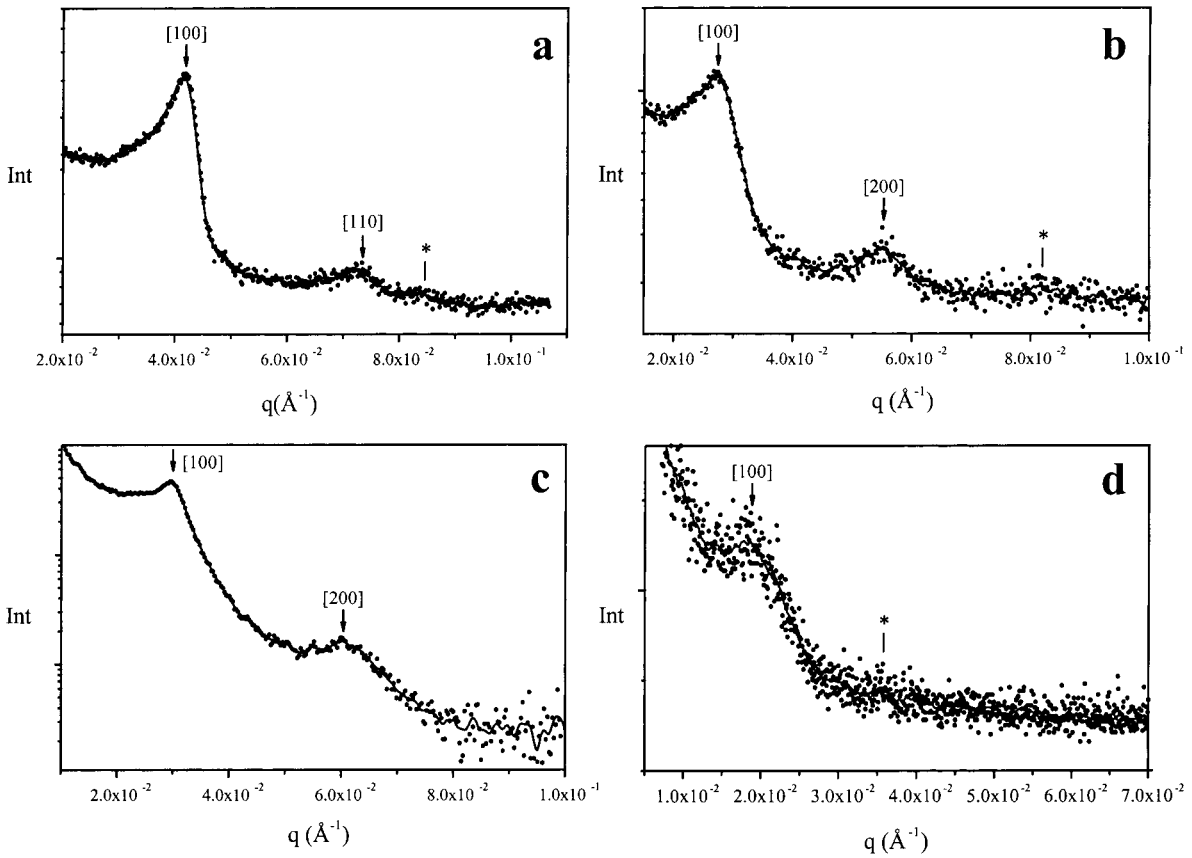

Figure 2. Small-angle X-ray scattering intensity profiles for solid films of (a) PS-*dendr*-$(COOH)_4$, (b) PS-*dendr*-$(COOH)_8$, (c) PS-*dendr*-$(COOH)_{16}$, and (d) PS-*dendr*-$(COOH)_{32}$. The positions marked with an asterisk correspond to positions at which higher-order peaks are expected for the geometry of the corresponding lattice in each case.

Table 1. Characterization of the Different Block Copolymers

block copolymer	f_{PS}[a] PS block	M_w (g/mol)
PS-*dendr*-$(COOH)_4$	0.87	3676
PS-*dendr*-$(COOH)_8$	0.75	4288
PS-*dendr*-$(COOH)_{16}$	0.60	5320
PS-*dendr*-$(COOH)_{32}$	0.42	7608

[a] f_{PS} is the molar fraction of the polystyrene block in the polymer.

state, it is assumed the block copolymers have the amine−carboxylic acid form and not the zwitterionic form, as they have in water; however, some acid−base reactions cannot be ruled out. The molar weight and molar fraction of polystyrene in the block copolymers are given in Table 1, showing that the block lengths are shorter than those of many block copolymers studied in detail before.[9−13] The morphology of these dendritic−linear block copolymers has been examined by using SAXS, TEM, and XRD techniques.

Small-Angle X-ray Scattering. The SAXS profiles of the acid-functionalized polystyrene−dendrimer diblock copolymers for four different generations of dendrimer are shown in Figure 2.

The scattering of PS-*dendr*-$(COOH)_4$ shows two clear diffraction peaks. The higher-order reflections are found at multiples of $\sqrt{3}$ and $\sqrt{4}$ of the first maximum, although the peak corresponding to the 200 position is hardly visible. This sequence of spacings corresponds to the geometry of hexagonally packed cylinders (hpc). In the case of PS-*dendr*-$(COOH)_4$, the volume of the dendrimer block is small compared with the volume of the polystyrene block and the dendritic part segregates, forming cylinders that are surrounded by a PS matrix. The distance between the centers of these cylinders is 86 Å, as determined from the experimental data. Therefore, the radius of the cylinders is 43 Å, and consequently, the conformation of the PS block is between all-trans and random coil.[21] A cylindrical structure is normally observed for linear block copolymers that possess a volume fraction of the apolar block of ca. 0.65−0.80.[22] However, in the case of PS-*dendr*-$(COOH)_4$, the molar fraction[23] of the PS block (f_{PS}) is nearly 0.90 (see Table 1). At this high value, an ordinary block copolymer with a low degree of polymerization is near the order−disorder transition, and a spherical morphology is expected to appear. Hence in this case, the χ value must be quite high, resulting in a large χN parameter. Additionally, due to the branched form of the dendritic block, the interface is forced to curve toward the PS side supporting the formation of well-ordered hexagonally packed cylinders (hpc), instead of a cubic array of spheres.

In the SAXS profile of PS-*dendr*-$(COOH)_8$, the peak sequence confirms that the microphase separation takes place in a lamellar structure. X-ray diffraction patterns show two reflections corresponding to the signals with the Miller indices $hkl = 100$ and 200, as expected for a one-dimensional lattice. The molar fraction of the PS block is 0.75, which in the case of a linear block copolymer would correspond with an hpc morphology. For PS-*dendr*-$(COOH)_8$, as in the case of PS-*dendr*-$(COOH)_4$, the interface PS−dendrimer becomes probably more flat than a corresponding linear block copolymer of the same composition due to the more compact shape of the dendritic block. The distance found between

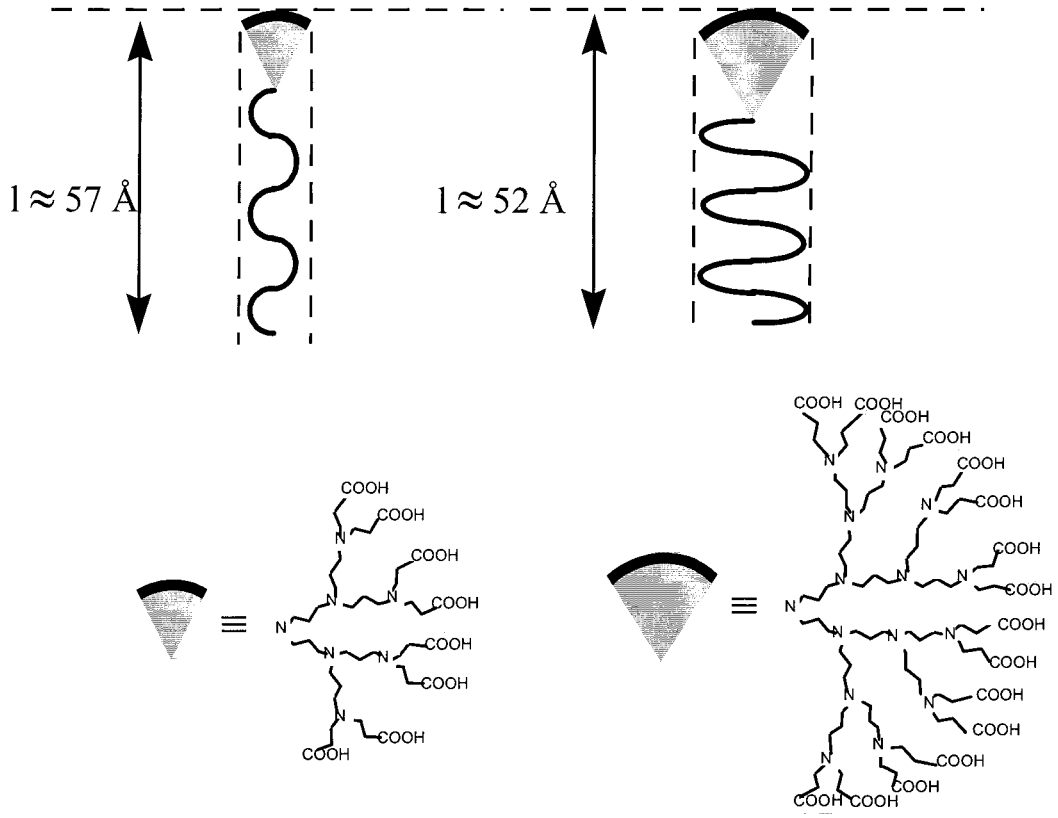

Figure 3. Schematic representation of PS-*dendr*-$(COOH)_8$ and PS-*dendr*-$(COOH)_{16}$ molecules in a layer. The diameter of the cylindrical volume occupied by the molecule increases upon dendrimer generation.

two layers is determined at 114 Å. In this lamellar lattice the molecules occupy a cylindrical volume[19] (see Figure 3). The PS chains are probably in a more stretched conformation than in PS-*dendr*-$(COOH)_4$, adapting their form to the space available between the molecules for an optimal packing. Since the polystyrene chains are atactic, they are not able to pack in a well-defined pattern, and they are present in a noncrystalline phase with a conformation between all-trans and random coil.

PS-*dendr*-$(COOH)_{16}$ is also found to be ordered in a lamellar phase. The distance between two layers is in this case determined at 105 Å. As the volume of the dendritic part increases, the cross section of the cylindrical space where the polymers are located will increase too, due to the increase in diameter of the volume occupied by the dendrimer block (see Figure 3). Moreover, the PS chains will have more space to adopt a more random conformation than in the case of PS-*dendr*-$(COOH)_8$; this effect leads to a shorter distance between the planes in the lamellar phase. Probably because of the limited conformational freedom of the dendrimer block, the PS block is able to adapt its conformation in order to produce an optimal packing in the lattice.

Interestingly and contrary to that expected, the long-range spatial order is less pronounced for the higher generations. The signals obtained for PS-*dendr*-$(COOH)_{32}$ are less defined than for the smaller generation dendrimers. No clear second-order peaks are visible. Since the degree of macroscopic orientation is low in this sample, it is difficult to determine whether the morphology of the lattice is of a lamellar or cylindrical nature. At $q = 0.036$ Å^{-1} a very weak signal seems to appear. In view of the ratio of the first and this weak second peak being ≈1.8 (corresponding to a 110 reflection), the structure is proposed to be of the hpc nature. For PS-*dendr*-$(COOH)_{32}$, the volume of the dendrimer part is large compared with the polystyrene part, and the microphase separation seems to be energetically favorable, but the interface is not as well-defined as in the case of smaller generations, and other structures, like lamellae, cannot be discarded.

Transmission Electron Microscopy. The microdomain structures were examined by transmission electron microscopy; Figure 4 shows typical TEM pictures obtained for the ultrathin sections of the films, stained with ruthenium tetraoxide. The dark parts in the photographs correspond to dendrimer domains, selectively stained. From the micrographs, highly ordered as well as somewhat disordered regions can be observed in all samples. This could be due to sample preparation; however, the disordered regions were clearly larger as the dendrimer generation of the sample increased. Figure 4a,b shows two different cross sections of the same sample, PS-*dendr*-$(COOH)_4$; in Figure 4a the plane of the section is perpendicular to the cylinders, and the hexagonal packing of the cylinders is clearly observed. From this picture the distance between two centers is about 8 nm, being in agreement with the spacing obtained from the position of the 110 peak in SAXS measurements ($d_{110} = 43$ Å). In Figure 4b the cross-sectional plane is parallel to the cylinders, and the same distance can be measured. However, TEM pictures are obtained by staining and therefore only provide an approximate estimation of the spacing in the sample.

Parts c and d of Figure 4 show the lamellar microdomains of PS-*dendr*-$(COOH)_8$ and PS-*dendr*-$(COOH)_{16}$, respectively. Both samples exhibit amorphous regions between the well-defined morphologies. The distance

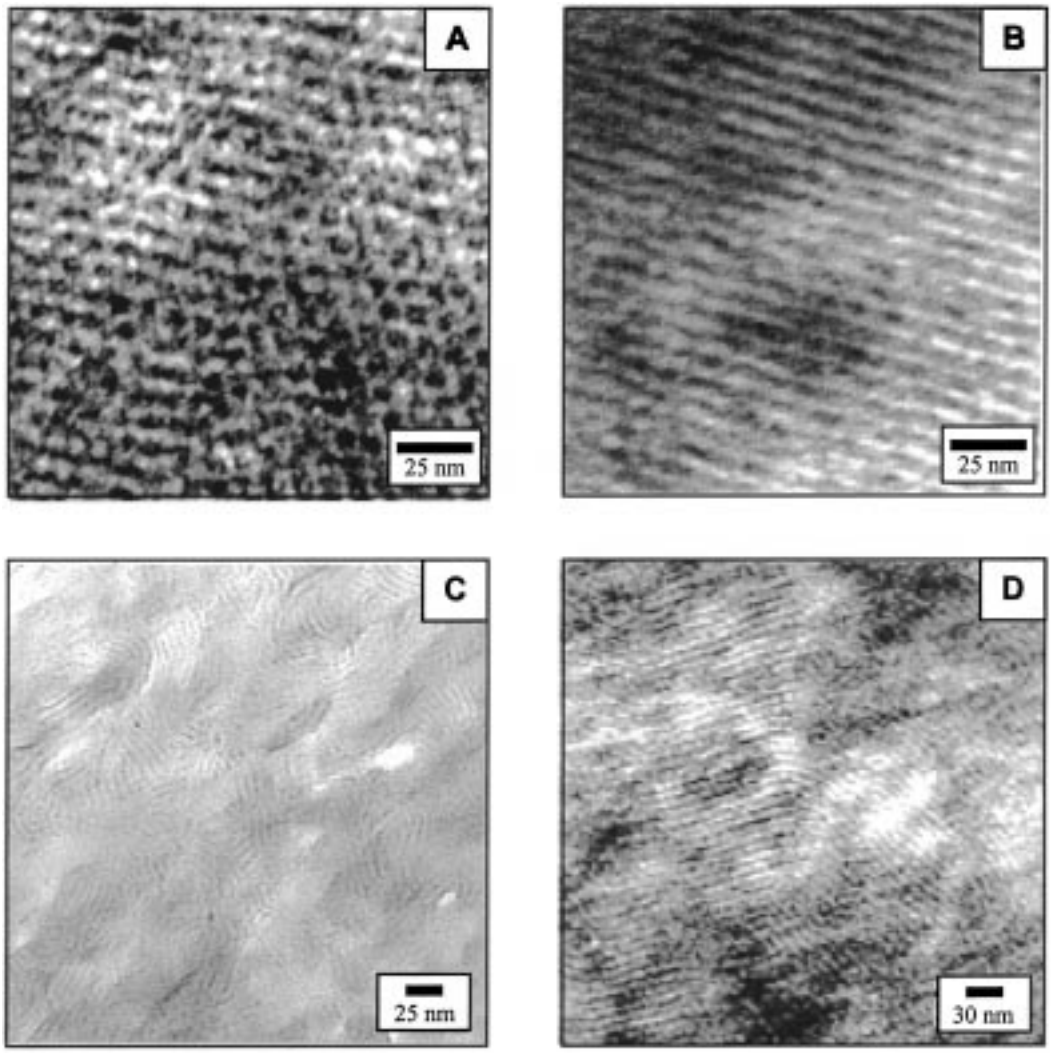

Figure 4. TEM picture of solid films of (a) PS-*dendr*-$(COOH)_4$ section across the cylinders present in the lattice, (b) PS-*dendr*-$(COOH)_4$ section along the cylinders present in the lattice, (c) PS-*dendr*-$(COOH)_8$, lamellar lattice, and (d) PS-*dendr*-$(COOH)_{16}$, lamellar lattice.

between the lamellae is in both cases ca. 10 nm. However, these values are estimated and do not account for the change in the apparent spacing with possible orientation of the domains with viewing angle in the TEM.

Unfortunately, no TEM pictures of PS-*dendr*-$(COOH)_{32}$ could be made. The ultrathin section of the film could not be obtained because of the high hydrophilicity of the polymer, so that instead of floating in water after the process of cutting, it interacted with the solvent, sinking in it.

X-ray Diffraction. X-ray diffraction has been carried out on a *cast film* of PS-*dendr*-$(COOH)_8$ on a silicon plate. The diffraction patterns display a bilayer thickness of 126 Å at a relative humidity of 20%; the relative humidity in the air was varied between 90% and 0%, to see whether the hydration layer of the dendrimer headgroup could introduce some changes in the layer thickness, but since the signals were very broad, no quantitative analysis of the results was possible. However, a clear shift of the first-order peak to smaller θ values seems to indicate that swelling of the layers took place at high humidity percentages.

Discussion

In this paper, we have studied the solid-state properties of a novel type of hybrid dendritic−linear block copolymers using SAXS, TEM, and XRD. By comparing the experimental SAXS results of the different generations of PS-*dendr*-$(COOH)_n$, it is striking that the second-order peaks are weaker for the higher generations, which is assumed to be due to the poor regularity within the films. This assumption is corroborated by transmission electron microscopy techniques. This effect is probably caused by interpenetration of the PS in the interior of the poly(propylene imine) dendrimer phases, confirming the nonionic character of the acid-functionalized poly(propylene imine) dendrimer block. SAXS, TEM, and XRD experiments performed with primary amine-functionalized dendrimers, PS-*dendr*-$(NH_2)_n$, did not show any evidence of microphase separation for any generation.[24] These results suggest that no segregation takes place between styrene and propylene imine monomers in the bulk, which is in agreement with theoretical calculations of the χ parameter for this system.[25] Only upon protonation is the amine-functionalized dendrimer incompatible with polystyrene. Consequently, the microphase separation observed for acid-functionalized dendrimers is more likely to be due to the segregation of carboxylic end groups from the PS phase than to incompatibility effects between the PS block and the tertiary amines of the dendrimer block. The degree of polymerization N_A increases with the different genera-

tions dendrimer, but the larger the dendrimer block becomes, the larger also becomes the distance between the interface and the polar carboxylic end groups. The interface between the different domains is therefore not well defined, yielding a more mixed material, and the material can be regarded as a "triblock" copolymer.

By now comparing the observed morphologies for the dendritic−linear polymers with the ones expected for linear diblock copolymers, it is clear that architecture significantly influences the microdomain structure at a given volume fraction. It is characteristic that in the case of $f_{PS} = 0.87$ linear diblocks form spherical morphologies, while copolymer PS-*dendr*-$(COOH)_4$ has a cylindrical structure of dendrimers in a PS matrix. In the case of $f_{PS} \approx 0.75$, a cylindrical structure will be expected for a linear diblock copolymer, while PS-*dendr*-$(COOH)_8$ forms a lamellar structure. It has been observed before that the phase diagram in the strong segregation limit for block copolymers of type A_nB is shifted toward higher volume fractions of the linear B block.[10] This aggregation behavior can be explained in terms of the local preferred curvature of the A−B interface. The higher the dendrimer generation, the higher the curvature toward the PS phase will be. Dendrimers are highly branched polymers, and the high degree of branching of these molecules limits significantly their conformational freedom.[26] Recently, comparison experiments of dendrimers with their analogous linear molecules[27] did show that dendrimers possess much lower hydrodynamic volume values than linear molecules with the same molar weight, indicating that dendrimers behave as flexible globular-like molecules.

Conclusions

In summary, although all of the molecules are of much lower molecular weight than most of the linear diblock copolymers that have been well-studied, we have shown that, for asymmetric diblock copolymers based on a dendritic block, microdomains can be formed in which the polar dendritic block segregation is probably due to incompatibility effects between the carboxylic groups and the polystyrene block. By increasing the dendrimer generation, the structures change from hexagonal to lamellar structures, and the low-range spatial order decreased in the lattices. The phase diagram in the strong segregation limit for dendritic−linear diblock copolymers is shifted toward higher volume fractions with respect to the theoretical phase diagram, calculated for linear block copolymers. These new macromolecules provide the necessary materials for morphological studies that can reveal the influence of molecular architecture and chemical functionality on the structure of microphase-separated block copolymers.

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