Synthesis and Morphology Studies of a Polystyrene−Poly(arylene ether sulfone)−Polystyrene Coil−Semirod−Coil Triblock Copolymer

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ABSTRACT: A new ABA-type triblock copolymer was synthesized by coupling reaction of anhydride and amine-functionalized telechelic polymers. The two blocks of the copolymer, polystyrene end-functionalized with anhydride group (PS-anh) and poly(arylene ether sulfone) functionalized with aromatic amine groups at the termini (PAES-amn), were synthesized by living anionic and condensation polymerization, respectively. The block copolymer was characterized by size exclusion chromatography (SEC), thermal (DSC and TGA) studies, and the morphology investigated by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The microstructure of the block copolymer was affected by the volume fraction of the constituent blocks.

Introduction

There has been increasing scientific and technological interest in block copolymers since they offer products which can incorporate the desirable properties of two or more homopolymers.[1] Consequently, block copolymers are widely used in a variety of conventional applications including thermoplastic elastomers, impact modification, compatibilization, pressure-sensitive adhesion, foams, dispersion agents, and solubilizers.[2] Because of thermodynamically immiscible constituent blocks and the packing constraints imposed by the connectivity of each block, the copolymers form various self-assembled micro- and nanostructures. Typical self-assembled structures include spheres, cylinders, lamellae, and bicontinuous gyroid morphology.[3] The formation of the ordered microstructure is affected by composition and interactions between the component blocks, sample preparation, and the addition of diluents or another homopolymer.[3,4]

In rod−coil block copolymers, the chain conformation of rigid rod and flexible coil blocks can control their phase behavior and associated material properties. Various types of rod−coil block copolymers have been reported.[5] The most widely used synthetic approach to these materials has employed polymer analogous reactions such as living anionic and living free-radical polymerizations.[6,7] Several block copolymers have been synthesized by coupling reactions among telechelic polymers.[8] A number of coil−rod−coil ABA-type triblock copolymers have been studied in which the rod block is a small molecule or an oligomer.[9] These low molecular weight polymers are shown to form diverse morphology depending on the structural features, solvents, and additives. So far, there has been no report on coil−rod−coil ABA-type triblock copolymers in which the rod block is a true polymer. Herein we report the synthesis, characterization, and morphology studies of a new coil−semirod−coil triblock copolymer consisting of polystyrene (PS) and poly(arylene ether sulfone) (PAES) segments through a coupling reaction. Polystyrene end-functionalized with anhydride group (PS-anh) and poly(arylene ether sulfone) functionalized with aromatic amine groups at the termini (PAES-amn), synthesized by living anionic and condensation polymerization, respectively, were coupled, affording the desired triblock copolymers in quantitative yields. This synthesis protocol is designed for further expansion in selectively introducing $-SO_3H$ groups into the PAES or PS blocks in order to use the resulting triblock copolymers as membranes in fuel cells.

Experimental Section

Materials. Monomers and solvents were purified according to the usual procedures. Styrene was purchased from Aldrich and purified by distillation over dibutylmagnesium under high vacuum after removal of the inhibitor. 4,4′-Hexafluoroisopropylidene diphenol (F6-BPA, Aldrich) was recrystallized from hot toluene. 3-Aminophenol (Fluka) was sublimed at 120 °C in vacuo. 4-Fluorophenyl sulfone (4-FPS, Aldrich) and anhydrous potassium carbonate (Aldrich) were used without further purification. *N*,*N*-Dimethylacetamide (DMAc, Aldrich) and *tert*-butylbenzene (Junsei) were purified by distillation from CaH_2 under reduced pressures.

Synthesis of the Telechelic Polymers. Polystyrene end-functionalized with anhydride group was synthesized by means of anionic living polymerization. Detailed experimental procedure and the characterization of the polymer were reported by us before.[10] Poly(arylene ether sulfone) end-functionalized with amino group was synthesized by the direct aromatic nucleophilic substitution polycondensation of F6-BPA, 4-FPS, and 3-aminophenol following the procedure reported in the literature.[11] Typical procedures for the synthesis of the telechelic homopolymers are given in the Supporting Information.

Synthesis of the Triblock Copolymer from the Telechelic Polymers. PAES-amn (0.60 g, 1 equiv) was dissolved in dried DMAc (10 mL) in a 50 mL two-neck flask equipped with a nitrogen inlet. After PAES-amn was completely dissolved, PS-anh (1.71 g, 2.2 equiv) was added. The mixture was stirred at room temperature for 24 h to afford poly(amic acid) in solution. For imidization, a mixture of acetic anhydride and pyridine (2:1 v/v, 3 mL) was added to the poly(amic acid) solution with stirring at room temperature for 24 h.[12] The polymer was precipitated in methanol and dried under vacuum at 50 °C.

Characterization. The polymers were characterized by ^1H NMR spectroscopy with a JEOL JNM-LA 300 WB FT-NMR in $CDCl_3$ and DMSO-d_6. The molecular weights and molecular weight distributions were determined by size exclusion chromatography (SEC, Waters model 515) using polystyrene standards for calibra-

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Table 1. Molecular Weight Data of the Telechelic Polymers and Triblock Copolymers[a]

telechlic homopolymer [b]		PS-*b*-PAES-*b*-PS triblock copolymer [c]				
			M_n, kg mol^{-1}			
PS-anh M_n, kg mol^{-1} (M_w/M_n)	PAES-amn M_n, kg mol^{-1} (M_w/M_n)	sample (PS−PAES−PS)	calcd	obsd	M_w/M_n	f_{PAES}[d]
6 (1.06)	6 (2.23)	TE-1 (6−6−6)	18	18.3	2.52	0.33
6 (1.06)	31 (2.45)	TE-2 (6−31−6)	43	43.9	2.64	0.72
20 (1.06)	31 (2.45)	TE-3 (20−31−20)	71	73.5	2.73	0.43

[a] M_n and M_w/M_n were measured by SEC in THF at 40 °C with the polystyrene standards. [b] M_w/M_n of PS-anh and PAES-amn polymers are presented in parentheses. [c] The total M_w and M_n values were determined relative to polystyrene standards. [d] Volume fraction of PAES block.

tion. Titration of terminated diamine in PAES-amn was carried out with an Auto-titrator 670 (Metrohm). The thermal properties of polymers were determined with a TA Instrument 2100 series. Glass transition temperatures (T_g) of polymers were measured at a heating rate of 5 °C/min in N_2 gas. Thermal degradation temperatures (T_d) were measured at a heating rate of 10 °C/min under N_2. The temperature at which the weight loss was 5% was considered as an index of thermal stability.

Atomic force microscope (AFM) images were acquired with a Nanoscope III Dimension 3000 (Digital Instruments Inc., Santa Barbara, CA). SuperSharp Silicon tapping mode with a cantilever resonance frequency of ca. 330 kHz and scan rates of 0.5 Hz were used (NanoSensors, Wetzlar-Blankenfeld, Germany). The tip of the cantilever had a nominal radius of curvature of ca. 2 nm. The samples for AFM images were prepared by spin-casting of THF solution (1.5 wt %) onto the silicon wafer substrate and dried at 60 °C for 4 h. Silicon wafer was cleaned by sonication in ethanol/water (1:1, v/v) for 5 min prior to use. Oxidation of the silicon wafer was carried out by treatment with a mixture of hydrogen peroxide (30%, w/v) and sulfuric acid (96%) (20:80, v/v) for 5 h. Transmission electron microscope (TEM) images were obtained using an EF-TEM, EM 912 (OMEGA ZEISS, Germany). The copolymer samples for TEM images prepared in THF (1.5 wt %) were cast on carbon-coated copper grid without any staining and then annealed for 6 h at 60 °C.

Results and Discussion

Synthesis of the Telechelic Polymers. The anhydride end-functionalized polystyrene was synthesized by living anionic polymerization, followed by termination with 6-bromo-3-methylene-1-hexene. The butadiene terminus was converted into anhydride group through Diels−Alder reaction with maleic anhydride. The molecular weights of the resulting PS-anh were well controlled, and molecular weight distributions were quite narrow, all M_w/M_n values being 1.06 (Table 1). The ^{1}H NMR spectra of the samples show a disappearance of the resonances at 5.13 ppm corresponding to vinyl protons of the butadienyl group after the cycloaddition reaction. More detailed results were reported in our previous work.[10a] The results indicate that polystyrene end-functionalized with anhydride group was successfully synthesized.

The poly(arylene ether sulfone)s end-functionalized with amine at the termini were synthesized by condensation polymerization, followed by treatment with 3-aminophenol. For the PAES-amn sample of molecular weight 6 kg mol^{-1} (PAES-6) the ^{1}H NMR spectrum showed a peak at 5.3 ppm corresponding to the amine group. In the case of PAES-6 with short backbone chain, the functionality of the polymer could be confirmed from ^{1}H NMR analysis. ^{1}H NMR determination of the amine groups for the high molecular weight homopolymers of molecular weights 20 kg mol^{-1} (PAES-20) and 31 kg mol^{-1} (PAES-31) were not possible due to weak amine proton signals. For these polymers functionality were determined by auto-titrator, and the values were 1.9 with an error margin of ±0.1.

Synthesis of the Triblock Copolymer. The new coil−semirod−coil block copolymers consisting of PS and PAES segments were successfully synthesized by coupling reaction between anhydride- and amine-ended telechelic polymers of varying molecular weights, resulting in tailor-made triblock copolymers as listed in Table 1.[13] The copolymers demonstrated monomodal SEC distribution (shown for the sample TE-2, Figure 1) without any shoulders and tailings after coupling reaction. The calculated and experimental molecular weights matched, indicating that the architecture of copolymers can be controlled by the synthetic procedure. The results of DSC analysis (Figure S1, Supporting Information) show that the glass transition temperatures of PS-anh and PAES-amn are at around 103 and 187 °C, respectively, which agreed with the known T_g values of the corresponding PS and PAES homopolymers.[2a] The block copolymers also showed T_g values at about 105 and 185 °C. The TGA traces (Figure S2, Supporting Information) show that the triblock copolymers are thermally more stable than PS but less stable than the PAES homopolymers. For the copolymer, two degradation temperatures (T_d) were clearly seen: one at ∼400 °C pertaining to degradation of the PS blocks and the other at ∼500 °C when the degradation of PAES block ensues. Block copolymers exhibited high-temperature stability due to high thermal and oxidative stability of phenyl ether and phenyl sulfone groups in the PAES block.

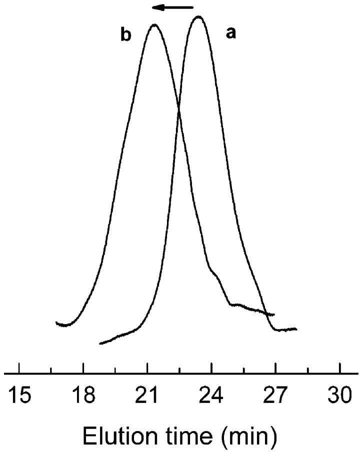

Figure 1. (a) SEC trace of the homopolymer PAES-31 and (b) the triblock copolymer TE-2.

Morphology Studies. In block copolymers, the molecular weights, compositions, solvent, temperature, additives, and the nature of the substrate determine the morphology.[14] For a block copolymer such as polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) with a PMMA volume fraction f_{PMMA} of 0.25, when cast on a neutral substrate that has a layer of random copolymer PS-*r*-PMMA, the PMMA domains of PS-*b*-PMMA form a cylindrical array in the PS matrix.[15] To generate this morphology, the copolymer is annealed at a temperature higher than the T_g of both the blocks.[15c] Slow evaporation of solvent over a week from a mixture of polystyrene-*b*-polyisoprene (PS-*b*-PI) and PS homopolymer generated a bicontinuous gyroid structure.[16] In the present study the PS-*b*-PAES-*b*-PS triblock

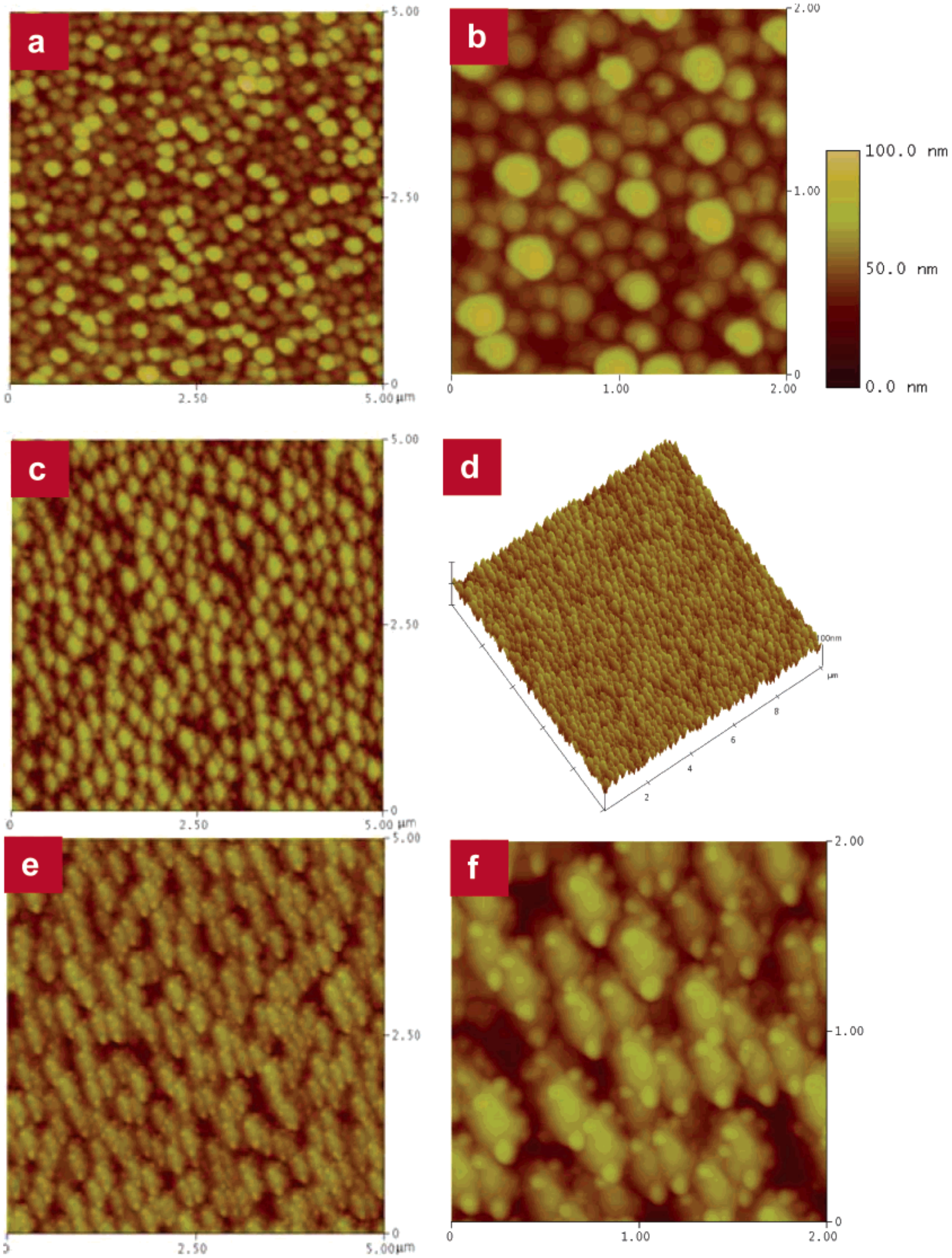

Figure 2. AFM images of PS-*b*-PAES-*b*-PS block copolymers. Films were spin-cast from 1.5 wt % THF solution. (a) TE-1, (b) magnified image of TE-1, (c) TE-2, (d) side view of TE-2, (e) TE-3, (f) magnified image TE-3. Magnified image of TE-2 is given in the Supporting Information, Figure S4 (see Table 1 for sample details).

copolymer samples for AFM images were prepared by spin-casting of THF solution on the silicon substrate and drying at 60 °C, well below the annealing temperatures of the constituent blocks. Thus, the AFM images of the copolymers are those of the micelles generated by a solubility difference of the PAES and the PS blocks in the selected solvent.

We investigated the effect of the weight fraction of PAES block (f_{PAES}) on the shape and ordering of the micelles. Figure 2 shows the tapping-mode AFM images of block copolymers with different f_{PAES} values. Block copolymers form interestingly different morphologies not observed in PAES homopolymer (Figure S3, Supporting Information). The homopolymer showed random distribution of the micelles of irregular shape due to aggregation. In the triblock copolymer the micelles are of uniform shape. The AFM image of TE-1 shows spherical aggregates (Figure 2a) of average size 250 nm. A close look at the magnified image (Figure 2b) shows a larger spherical micelle to shadow a smaller one beneath, reminiscent of a hockey puck micelle.[4] We ascribe the larger spherical aggregates to top PS block, which overlaps the short PAES block and masks it from a direct view. As f_{PAES} increases from 0.33 (TE-1) to 0.72 (TE-2), the morphology changed from spherical to ellipsoidal shape of average length 300 nm and width 170 nm. Further, the ellipsoids in TE-2 form a near regular assemblage, unidirectional

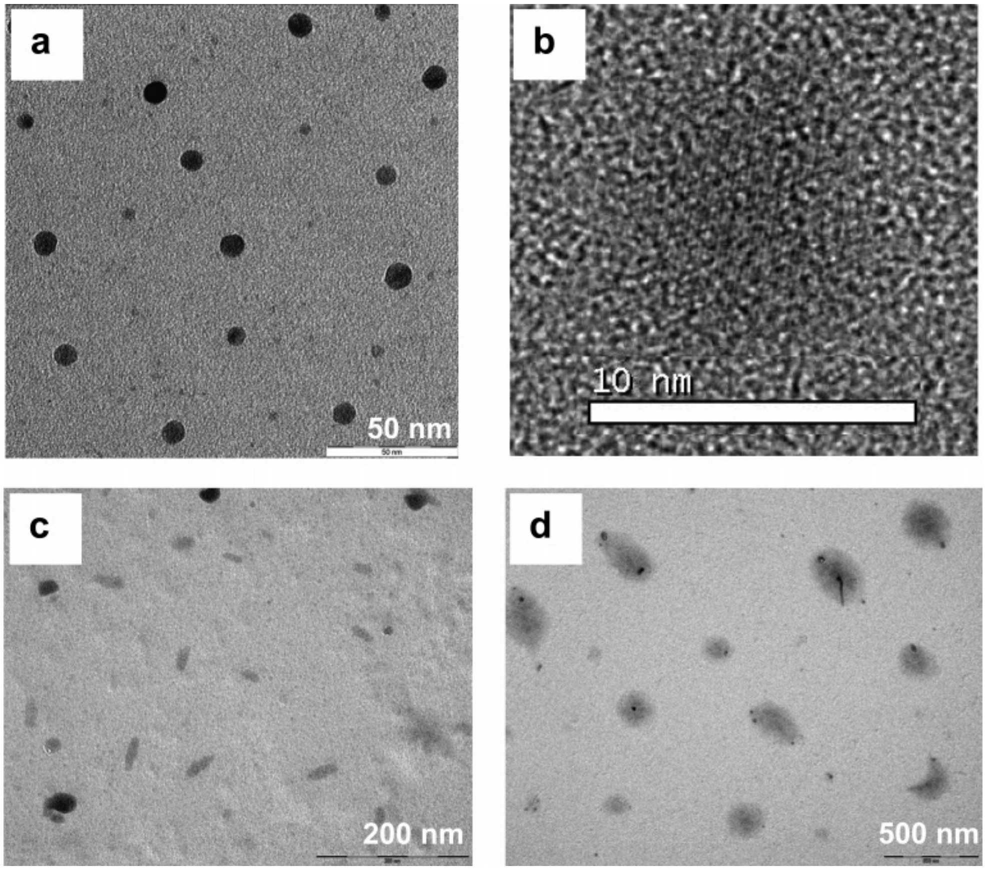

Figure 3. TEM images of PS-*b*-PAES-*b*-PS block copolymers from 1.5 wt % THF solution on carbon-coated copper grid (no staining). (a) TE-1, (b) HRTEM of TE-1, (c) TE-2, (d) TE-3 (see Table 1 for sample details).

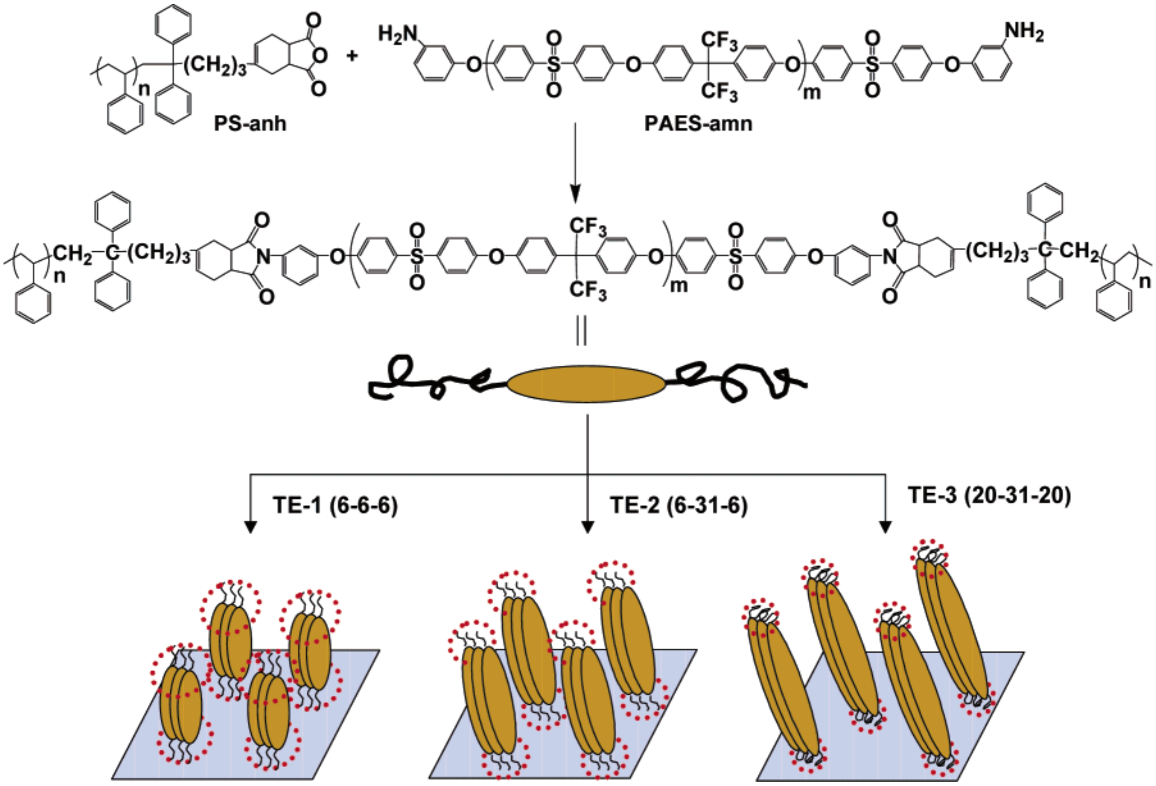

Figure 4. Synthesis of the triblock copolymer and the schematic model showing the packing arrangement for TE-1, TE-2, and TE-3. The PAES block is represented by the ellipsoids and the PS blocks as chains. The dotted circles represent the PS aggregates.

and oriented at an angle away from the normal to the substrate surface. In TE-2, the PAES block is longer in comparison to that in TE-1. Since the coil length in TE-2 is the same as that in TE-1, change of shape from spherical to elliptical as well as an enhanced order in the arrangement of the micelles in TE-2 is a direct consequence of the increased PAES length.

In the case of TE-3, the molecular weight of PAES block is same as that of TE-2, but the molecular weight of the PS blocks is high. The PS domains now appear as two independent spherical aggregates decorating the two ends of the ellipsoids of average length 440 nm and width 250 nm. Besides, the degree of tilt is more than that in TE-2, large enough to allow a clear view of the PAES blocks. It is known that a high coil volume fraction in rod−coil diblock copolymer favors a tilted nanostructure as more headroom is required for the space-demanding coil block.[5f] Furthermore, in rod−coil diblock copolymers the tilt angle is determined not only by the packing requirement but also by the crystallization of the rod blocks.[17] Thus, tilting of the elliptical micelles could be a consequence of enhanced steric demand of the PS block with increasing molecular weight as well as the propensity of the PAES block to crystallize. Furthermore, going from TE-1 to TE-3, the PS domain appears to be progressively decreasing in size. This again is a consequence of the increasing tilt of triblock copolymer from TE-1 to TE-3 coupled with the AFM tip convolution effect.

TEM pictures (Figure 3) of the TE-1 show the micellar features as expected. However, the size is greatly reduced to an average diameter of 8 nm, in contrast to the size inferred from the AFM measurement. The high-resolution TEM (HR-TEM) picture of a micelle shows aligned fine lines in the core, which could originate from the π-stacked PAES chains. TE-2 forms elliptical micelles of average length 35 nm and width 12 nm. For TE-3 the size of the micelles increased significantly to an average length of 265 nm and width 200 nm. Repeated TEM experiments showed that the above sizes of the micelles are not absolute and varied with sampling conditions, such as the differences in the nature of the substrates and the solvent evaporation rates. Variation in size could also be attributed to the large polydispersities of the copolymers. Nevertheless, the spherical shapes for TE-1 and elliptical shapes for TE-2 and TE-3 were always retained. The TEM picture of TE-3 shows the PS blocks as two dark dots at the termini of the relatively lighter PAES block (see Figure S5, Supporting Information, for a large-area picture). Though this was not clearly seen in all the micelles, the pattern was unmistakable. The dynamic light scattering studies of the polymer solutions at a concentration same as that for preparation of AFM and TEM samples (1.5 wt % in THF) did not show any evidence of aggregation. The polymer solutions were too dilute and seemingly below the critical micellar concentrations. In such solutions, the block copolymers are suggested to exist as unimers.[18] Upon solvent evaporation the unimers self-assemble on the substrates furnishing the observed morphology.

Thus, we observe a triblock copolymer to form a typical micelle with a semirod midblock decorated at the termini with the coil blocks. For the three copolymers of different composition, the observed morphology is schematically illustrated in Figure 4. We envisage that differences in solubility of the PS and PAES blocks coupled with the tendency of the PAES block to π-stack are the driving forces for self-assembly generating the typical morphology not seen before. Detailed studies of the triblock copolymer morphology with HRTEM studies are under way with copolymer samples of varying PAES and PS fractions.

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Supporting Information Available: Experimental details for the synthesis of the telechelic homopolymers; DSC and TG data of the triblock copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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