

Synthesis and Microphase Separation of Linear Triblock Terpolymers of Polystyrene, High 1,4-Polybutadiene, and High 3,4-Polyisoprene

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ABSTRACT: We introduce a new combination of diene/diene microstructures to form microphase-separated ABC terpolymers. The synthesis and morphology of two triblock terpolymers of the poly-(butadiene-*b*-styrene-*b*-isoprene) (BSI) type and one poly(styrene-*b*-butadiene-*b*-isoprene) (SBI) type are reported. The microstructure for the PB block was 92 wt % 1,4- and 8 wt % 1,2- and for the PI block 54 wt % 3,4-, 16 wt % 1,2-, and 30 wt % 1,4-. A three-component microphase-separated system occurred even when the two diene blocks were adjacent, as in the SBI sequence, leading to the conclusion that the PB:PI 1,4/3,4 diene combination has a larger Flory–Huggins χ parameter than the other three possible combinations of PB:PI diene microstructures. A new type of cylindrical microdomain structure with alternating types of diene regions along the cylinder axis is observed.

Introduction

Within the past 30 years, experimental procedures have been established for the synthesis of well-defined ABC linear triblock terpolymers. Most of the materials thus far produced consist of polystyrene (PS), a polydiene (usually polybutadiene (PB) or polyisoprene (PI)), and a third block. Third components that have been used are poly(α -methylstyrene),¹ poly(ethylene oxide)² (PEO), poly(4-vinylpyridine)^{3,4} (P4VP), poly(ethylene sulfide),⁵ poly((4-vinylbenzyl)dimethylamine),^{6–10} or especially poly(2-vinylpyridine)^{11–19} (P2VP). Interesting microdomain structures have been found in such ABC materials. Stadler et al.^{20–29} examined the morphological behavior of an extensive set of ABC triblocks, where A is PS, B is PB (90% 1,2-), and C is poly(methyl methacrylate) (PMMA). In some cases^{21,28,30} the middle block was hydrogenated, leading to poly(ethylene-*co*-butylene) and a strong increase in the χ_{AB} and χ_{BC} parameters. Hydrogenation sometimes resulted in a change of the observed microdomain morphology. Several novel morphologies were obtained by the Stadler's group such as the lamellae-sphere ("ball at the wall"³²)/lamellae-cylinder/cylinder-ring combination phases^{20,30} and the "knitting-pattern"^{28,34} structures. Also, the same group^{31–34} made an extensive study of the dependence of the structure on the sequence of components as well as the casting solvent. Additionally, the compositional ranges of these morphologies (i.e., the knitting pattern) have been studied.³⁵ The morphological phase diagrams of ABC triblock terpolymers have also been studied theoretically in the strong segregation limit³⁶ (SSL).

Since there are three interaction parameters, χ_{AB} , χ_{BC} , and χ_{AC} , the microphase separation of ABC triblocks is more complicated than for diblocks. The microdomain structure of terpolymers depends not only on the interaction parameters but also on the overall molecular weight, the two volume fractions, and additionally the

sequence of the blocks in the chain (i.e., whether it is A–B–C, B–C–A, or C–A–B). Indeed, a lamellar morphology is formed in the system PI-*b*-PS-*b*-P2VP (ISV) (total molecular weight 58K) with volume fraction 0.33/0.33/0.33,^{13,14,37} whereas a hexagonally ordered coaxial cylinder phase is obtained in the SIV system (total molecular weight 43K) with the same composition and cast from the same solvent.¹⁵

For terpolymers containing two dienic blocks, one needs to carefully consider the type and relative amount of the particular block stereoisomers since local structure influences the segment–segment interaction parameter. The possible segment microstructures for PB are 1,4-*cis*, 1,4-*trans*, and 1,2-. In a nonpolar synthesis procedure the resultant microstructure of a PB is predominantly 1,4- (92 wt % 1,4- and 8 wt % 1,2-). For the PI case, because of the methyl group, more microstructures are possible: *cis* or *trans* 1,4- as well as the 3,4- and the 1,2-microstructure. In a nonpolar synthesis procedure the resultant microstructure of a PI is 90 wt % 1,4- (70% *cis* and 20% *trans*) and 10 wt % 3,4-. There are four possible combinations of PB and PI microstructures: 1,4-/1,4-, 1,2-/1,4-, 1,2-/high 3,4-, and 1,4-/high 3,4-. When the 3,4-microstructure of PI is significantly increased (~50–60%), then the 1,2-microstructure is increased as well (15–25%). To date, the first three combinations of diene pairs have been explored and the interaction parameters found sufficiently small such that either copolymers or even blends of diene pairs form simple mixed homogeneous phases for typical molecular weights. The segment–segment interaction parameter of diblock copolymers of predominantly 1,4-polybutadiene and predominantly *cis*-1,4-polyisoprene with either or both of the corresponding linear homopolymers has been investigated.^{38,39} Ternary blends of the two homopolymers with the diblock and binary blends of a single homopolymer with the diblock were one or two phase materials depending on the sample composition, the ratio, and the number of diene units in the diblocks. Contrast in the TEM images between the two phases was obtained using the ebonite method.⁴⁰ This method employs molten sulfur to transform the

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polydienes into ebonite, making the near-surface harder. In addition to using sulfur as the hardening agent, a sulfenamide-type accelerator and zinc stearate are added (90:5:5). The development of contrast between the phases is dependent upon the relative reactivity of the hardening agent and the particular diene. The harder phase (higher sulfur and zinc content) appears darker than adjacent softer phases due to the greater electron scattering by the sulfur and zinc atoms. Cohen and Wilfong⁴¹ calculated χ for different diene pairs, obtaining room temperature values of 0.081 and 0.048 for 1,4-PI/1,4-PB and 1,4-PI/1,2-PB, respectively. A set of experimental results has also been reported for the particular binary system 1,2-PB/1,4-PB. The solubility parameter values,⁴² δ , of polystyrene, 1,4-polybutadiene (92 wt %), and 1,2-polybutadiene (95 wt %) are 9.1, 8.4, and 8.1 (cal/cm³)^{1/2}, respectively, and that of toluene is 8.9 (cal/cm³)^{1/2}. Polyisoprene of the present samples has a high 3,4-microstructure, suggesting a solubility parameter higher than for cis-1,4-PI [$\delta = 8.2$ (cal/cm³)^{1/2}].

The synthesis and morphological characterization of a terpolymer containing PB and PI have been reported in the literature.^{43,44} The ternary polymers⁴³ were synthesized by sequential anionic polymerization of isoprene, butadiene, and styrene, leading to poly(1,4-isoprene-*b*-1,2-butadiene-*b*-styrene). Four samples were synthesized: I₅₀B₄₄S₆⁴⁸, I₄₅B₄₅S₁₀⁶⁰, I₄₆B₃₈S₁₆⁷⁴, and I₃₇B₃₇S₂₆⁷⁰ (where the subscripts correspond to the composition of each block and the superscripts correspond to the total \bar{M}_n of the triblock polymer). Neumann et al. concluded that the triblock material behaved essentially as a pseudo-diblock copolymer consisting of a mixed poly-1,4-isoprene/poly-1,2-butadiene block segregated from the polystyrene block. Well-defined microphases⁴⁴ of the hydrogenated poly(ethylene-*alt*-propylene)-*b*-poly(ethylene-*co*-butylene)-*b*-styrene indicated an increase in χ_{AB} . The χ parameter for a pair of dienes with high 1,4-PB and PI with high (54 wt %) 3,4-microstructure has not yet been reported in the literature. It is already known⁴⁵ that an increase in the interaction parameter χ_{AC} generally has very small contribution on phase behavior once the A and C end blocks of the ABC linear triblock copolymer are segregated. This is due to the fact that many of the obtained morphologies do not possess any A/C interfaces, leading to free energies independent of χ_{AC} .

In the present work, we prepared a series of terpolymers, two of the BSI type with approximate block volume ratios of 1:1.2:1.3 and 1:2.7:1 and one SBI triblock with a volume ratio of 1:1.2:1. In the BSI polymers, the middle styrene block has a variable length while the length of the two diene end-blocks is kept approximately constant. Our nomenclature for the samples is ABC-*X*/*Y*/*Z*, where *X*, *Y*, and *Z* indicate the molecular weight in kg/mol of the A, B, and C blocks, respectively. Our goal was to study the variation of equilibrium morphology with composition via transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) and to examine how the sequence of the blocks and the diene microstructure (high 3,4-PI blocks) influence the microphase behavior, especially with regard to the mixing of the two diene blocks.

Experimental Section

All triblock terpolymers were prepared by anionic polymerization using high-vacuum techniques in evacuated, *n*-BuLi-

washed, benzene-rinsed glass vessels. The purification procedures for monomers (styrene, butadiene, and isoprene), solvents (benzene, THF), and initiator (synthesis and use of *sec*-BuLi) to the standards required for anionic polymerization have been described in detail elsewhere.⁴⁶ The molecular characterization was carried out via size exclusion chromatography (SEC), low-angle laser light scattering (LALLS), and membrane osmometry (MO). More details are given elsewhere.⁴⁷ The \bar{M}_w values from LALLS were obtained from the $(Kc/\Delta R_\theta)^{1/2}$ vs c plots (ΔR_θ , excess Rayleigh ratio; K , combination of known optical constants; c , concentration), and the correlation coefficient was better than 0.99. \bar{M}_n values from MO were calculated from the corresponding $\sqrt{\pi}c$ vs c plots, where π is the osmotic pressure and c is the concentration. Square root plots were used in calculating both the \bar{M}_w and \bar{M}_n in order to minimize the curvature due to the third virial coefficient.

¹H NMR determination of the composition and the microstructure of the materials was carried out in CDCl₃ at 30 °C using a Varian Unity Plus 300/54 instrument. The typical microstructure which is characteristic of anionic polymerization of butadiene in benzene (92 wt % 1,4- and 8 wt % 1,2-) was observed for the BSI terpolymers. For the polyisoprene block a microstructure was observed different from that of the usual anionic polymerization of isoprene in benzene. Since a small quantity of polar solvent was used (THF, 1 mL), the microstructure of PI was 54 wt % 3,4-, 16 wt % 1,2-, and 30 wt % 1,4-. The lower 1,4 content is due to the delocalization of the negative charge among the three final carbons of the living chain (loose ion pairs). By introducing a small quantity of polar solvent in the mixture, the initiation rate of the styrene toward the PB-Li⁺ macroinitiator was increased. For the SBI case the microstructures were 92 wt % 1,4- and 8 wt % 1,2- for PB and 53 wt % 3,4-, 14 wt % 1,2-, and 33 wt % 1,4- for PI. The procedure used for the synthesis of the SBI was exactly the same as in the BSI sequence, and the small amount of THF was added before the polymerization of the isoprene. NMR results show that the chain microstructure for SBI and BSI samples is essentially the same within experimental error.

DSC experiments, employing a TA Instruments DSC 2910 modulated DSC, were used in order to obtain preliminary information about the microphase separation of the three components. Three different glass transition temperatures were exhibited. The values were $T_{g1} \sim -80$ °C, $T_{g2} \sim -30$ °C, and $T_{g3} \sim 100$ °C. According to the literature,⁴⁸ the first and last values correspond approximately to 1,4-PB and PS, respectively. If the chains were mixed, the values would be higher for the PB and lower for the PS, which is not observed, leading to the conclusion that the third T_g corresponds to the high 3,4-PI component. The PI T_g is significantly different compared to that of high 1,4-PI (~ -60 °C) and that of the 1,4-PB (~ -80 °C). The observation of three different glass transition temperatures thus suggests a well-microphase-separated system.

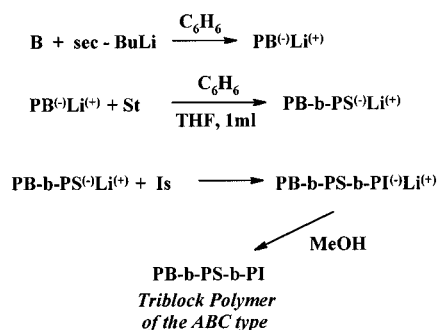
SAXS and TEM were employed for the morphological characterization of the polymers. More details are given elsewhere.⁴⁹ Approximately 0.7 mm thick films of the materials were cast from a dilute solution (~ 4 wt %) in toluene, which is a nearly nonselective solvent for a styrene/isoprene/butadiene system, over a period of 1 week at ambient conditions. To obtain near-equilibrium morphologies, the films were annealed above the T_g of the PS component for 7 days (at 130 °C) under vacuum. For TEM investigation, 500–1500 Å thick sections were cryomicrotomed, and the sections were picked up on 600 mesh copper grids. The grids were then placed in the vapors of a 4% OsO₄-water solution for selective staining of the two diene phases. The SAXS diffraction patterns were obtained at room temperature on the Time-Resolved Diffraction Facility (station X12B) at the National Synchrotron Light Source at Brookhaven National Laboratory (BNL) using a custom-built two-dimensional detector (10 × 10 cm, 512 × 512 pixels) interfaced to a real-time histogramming memory system.⁵⁰

Table 1. Molecular and Microdomain Characteristics of the ABC Triblock Copolymers

sample	total $\bar{M}_w^a \times 10^{-3}$	total $\bar{M}_n^b \times 10^{-3}$	\bar{M}_w/\bar{M}_n^c	ϕ_{PB}	ϕ_{PS}	ϕ_{PI}	morphology	d_1 (Å)
BSI-25/28/32	91	85	1.06	0.29	0.36	0.35	lamellar	520
BSI-37/80/32	161	149	1.07	0.23	0.56	0.21	cylindrical	560
SBI-45/48/40	142	133	1.06	0.32	0.37	0.31	lamellar	785

Results and Discussion

Synthesis. Three polymers were synthesized using the technique of sequential addition of monomers. Two of the samples are of the ABC type, where A is high 1,4-PB, B is PS, and C is high 3,4-PI, and the third is of the BAC type. The reactions are the following:



In the case of the BAC type linear triblock polymer, the sequence of the monomers added is the only change in the aforementioned reactions. First we polymerize the styrene, then the butadiene, and finally the isoprene.

To increase the initiation rate of the styrene toward the $\text{PB}^{\ominus}\text{Li}^{\oplus}$ macroinitiator for the ABC triblock terpolymers, a small amount of THF (1 mL when the volume of the benzene, which was the initial polymerization solvent, varied from 150 to 300 mL) is added. Thus, the styrene polymerization has a fast initiation step, and the narrow distribution of the intermediate diblock product is ensured. The microstructure change in the PI component is significant, as indicated by ^1H NMR spectroscopy, compared to a PI synthesized by anionic polymerization of isoprene in nonpolar environment. In the case of the SBI sample, a small quantity of THF is also added to the benzene (which was the solvent for preparing the first two blocks). After the polymerization of each component, a small amount (~ 1 g) was removed from the apparatus for characterization via SEC, LALLS, and MO. A typical SEC example is shown in Figure 1. The molecular characteristics for the four samples are shown in Table 1. The good agreement between the molecular characterization results indicates the high degree of homogeneity in molecular weight and composition for the final terpolymers.

Microphase Separation Behavior. TEM images of BSI 25/28/32 and SBI 45/48/40 show well-ordered lamellae (Figure 2). There are three levels of image contrast in each sample, indicating that the two diene blocks are microphase-separated. It should be noted that the staining time in the vapors of a 4% OsO_4 -water solution is very crucial, since the two dienes could be over-stained, yielding a misleading apparent two-phase contrast. Staining for 1 h or less allows distinction of the two types of diene domains. The TEM images of the BSI 25/28/32 sample reveal an alternating black/white/gray/white/black ... sequence. The thickness of the gray and black layers is approximately equal (even though the volume fractions of the B (0.29) and I (0.35) blocks

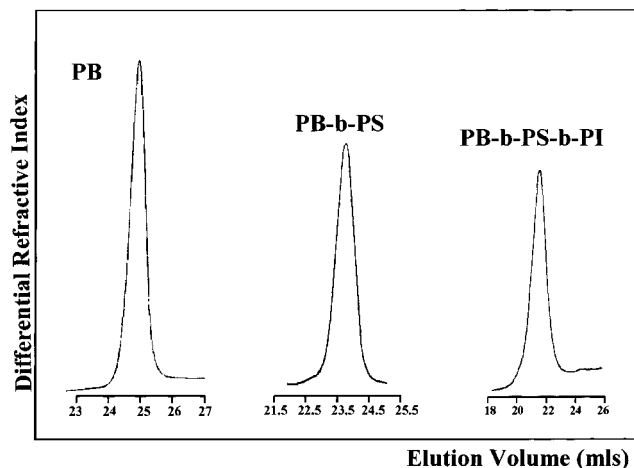


Figure 1. SEC chromatographs of the precursor (PB), the intermediate diblock (PB-*b*-PS), and the final triblock copolymer (PB-*b*-PS-*b*-PI, sample BSI-25/28/32).

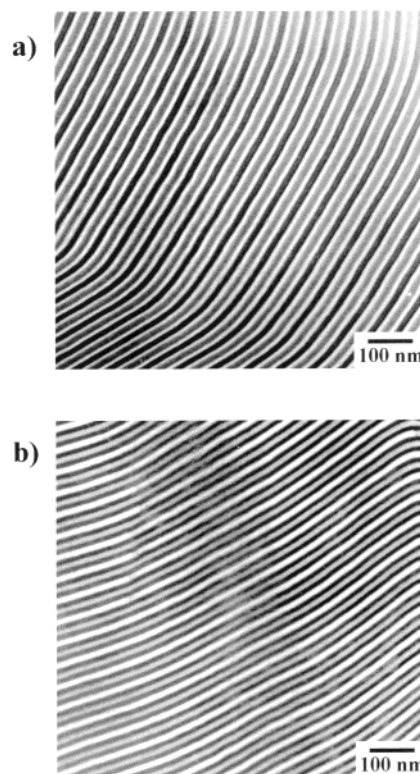


Figure 2. (a) Bright field TEM image of the three-phase four-layer lamellae of the BSI-25/28/32. Both diene phases stain with OsO_4 , and so the PS phase appears lightest. (b) Bright field TEM image of the three-phase four-layer lamellae of the SBI-45/48/40. In this case, the darkest diene phase corresponds to the PB and the gray contrast regions correspond to the PI.

are not equal), so we cannot distinguish which of the two diene chains is more preferentially stained. In the SBI 45/48/40 sample the TEM image (Figure 2b) shows an alternating white/black/gray/black/white ... sequence. The component forming the bridge block is thus more heavily stained (darkest layer), allowing us to definitively assign the PB as the darker domain and the PI

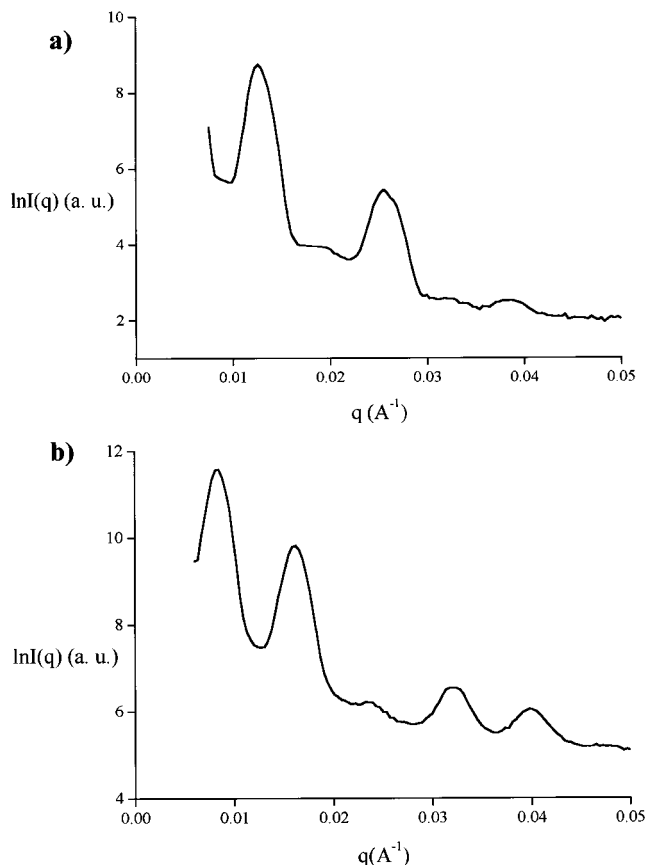


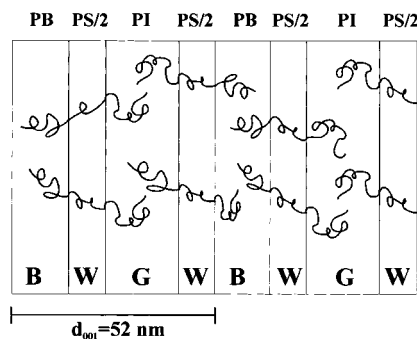
Figure 3. SAXS plots of $\ln I(q)$ vs q : (a) sample BSI-25/28/32; (b) sample SBI-45/48/40.

as the gray domain. The lamellar morphologies evident from the TEM images are confirmed from the SAXS patterns (Figure 3a,b). The mass densities of PI and PB are nearly equivalent (0.903 and 0.9 g/mol, respectively), so their electron density is approximately the same; therefore, the SAXS patterns reflect scattering from a two-density system. Peaks with scattering vector ratios q_{i1}/q_1 of 1:2:3 are resolved for the BSI sample, and peaks up to fifth order are obtained for the SBI sample. The third peak in both samples is very weak due to the fact that the volume fraction of the PS component is not too different from 0.33 (form factor cancellation of third-order lattice peaks). The d_{001} spacings are given in Table 1. A schematic of the three-microphase four-layer ABC lamellar morphologies exhibiting typical chain conformations is shown for both samples in Figure 4.

TEM images of BSI 37/80/32 with $\phi_{PI} = 0.23$ and $\phi_{PB} = 0.21$ exhibit a type of cylindrical morphology with an average cylinder radius of about 200 Å (Figure 5a). If the two dienes were mixed, the pseudo-two-component diblock would have volume fractions of 0.56 and 0.44, suggesting a lamellar morphology, which is not the case. The SAXS $I(q)$ vs q plot is shown in Figure 5b. There are three peaks at low q and a weak broader peak just beyond $q \approx 0.04 \text{ nm}^{-1}$. The q_{i1}/q_1 ratios from the SAXS patterns are approximately 1.0:1.55, 1.96, 3.8 Å.

The cylindrical structure of the BSI-37/80/32 may be one of the following possibilities previously mentioned in the literature: (i) two different cylindrical domains (PB and PI) within the PS matrix domain arranged on a square or a hexagonal lattice or (ii) a single kind of mixed diene cylinder in the PS matrix on a square or a hexagonal lattice. Because of the closeness of the volume

a. Sample BSI-25/28/32



b. Sample SBI-45/48/40

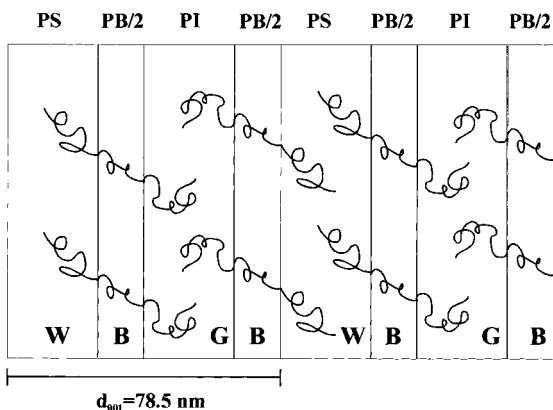


Figure 4. A typical schematic of the three-microphase four-layer ABC lamellar morphologies for (a) sample BSI-25/28/32 and (b) sample SBI-45/48/40.

fractions of the two dienes, the radii of the respective cylinders in a single type of mixed cylinder structure vs that of an array of two types of diene cylinders would be essentially indistinguishable. For example, in the case of two different (PB and PI) cylindrical domain types on a square lattice, the calculated radii of the respective cylinders are approximately 220 and 200 Å. In the case of hexagonal packing, for two types of diene cylinders on a hexagonal lattice, the calculated radii are approximately 235 and 215 Å. Thus, the calculated cylinder sizes based on various candidate structures are not very different so a definitive structural assignment is not possible on this basis. Close examination of TEM images shows dark circular regions (end-on views) which appear approximately on a hexagonal lattice. Striped regions of alternating gray, white, black, white, gray ... domains (oblique views) are also apparent. The dark stripes are narrower than the gray stripes. In some areas certain stripes alter in thickness and in contrast along their length while the adjacent stripes exhibit antisymmetric variations in thickness and contrast. This suggests a model with axial alternation of the cylindrical component diene (for either square or hexagonal packing) as schematically depicted in Figure 6. Such a three-microphase alternating stripe model is similar to that seen in PS/PB/PMMA lamellae.⁵³

Conclusions

ABC terpolymers have been synthesized with two diene components. The increased 3,4-microstructure in the PI component increases the Flory–Huggins interaction parameter between PB and PI and leads to a three-

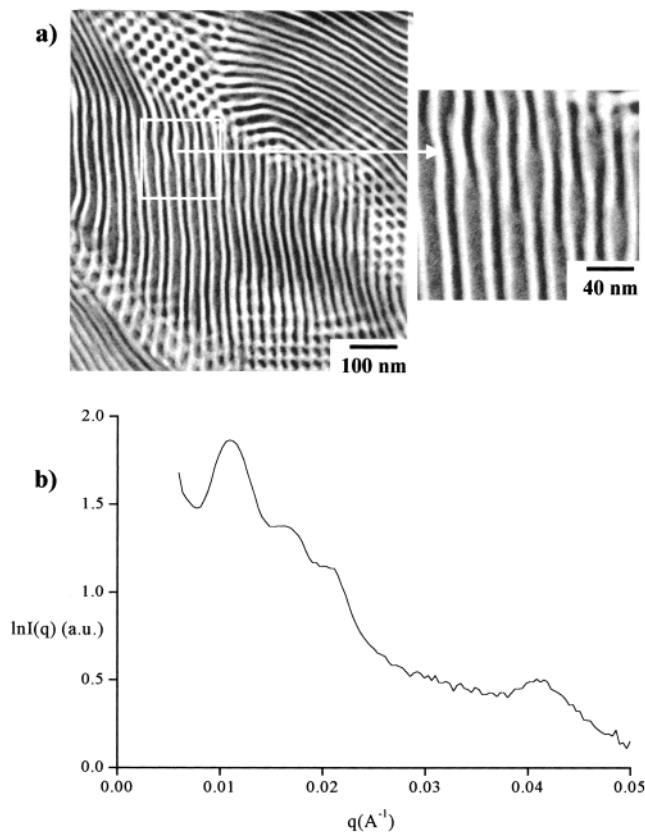


Figure 5. (a) Bright field TEM image of the BSI-37/80/32 sample, showing cylindrical morphology. The magnified portion of the image shows alterations in the cylinder contrast along the axial direction. These alterations are antisymmetric between adjacent cylinders. (b) Corresponding SAXS pattern of BSI-37/80/32 exhibiting peaks characteristic of cylinders.

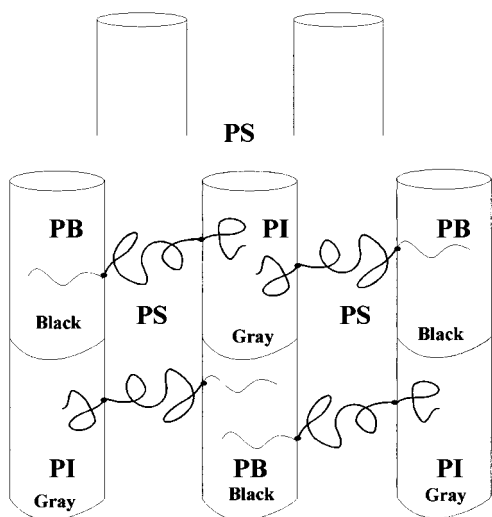


Figure 6. Model adopted for the explanation of the cylindrical morphology. The interface between the two dienes inside each cylinder should be of low energy. For this model, the top view leads to dark circular regions on a hexagonal lattice, whereas the site view gives parallel stripes of alternating gray/black contrast along the axes of the cylinders.

microphase system rather than a mixed-diene system. Changing the sequence from BSI to SBI did not change the lamellar morphology although previous studies have shown that the sequence sometimes affects the morphology.¹⁵ A new model exhibiting alternating diene regions along the cylinder axis is suggested for a nearly symmetric minority diene BSI polymer.

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