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Registry No. (Ethylene)(propene) (copolymer), 9010-79-1; (ethylene)(1-octene) (copolymer), 26221-73-8.

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Horizontally Oriented Microdomains of Block Copolymers by Means of Segment–Segment Interactions

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ABSTRACT: Well-defined poly(styrene-*block*-isoprene) diblock copolymers were prepared by sequential anionic addition. Composite films were fabricated by casting these block copolymer solutions on a surface of cross-linked polystyrene as a substrate film and by varying the casting solvent. The control of horizontally oriented microdomains of block copolymers is discussed in terms of the morphology of the composite films.

Introduction

Block copolymers composed of incompatible block segments generally form a microdomain structure in the solid state as a consequence of microphase separation of the constituent block chains. The morphology of diene-containing block copolymers has been most extensively studied and found to depend, according to Molau's rule,[1] on the conditions of preparation, for example, the type of casting solvent.[1-3] These studies have been concerned with the morphology of the microdomain in solids. O'Malley et al.[4] have investigated the surface properties of block copolymers and, in particular, their surface composition and topography at the air–copolymer interface. They have made clear that the surface and bulk were not identical because of the significant differences in the solid-state surface tension of each block. More recently, Hasegawa et al.[5] have studied the morphology of the microdomains of an AB diblock copolymer formed as a consequence of liquid–liquid microphase separation of the constituent polymer A and B at or near the air–polymer interface in constrast to the morphology in the bulk. It was found that the morphology at the surface was dramatically affected by the surface free energy. In preceding papers,[6-9] we have established a preparation method for vertically oriented microdomains of block and graft copolymers or polymer blends by means of an epitaxial growth of a microdomain pattern on the surface of the substrate film.

In this paper, well-defined poly(styrene (S)-*block*-isoprene (I)) diblock copolymers were prepared by sequential anionic addition. The aim of this work is to describe the control of the microdomain structure (horizontally oriented lamellar and cylindrical microdomains) of poly(S-*b*-I) diblock copolymers by means of the segment–segment interactions between one component of diblock copolymer and substrate film.

Experimental Section

Polymer Synthesis. Poly(S-*b*-I) diblock copolymers were prepared by living anionic polymerization techniques. Styrene was first dried over a mixture of calcium hydride–lithium aluminum hydride and then purified with triphenylmethylsodium in vacuum. Isoprene was dried over calcium hydride and then purified with *n*-butyllithium (*n*-BuLi) in vacuum. Benzene was

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used for a polymerization solvent. Benzene was dried over sodium metal wire and then purified with *n*-BuLi under vacuum. Block copolymers were prepared by the usual sequential anionic addition, using *sec*-BuLi as an initiator in benzene in a sealed glass apparatus under a pressure of 10^{-6} mmHg. At the end of the polymerization of the first styrene monomer, an aliquot was taken out to recover the polymer for characterization. The polymerization techniques are almost the same as those employed in previous work.[10] The product was purified three times by reprecipitation from the benzene solution with methanol. The microstructure of the polyisoprene (PI) blocks obtained from the above method contained 50% 3,4- and 50% 1,4-structures (60% cis, 40% trans).[11]

Cross-linked (*S*)-2-hydroxyethyl methacrylate ((*S*)-HEMA) copolymer was used for the substrate film. The free radical copolymerization of styrene with HEMA was carried out in *N*,*N*-dimethylformamide (DMF) initiated by 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70: Wako Pure Chemical Ind. LTD.) at 40 °C in a sealed ampule under high vacuum. V-70 is a white crystalline powder (decomposition temperature 50–96 °C; 10-h half-life decomposition temperature at 30 °C in toluene). The reactivity ratios of styrene (M_1) and HEMA (M_2) systems were $r_1 = 0.53$ and $r_2 = 0.59$ in DMF.[12]

Molecular Characterization. The number-average molecular weight ($\bar{M}_n$) of PS precursors was determined by gel permeation chromatography (GPC; Toyo Soda high-speed liquid chromatograph HLC 802-A), with tetrahydrofuran (THF) as eluent at 38 °C, a TSK gel GMH column, and a flow rate of 1.0 mL/min. The $\bar{M}_n$ of poly(S-*b*-I) block copolymers was also determined by universal calibration[13] (log $[\eta]M$ versus elution volume) on a GPC. The intrinsic viscosity $[\eta]$ of block copolymers was measured in THF at 38 °C with a Ubbelohde viscometer. The content of PI blocks was determined by ^{1}H NMR (90 MHz, JEOL FX-90Q NMR spectrometer) in $CDCl_3$. The HEMA content of (*S*)-HEMA copolymer was also determined by ^{1}H NMR in $CDCl_3/CD_3OD$ mixed solvent at $\delta = 6.2$–7.1 (aromatic proton) and $\delta = 3.5$ and 3.9 (methylene proton of HEMA pendant chain).

Fabrication of Composite Film. The (S)-HEMA copolymer (HEMA units, 14.9 mol %) film (40 μm thick) was cast from a 0.03 g/mL benzene solution on a Teflon sheet (0.11 mL/cm^2). Once the film of this copolymer had been soaked in aqueous solution of 0.24 N HCl and 5% glutaraldehyde for 24 h, the resultant film was washed with acetone and dried under vacuum (this film was cross-linked with formal links). The composite film was made by placing a benzene or cyclohexane solution (0.8 wt %) of the block copolymers on top of the film of cross-linked (S)-HEMA copolymer. After evaporating the solvent as gradually as possible at room temperature, the film was dried under vacuum for 2 days.

Morphology. Ultrathin film specimens of poly(S-*b*-I) diblock copolymers were prepared for electron microscopy by placing a drop of a 1 wt % benzene or cyclohexane solution on a microscopy mesh coated with a carbon film and evaporating the solvent as gradually as possible at room temperature. Benzene is a common good solvent for both components. Cyclohexane is good solvent for PI but a Θ solvent for PS at 34 °C. This specimen was exposed to the vapor of osmium tetraoxide (OsO_4) for 24 h at room temperature. The composite films, stained with OsO_4, were embedded in a epoxy resin and cut perpendicularly to the film interfaces into ultrathin sections (about 700–1000 Å thick) using an ultramicrotome (Hitachi UM-3 ultramicrotome). The ultrathin sections were further exposed with the vapor of OsO_4. Morphological results were obtained on a Hitachi H-600A transmission electron microscope (TEM).

Results and Discussion

Polymerization of Block Copolymer. The results of polymerization reactions are shown in Table I and Figure 1 shows typical sets of GPC profiles of PS precursor and poly(S-*b*-I) diblock copolymer SI1. The conversions are almost 100% within experimental error, in both cases. The molecular weight observed is close to the value expected from the feed ratio of monomer and initiator used. The GPC elution peak of SI1 is shifted to the side of high molecular weight, as compared with its precursor. The GPC profiles show that both PS precursor and SI1 diblock copolymer have a single and narrow molecular weight distribution.

Table I
Characterization of Poly(S-*b*-I) Diblock Copolymers and Microdomain Spacings

sample	$10^{-4}\bar{M}_n$ PS[a] block	$10^{-4}\bar{M}_n$ block[b] copolym	wt fractn[c] of PS blocks	shape[d]	domain spacing,[e] nm $\bar{D}_{PS}$	$\bar{D}_{PI}$	$\bar{C}_{PI}$
SI1	3.5	5.7	0.60	L	16.2	20.9	
SI2	2.2	3.1	0.72	C_{PI}			6.6

[a] Determined by GPC. [b] Determined by universal calibration on GPC. [c] Determined by ^{1}H NMR. [d] Specimen was cast from benzene: L, lamellae; C_{PI}, PI cylinders. [e] Determined by TEM micrograph of specimen cast from benzene. $\bar{D}_{PS}$ and $\bar{D}_{PI}$ are the average domain distances of PS and PI lamellae, respectively. $\bar{C}_{PI}$ is the average diameter of PI cylinders.

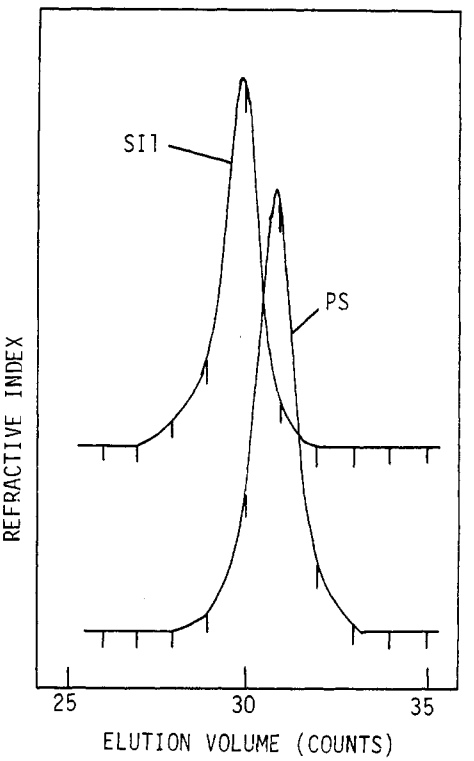
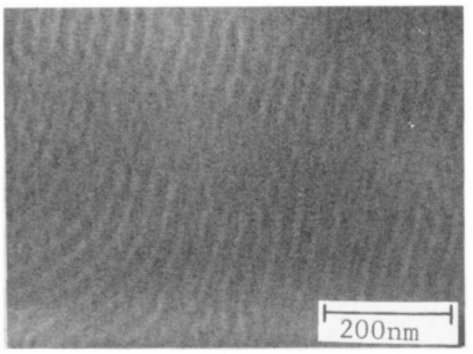


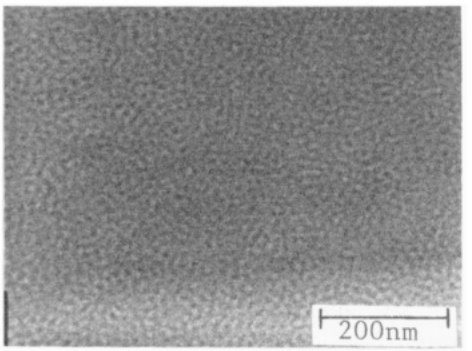
Figure 1. GPC profiles of SI1 diblock copolymer and its PS precursor.

TEM micrographs of the diblock copolymer SI1 and SI2 ultrathin film specimens cast from benzene solution and subsequently stained with OsO_4 are shown in parts a and b of Figure 2, respectively. The dark portions are the selectively stained PI blocks. Benzene is a common good solvent for both components. The texture of SI1 specimen (PS weight fraction 0.60) showed PS–PI alternating lamellae. Cylindrical PI domains in the PS matrix were observed in the SI2 specimen (PS weight fraction 0.72). These results are the same as the morphology of the microdomain structures which depend solely on the composition.[14]

Morphology of Block Copolymer Films. Figure 3 shows a cross section of the SI1 film cast from benzene solution near the air–polymer interface. The arrow indicates the free surface of film. Near the free surface, alternating lamellar structures of PI and PS microphases are oriented with their interfaces parallel to the surface which contact air. At the free surface, however, the film is covered with a PI layer, which is thinner than the corresponding inner PI domains. These morphological results are the same as those reported by Hasegawa et al.[5] Ac-



(a) SI1



(b) SI2

Figure 2. TEM micrographs of diblock copolymer specimens formed by casting a benzene solution: (a) SI1; (b) SI2.

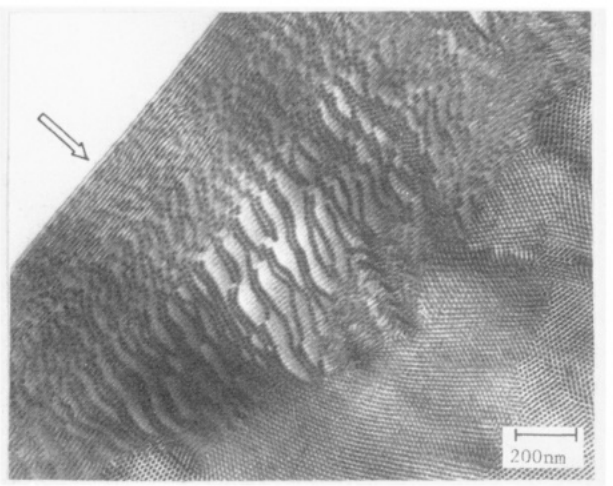


Figure 3. TEM micrograph of a cross section of a SI1 film specimen. The arrow indicates the free surface.

cording to this explanation, the outermost layer must consist of a single layer of PI block chains since the PI chain ends connected by the chemical junctions to PS chains cannot emerge from the air interface, while the inner layers are composed of bimolecular layers, since the block chains can emerge from the two opposing interfaces of the domains. There is a discrepancy between the microdomain morphologies of SI1 observed in the ultrathin film cast on a microscope grid (lamellae, see Figure 2a) and in the thin section of the thick-cast film (PI cylinders in the bulk), although both were cast from benzene solution. The bulk morphology of SI1 could be recognized to be PI cylinders which were observed from the radius direction. The thermal equilibrium morphology of SI1 seems to be PI cylinders in a PS matrix. It is well-known that the surface and bulk of block copolymers[4,15,16] or polymer blends[17] are not identical because of the significant differences in the solid-state surface tension of both components. The surface tensions of PS and PI are 36 dyn/cm[18] and 32 dyn/cm,[19] respectively. In our experimental results, the PI domains having lower solid-state surface tension are therefore accumulated at the air interface.

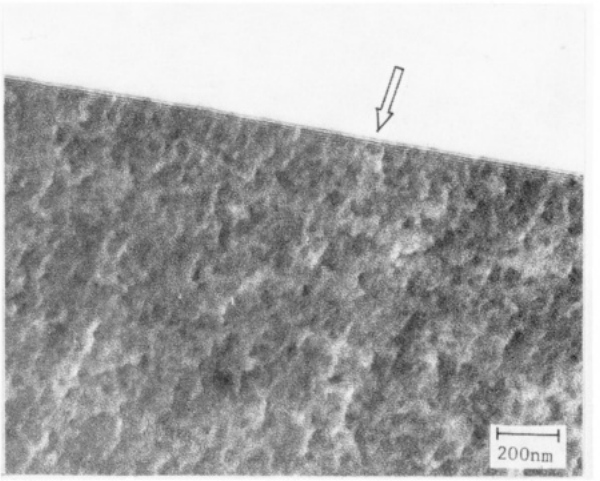
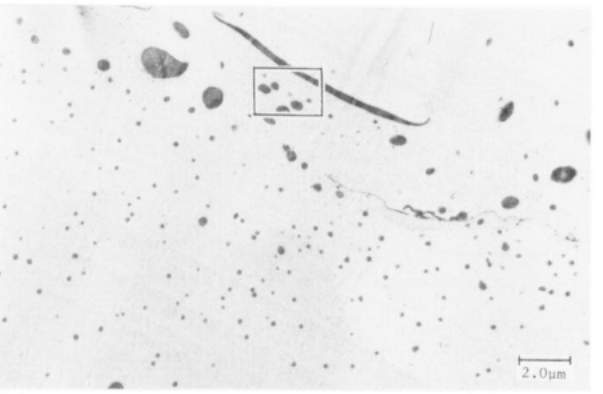
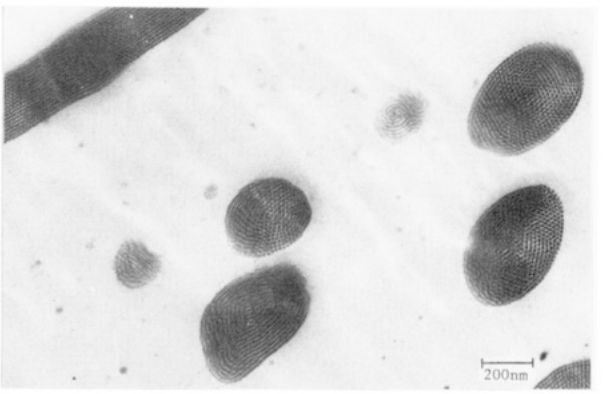


Figure 4. TEM micrograph of a cross section of a SI2 film specimen. The arrow indicates the free surface.



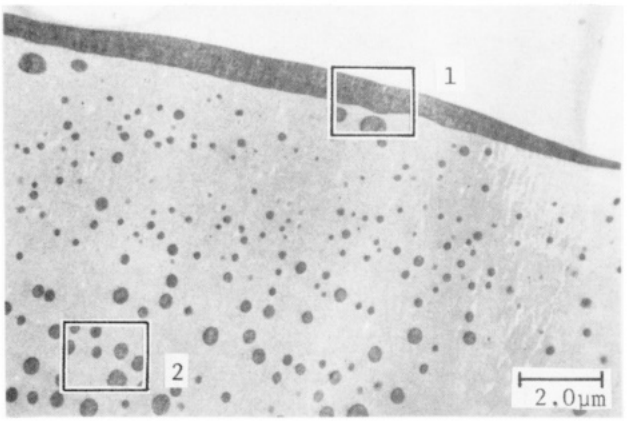
(a)



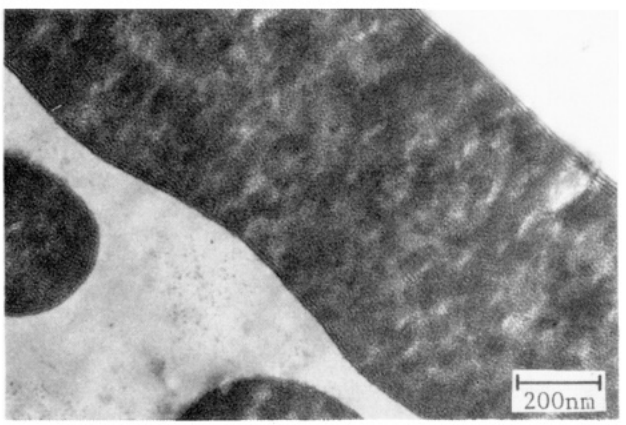
(b)

Figure 5. TEM micrographs of cross section of the composite film formed by casting a benzene solution of SI1 on the surface of cross-linked ((*S*)-HEMA) copolymer as a substrate film: (a) vertical sectional view of the composite film; (b) enlarged micrograph of the frame portion shown in (a).

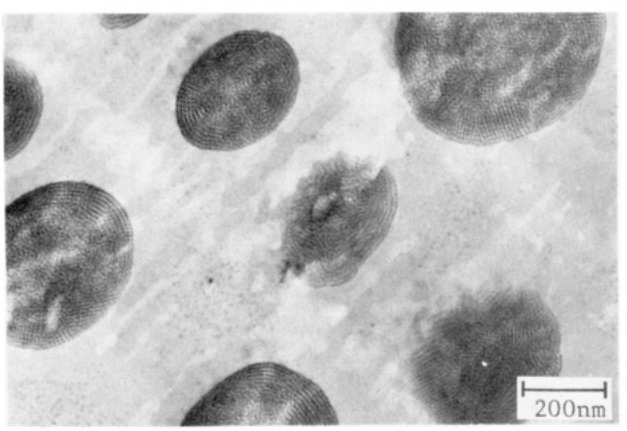
Figure 4 shows a cross section of the SI2 film cast from benzene solution near the air–polymer interface. It is also found from this micrograph that a thin PI layer is aligned with its interface parallel to the free surface. Subsequently, two or three alternating lamellar structures of PI and PS microphases are oriented parallel near the air–polymer interface. These lamellar structures seem to change into randomly oriented PI cylinders/PS matrix in the bulk. In general, lamellar microdomains in a poly(S-*b*-I) block co-



(a)

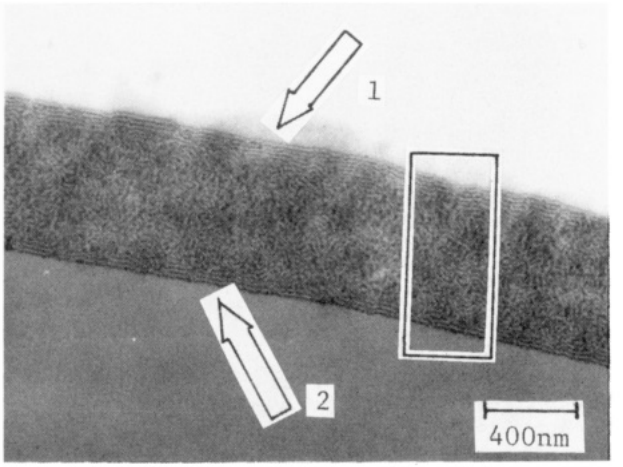


(b)

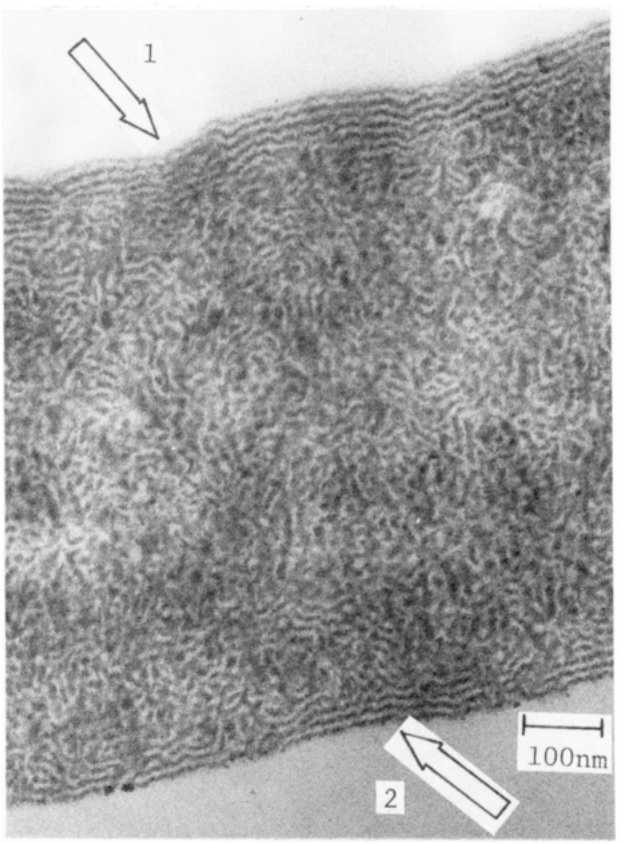


(c)

Figure 6. TEM micrographs of cross section of the composite film formed by casting a benzene solution of SI2 on the surface of the substrate film: (a) vertical sectional view of the composite film; (b) enlarged micrograph of the frame portion 1; (c) enlarged micrograph of the frame portion 2.



(a)



(b)

Figure 7. TEM micrographs of a cross section of the composite film formed by casting a cyclohexane solution of SI1 on the surface of the substrate film: (a) vertical sectional view of the composite film. The arrows 1 and 2 indicate the free surface and domain boundary between the upper layer and the substrate film, respectively; (b) enlarged micrograph of the frame portion shown in (a).

polymer film cast from solutions tend to align with their interfaces parallel to the film surfaces.[20,21]

Morphology of Composite Films. Figure 5a shows a cross section of the composite film formed by casting the benzene solution of a SI1 diblock copolymer on the surface of cross-linked (*S*)-HEMA copolymer as a substrate film. The bright part of the micrograph without structure corresponds to the cross-linked (*S*)-HEMA copolymer matrix and the dispersed dark layer or particles correspond to the microdomains of a SI1 diblock copolymer. This micrograph shows that the benzene solution of SI1 diblock copolymer dissolves into the cross-linked substrate film due to its low cross-linking density and then precipitates as diblock copolymer droplets as the solvent evaporates. Figure 5b is the enlarged micrograph of the frame portion shown in Figure 5a. The PS layer is aligned with its interface parallel or circular to the surface of the droplets by segment–segment interactions between substrate film and block copolymer chains. These results are very similar to special two-phase morphologies in some types of high-impact polystyrene.[22,23] For example, the domains of onion-skin morphology in high-impact polystyrene prepared

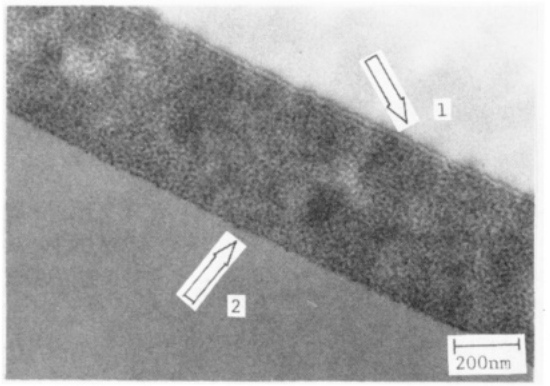


Figure 8. TEM micrograph of a cross section of the composite film formed by casting a cyclohexane solution of SI2 on the surface of the substrate film. The arrows 1 and 2 indicate the free surface and domain boundary between upper layer and substrate film, respectively.

by solvent evaporation from polystyrene/poly(styrene-*block*-butadiene) block copolymer blends.

Figure 6a shows a cross section of the composite film formed by casting a benzene solution of SI2 diblock copolymer on the surface of cross-linked (*S*)-HEMA copolymer as a substrate film. In this case also, the benzene solution of SI2 dissolves into the substrate film. Parts b and c of Figure 6 are the enlarged micrographs of the frame portions 1 and 2 shown in Figure 6a, respectively. Near the boundary surface of the substrate film, the onion-skin morphology of PS/PI lamellae is aligned with their interfaces parallel to the surface of the substrate film in several layers. These structures seem to change completely to a horizontally oriented PI cylinder/PS matrix structure in the bulk of the block copolymer layer or particles.

Figure 7a shows a cross section of the composite film formed by casting a cyclohexane solution of SI1 diblock copolymer on the surface of the substrate film. The arrows 1 and 2 indicate the free surface and domain boundary between upper layer and support film, respectively. Cyclohexane is a poor casting solvent for the PS segment. Therefore, it is considered that a cyclohexane solution of diblock copolymer may not dissolve into the substrate film, and PS block segments in cyclohexane solution of diblock copolymer are easy to absorb on the surface of the substrate film by intermolecular interaction of PS segments. In fact, it is found from this micrograph that the composite film is constructed with the bilayer of SI1 diblock copolymer and substrate film. Figure 7b is the enlarged micrograph of the frame portion shown in Figure 7a. At the lower surface of the upper layer, the PS layer is considered to be aligned with its interface parallel to the substrate film. This absorbed PS layer is not clear in the micrographs, because the PS blocks are not stained with OsO_4. As a result, several alternating PS/PI lamellae are oriented parallel to the surface of the substrate film. On the other hand, at the free surface of the upper layer, a thin PI layer is aligned with its interface parallel to the free surface of the film. Near the free surface, the alternating lamellar structures of PI/PS microphases are oriented parallel to the surface which contacts air. This morphological behavior was the same as the result obtained in the morphology of SI1 diblock copolymer film at or near the air–polymer interface. These alternating lamellar structures change to randomly oriented PI cylinder/PS matrix structure inside the block copolymer film. If the thinner upper layer of the SI1 diblock copolymer is formed by casting a cyclohexane solution on the surface of the substrate film, or if other casting conditions are chosen in this system (for example, film casting in the atmosphere of saturated cyclohexane vapor), it will be possible to fabricate horizontally oriented lamellar microdomain structures.

Figure 8 shows a cross section of the composite film formed by casting a cyclohexane solution of SI2 diblock copolymer on the surface of the substrate film. The arrows 1 and 2 indicate the free surface and domain boundary between upper layer and substrate film, respectively. It is also found from this micrograph that the composite film is constructed with the bilayer of SI2 diblock copolymer and substrate film. Near the boundary surface between the upper layer and the substrate film, the PS layer is considered to be aligned with its interface parallel to the surface of the substrate film. Subsequently, randomly oriented PI cylinder/PS matrix structures are formed away from the lower interface. At the upper surface of the cast film layer, a thin PI layer is aligned with its interface parallel to the free surface. The PS/PI monolamellar layer seems subsequently to orient with its interface parallel to the free surface. This texture shows that the greater part of upper layer SI2 diblock copolymer is constructed of randomly oriented PI cylinder/PS matrix microdomain structures.

We anticipate practical application of these horizontally oriented microdomains. One of them may have use as an anisotropic material. The information obtained from these results will be reported in the near future.

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Registry No. (Styrene)(isoprene) (block copolymer), 105729-79-1.

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