Orientation on microdomains of diblock copolymers

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Well defined poly(styrene-*block*-isoprene) and poly(styrene-*block*-2-vinylpyridine) diblock copolymers were prepared by sequential anionic addition. Films were fabricated by casting these diblock copolymer solutions on a Teflon sheet by varying the casting conditions. Morphological results of these ultrathin sections were obtained on a transmission electron microscope. The surface characterization of poly(styrene-*block*-2-vinylpyridine) film was carried out by X-ray photoelectron microscopy. Both surface and bulk morphologies of these diblock copolymer films (about 50 wt% polystyrene blocks) showed an interesting tendency, namely that alternating lamellar structures of two microphases were oriented with their interface parallel to the surface that contacts air.

(Keywords: diblock copolymer; transmission electron microscopy; X-ray photoelectron microscopy; surface and bulk morphologies; lamellar structure)

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[1–3]. These studies have been concerned with the morphology of microdomains in solids. Thomas and O'Malley[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 significant differences in the solid-state surface tension of each block. Hasegawa and Hashimoto[5] have studied the morphology of microdomains of an AB diblock copolymer formed as a consequence of liquid–liquid microphase separation of the constituent polymers A and B at or near the air–polymer interface in contrast to the morphology in the bulk. It was found that the morphology at the surface was dramatically affected by the surface free energy. More recently, we have investigated the control of the microdomain structure of poly(styrene-*block*-isoprene) (poly(S-*b*-I)) diblock copolymers by means of the segment–segment interactions between one component of the diblock copolymer and the substrate film[6]. Even if, in the diblock copolymer specimen (60 wt% polystyrene (PS) block) the thermal equilibrium morphology is polyisoprene (PI) cylinders in a PS matrix, some 10–100 layers of alternating lamellar structures of PI and PS microphases were oriented parallel near the air–polymer interface or near the boundary surface of the substrate film.

In this article, well defined poly(S-*b*-I) and poly(styrene-*block*-2-vinylpyridine) poly(S-*b*-2VP) diblock copolymers exhibiting about 50 wt% of PS blocks were prepared by sequential anionic addition. The aim of this work is to make clear the orientation on the surface and in bulk microdomain structures of both diblock copolymers by varying the casting conditions. Morphological results of these diblock copolymer films were obtained on a transmission electron microscope (TEM). The surface characterization of poly(S-*b*-2VP) film was carried out by X-ray photoelectron spectroscopy (x.p.s.).

EXPERIMENTAL

Polymer synthesis and characterization

The well defined poly(S-*b*-I) and poly(S-*b*-2VP) diblock copolymers used in this work were prepared by sequential anionic addition, like those used in the preceding papers[6,7]. The monodisperse poly(S-*b*-I) diblock copolymers were prepared by anionic addition, with s-butyllithium (s-BuLi) as initiator in benzene at 5°C. The microstructure of PI blocks obtained from the above method contained 50% 3,4- and 50% 1,4-structures (60% *cis*, 40% *trans*)[8].

The monodisperse poly(S-*b*-2VP) diblock copolymers were also prepared by anionic addition with n-BuLi as initiator in tetrahydrofuran (THF) at -78°C.

The number-average molecular weight $\bar{M}_n$ of PS prepolymers was determined with a Toyo Soda high-speed liquid chromatograph (g.p.c.) HLC-802A, with THF as eluent at 38°C, a TSK gel GMH column, and a flow rate of $1.0\,\mathrm{ml\,min^{-1}}$. The $\bar{M}_n$ of the diblock copolymers was determined by means of a Mechrolab model 501 membrane osmometer in benzene at 37°C. The molecular-weight distribution $\bar{M}_w/\bar{M}_n$ of diblock copolymers was determined by g.p.c. distributions after improvement by the reshaping method[9]. *Table 1* lists the characteristics and the domain sizes of poly(S-*b*-I) and poly(S-*b*-2VP) diblock copolymers.

Morphology of diblock copolymer films

Poly(S-*b*-I) diblock copolymer film (40 μm thick) was

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Table 1 Characteristics of poly(S-*b*-I) and poly(S-*b*-2VP) diblock copolymers and microdomain sizes

Specimen code[a]	$10^{-4}\bar{M}_n$		Content of PS block (wt%)	$\bar{M}_w/\bar{M}_n$[b]	Shape[e]	Domain size (nm)[f]		
	PS[b]	Block[c] copolymer				$\bar{D}_{PS}$	$\bar{D}_{PI}$	$\bar{D}_{P2VP}$
SI	1.1	2.1	54	1.03	L	7.8	8.3	–
SV	1.0	2.0	51	1.20	L	9.2	–	10.3

[a] SI, poly(S-*b*-I); SV, poly(S-*b*-2VP)
[b] Determined by g.p.c.
[c] Determined by osmometry
[d] Determined by g.p.c. distribution
[e] L, lamella
[f] $\bar{D}_{PS}$ ($\bar{D}_{PI}$, $\bar{D}_{P2VP}$), average domain distance of PS (PI, P2VP) lamellae

cast from a 0.03 g ml^{-1} benzene solution on a Teflon sheet (0.11 ml cm^{-2}) and the solvent was evaporated as gradually as possible under the saturated vapour of the casting solvent. Benzene is a commonly good solvent for both PS and PI components. This film was annealed at 90°C for 24 h. On the other hand, poly(S-*b*-2VP) diblock copolymer film was cast from 1,1,2-trichloroethane (TCE) or $CHCl_3$/1,4-dioxane 6/4 (v/v) mixture. The casting solvent was evaporated as gradually as possible under saturated vapour. Subsequent annealing treatment was not carried out for these films. Both TCE and $CHCl_3$ are good solvents for PS but somewhat poor for poly(2-vinylpyridine) (P2VP). The $CHCl_3$/dioxane 6/4 (v/v) mixture seems to be a relatively commonly good solvent for PS and P2VP components. Next, the films were embedded in an epoxy resin and cut perpendicularly to the film interfaces into ultrathin sections (about 700–1000 Å thick) using an ultramicrotome (Hitachi UM-3 ultramicrotome).

Sample preparation and instrumentation

The cast film of poly(S-*b*-2VP) (40 μm thick) was dried under vacuum for 2 days at room temperature. The sample film ($7 \times 20\,mm^2$) was coated on a copper sample holder with double-sided adhesive tape and copper wire, and was dried in an argon atmosphere at ambient temperature.

Spectra were recorded on a Spectoros XSAM 800 apparatus using Al Kα exciting radiation. Typical operating conditions were: X-ray gun, 14 kV and 20 mA; pressure in the analysis chamber, 5×10^{-8} Torr. Owing to the rather long analysis times required for the angular-dependent studies, a liquid-nitrogen-cooled sample holder was used throughout the experiments. A value of 285.0 eV was used for the C 1s core level of the hydrocarbon. Overlapping peaks were resolved into their individual components by use of a DEC PDP11/03L curve resolver. These studies have shown that the lineshapes are approximately Gaussian for individual components.

The angular-dependent x.p.s. studies were carried out as follows. The sample was rotated relative to the fixed energy analyser by angle θ, which is the angle between the normal to the sample and the slits in the analyser. Spectra were recorded at two different polar angles (θ), $\theta = 0$ and 80° with respect to the sample surface, to achieve effective sampling depths of ≈ 5 and ≈ 1 nm, respectively, where the mean free length (λ) is dependent on the 1/2 power of kinetic energy. The average values for λ as a function of kinetic energy for the polymer systems are ≈ 14, ≈ 22, ≈ 23 and ≈ 29 Å for kinetic energies of ≈ 969, ≈ 1170, ≈ 1202 and ≈ 1403 eV, respectively[10].

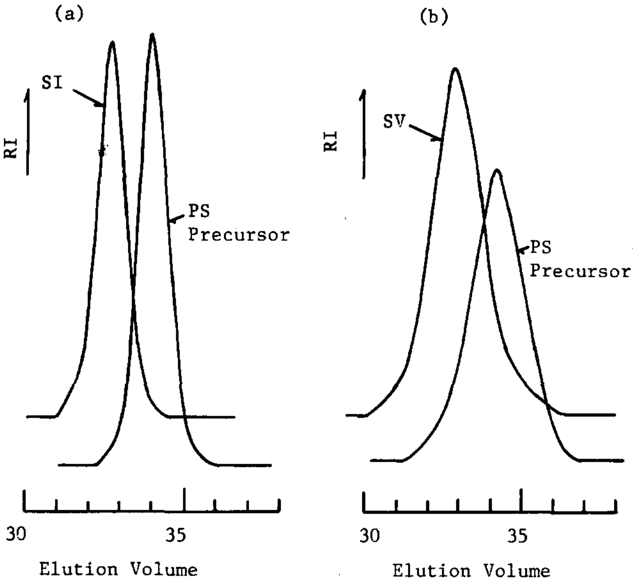


Figure 1 G.p.c. profiles of diblock copolymers and their PS precursors: (a) poly(S-*b*-I) diblock copolymer SI series; (b) poly(S-*b*-2VP) diblock copolymer SV series

RESULTS AND DISCUSSION

Figure 1a shows typical sets of g.p.c. profiles of PS precursor and poly(S-*b*-I) diblock copolymer SI. The conversion is almost 100% within experimental error. The molecular weight observed is close to the value expected from the feed ratio of monomer and initiator used. The g.p.c. elution peak of SI shifts to the side of high molecular weight, as compared with its precursor. The g.p.c. profiles show that both PS precursor and SI diblock copolymer have a single and narrow molecular-weight distribution. The observed $\bar{M}_w/\bar{M}_n$ of SI diblock copolymer is 1.03. *Figure 1b* shows typical sets of g.p.c. profiles of PS precursor and poly(S-*b*-2VP) diblock copolymer SV. Thus the g.p.c. profile of SV diblock copolymer prepared by anionic addition also has a single and relatively narrow molecular-weight distribution ($\bar{M}_w/\bar{M}_n = 1.20$).

Figure 2 shows a cross-section of the SI film cast from benzene solution near the air–polymer interface, in bulk and near the substrate–polymer interface. The upper and lower arrows indicate the free surface of the film and the surface that contacts the Teflon substrate, respectively.

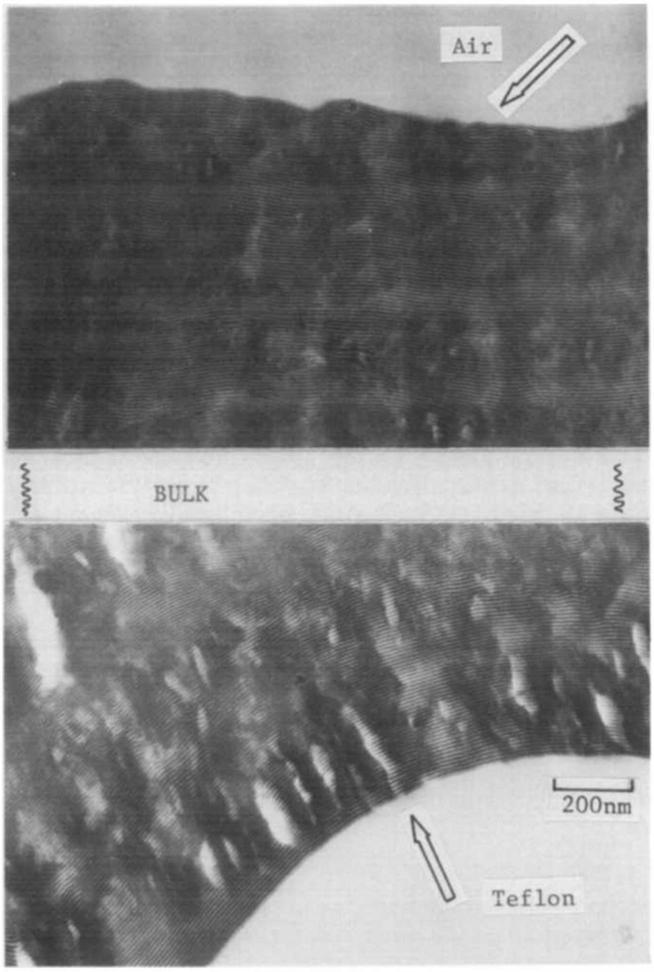


Figure 2 TEM micrographs of cross-sections of an SI film cast from benzene solution. The upper and lower arrows indicate the free surface of the film and the boundary surface that contacts the Teflon substrate, respectively

The dark portions are the selectively stained PI blocks. The thermal equilibrium morphology of SI (54 wt% PS block) is alternating lamellar structures of PI and PS microphases. The distribution of PI and PS domain sizes is very uniform owing to the monodispersity ($\bar{M}_w/\bar{M}_n = 1.03$) of SI diblock copolymer. Near the free surface, the alternating lamellar structures of PI and PS microphases are oriented with their interfaces parallel to the surface that contacts 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] and our previous work[6]. According to the explanation by Hasegawa *et al.*, 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. It is well known that the surface and bulk of block copolymers[4,11,12] or polymer blends[13] are not identical because of significant differences in the solid-state surface tension of both components. The surface tensions of PS and PI are 36 dyn cm^{-1} and 32 dyn cm^{-1}, respectively[14,15]. In our experimental results, the PI domains having lower solid-state surface tension therefore accumulate at the air interface. On the other hand, similar results are obtained in morphology near the boundary surface of the substrate film. Near the boundary surface of the Teflon substrate, the alternating lamellar structures of PI and PS microphases are oriented with their interfaces parallel to the surface that contacts Teflon. The surface tension of poly(tetrafluoroethylene) (Teflon) is 18.6 dyn cm^{-1} (ref. 16). At the boundary surface that contacts Teflon, the film is covered with a PI layer due to the segment–segment interaction between PI chains and Teflon substrate. Thus the thermal equilibrium morphology of SI (54 wt% PS block) cast on Teflon substrate is horizontally oriented PI and PS lamellar microdomains not only near the upper and lower film surfaces but also in bulk.

Figure 3 shows a cross-section of the SV film cast from TCE solution near the air–polymer interface and in bulk. The arrow indicates the free surface of the film. The dark portions are the selectively stained P2VP blocks. The thermal equilibrium morphology of SV (51 wt% PS block) is alternating lamellar structures of PS and P2VP microphases. TCE is a somewhat poor solvent for the P2VP segment. At the free surface, a PS layer is aligned with its interface parallel to the free surface of the film. Near the free surface, the alternating lamellar structures of PS and P2VP microphases are oriented parallel to the surface that contacts air. These horizontally oriented lamellar structures change to randomly oriented structures inside the diblock copolymer film. The surface tension of P2VP is estimated to be more than 40 dyn cm^{-1} from the relationship between the molar parachor and molar volume. Therefore, the PS domains having lower solid-state surface tension are considered to accumulate at the air interface.

The orientation on microdomains of block copolymers seems to depend strongly on the thermal history and casting conditions. *Figure 4* shows a cross-section of the SV film cast from $CHCl_3$/dioxane 6/4 (v/v) mixture near the air–polymer interface and in bulk. The arrow indicates the free surface of the film. This casting solvent seems to be a commonly good one for PS and P2VP components. The evaporating rate of casting solvent was very slow under the saturated vapour. It is found from this micrograph that the alternating lamellar structures of PS and P2VP microphases are oriented with their interfaces parallel to the surface that contacts air not only near the free surface but also in bulk. The distribution

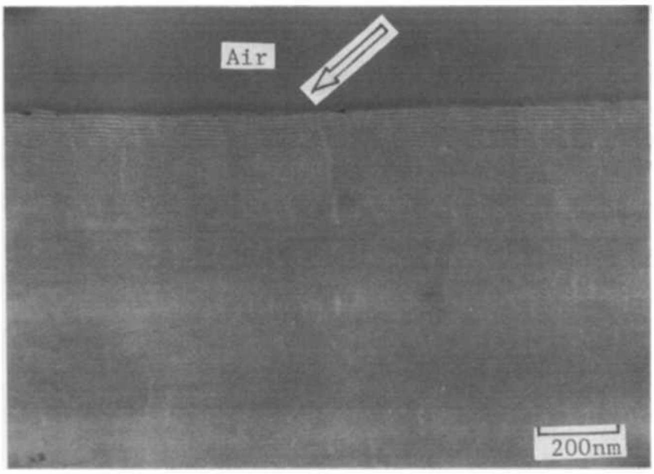


Figure 3 TEM micrograph of a cross-section of an SV film cast from TCE solution. The arrow indicates the free surface of the film

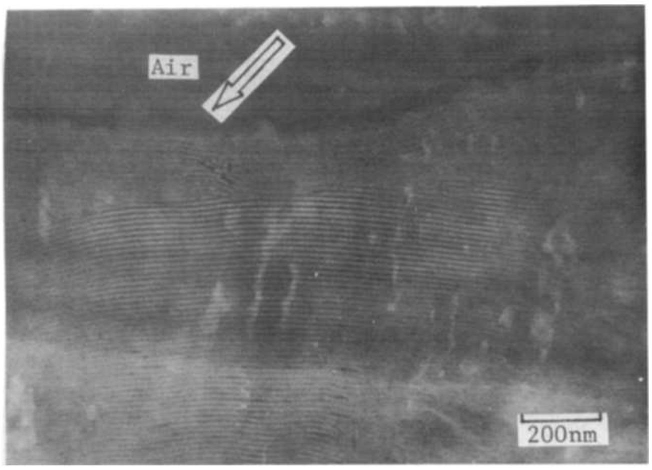
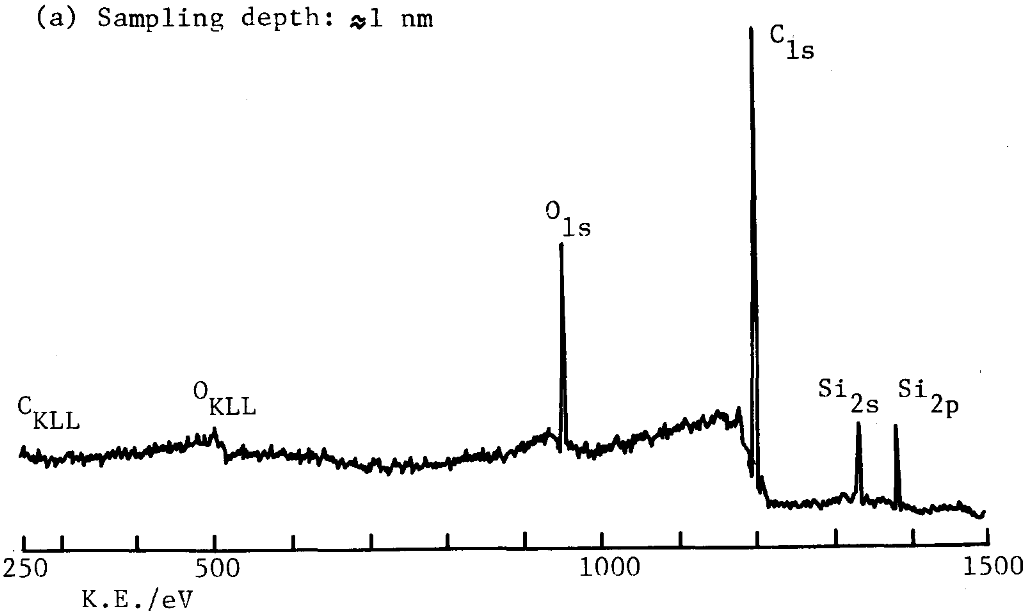


Figure 4 TEM micrograph of a cross-section of an SV film cast from $CHCl_3$/dioxane 6/4 (v/v) mixture. The arrow indicates the free surface of the film

of PS and P2VP domain sizes is uniform even in the SV diblock copolymer specimen exhibiting molecular-weight distribution 1.20. Hashimoto *et al.*[17] have reported that the uniformity of the microdomain sizes of block copolymers is much higher than the uniformity of molecular weights of the block copolymers forming the microdomains.

X.p.s. on poly(S-*b*-2VP) cast film is one of the best ways to inspect the orientation on microdomains near the free surface. *Figure 5* shows the x.p.s. survey scan (Al Kα; sampling depths ≈ 1 and ≈ 5 nm) of the cast film SV. Theoretical atomic percentages of SV are as follows: C, 86.17%; H, 7.17%; N, 6.66%. These spectra show the presence of surface oxygen (O 1s) and silicon (Si 2s and Si 2p). Confirmation of the presence of surface silicon was not obtained, and in this study we neglect the presence of this element. The x.p.s. survey scan at a sampling depth of ≈ 1 nm (*Figure 5a*) shows the presence of carbon alone. These results support the surface

(a) Sampling depth: ≈1 nm



(b) Sampling depth: ≈5 nm

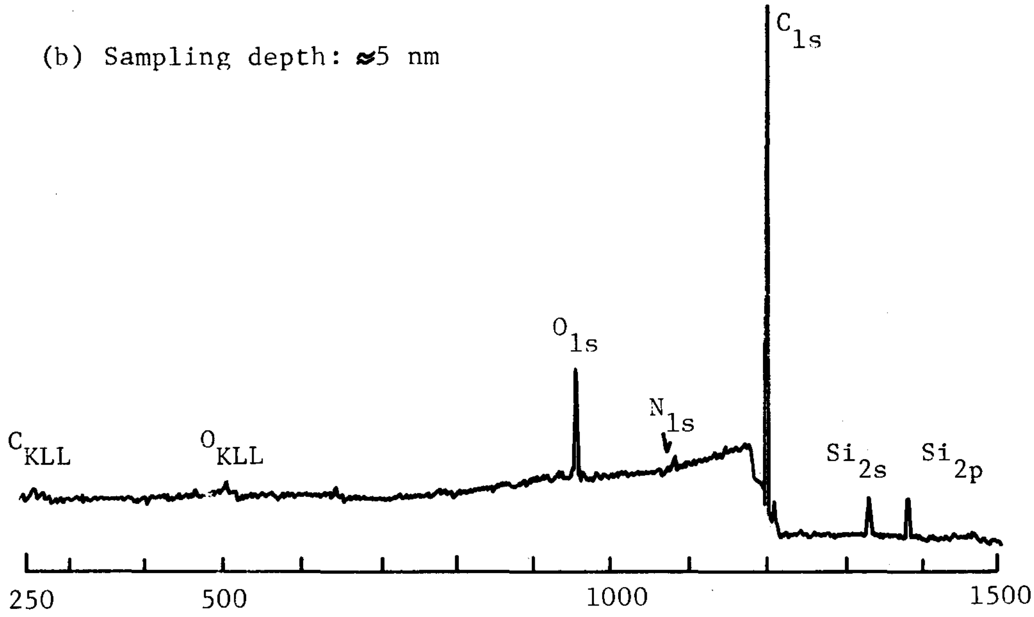


Figure 5 X.p.s. survey scan of cast film SV (Al Kα X-rays; K.E., kinetic energy): (a) sampling depth ≈ 1 nm; (b) sampling depth ≈ 5 nm

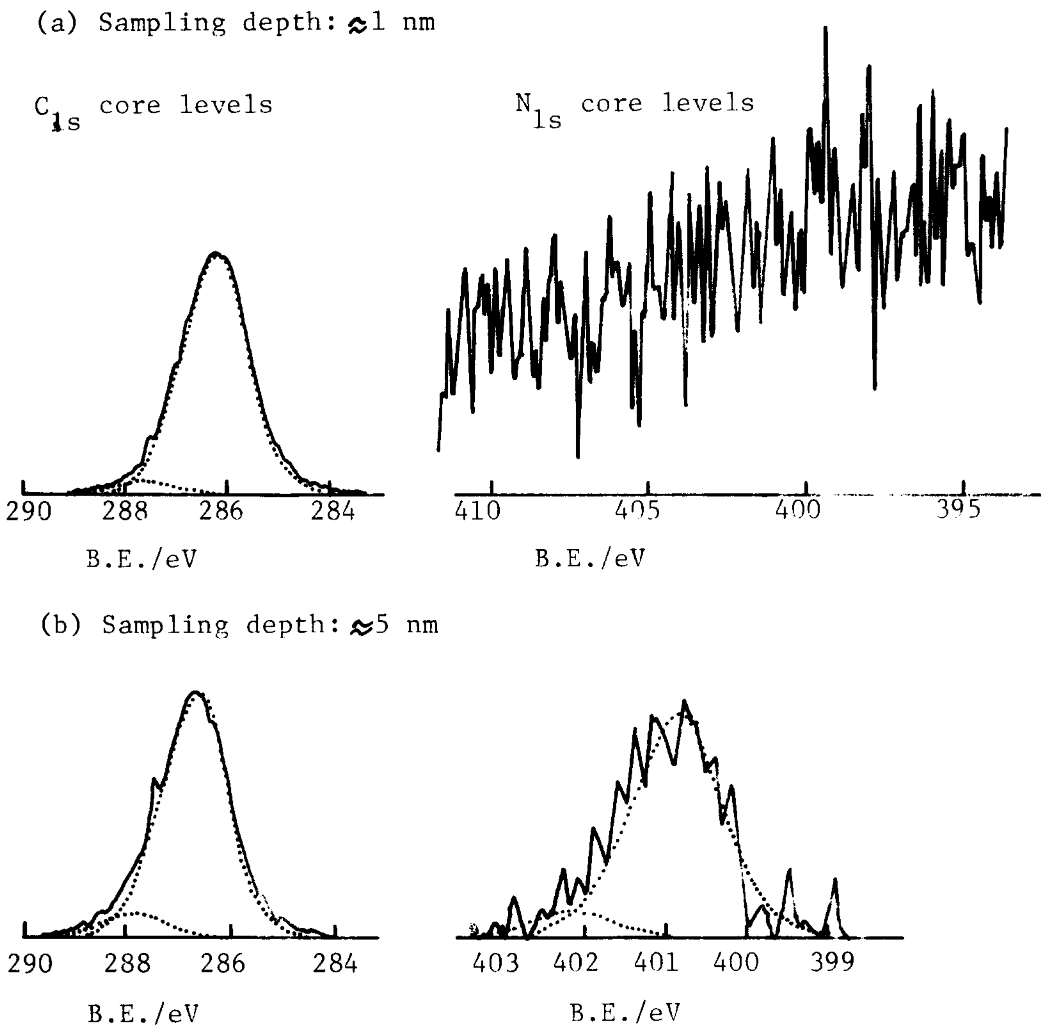


Figure 6 C 1s and N 1s core-level spectra of cast film SV (B.E., binding energy): (a) sampling depth ≈1 nm; (b) sampling depth ≈5 nm

morphology in which the cast film SV is covered with a thin PS layer at the free surface, as shown in *Figure 4*. On the other hand, the x.p.s. survey scan at a sampling depth of ≈5 nm (*Figure 5b*) shows the presence of carbon and nitrogen.

Figure 6 shows C 1s and N 1s core-level spectra at sampling depths of ≈1 and ≈5 nm. It is indicated from these core-level spectra that a small amount of nitrogen is detected at a sampling depth of ≈5 nm. The surface nitrogen content of SV film at a sampling depth of ≈5 nm calculated from the x.p.s. core-level data is 0.3%. The thickness of the outermost PS layer is judged to be about 4.5 nm, because this layer must consist of a single layer of PS block chains. These results are reasonable since the X-rays reach not only the outermost PS layer but the second layer of P2VP phase from the free surface at a sampling depth of ≈5 nm. Thus the x.p.s. core-level data also support the horizontal orientation on PS/P2VP lamellar microdomains of SV cast film.

CONCLUSIONS

In this work, we make clear that poly(S-*b*-I) and poly(S-*b*-2VP) diblock copolymers (about 50 wt% PS blocks and relatively narrow molecular-weight distribution) form horizontally oriented lamellar microdomains when these copolymers are cast from a non-selective solvent by means of the air–polymer and substrate–polymer interactions. We anticipate a practical application of horizontally oriented microdomains of PS and P2VP microphases. One of them may be as an anisotropic material for electrical conductivity. More recently, Möller and Lenz[18] have reported the electrical conductivity of a block copolymer film exhibiting a continuous P2VP/I_2 complex phase. Information obtained from our results will also be reported in the near future.

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