Phase separation in binary block copolymer blends

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The well defined poly(styrene(S)-b-isoprene(I)) and poly(S-b-2-vinylpyridine(2VP)) diblock copolymers were prepared by sequential anionic addition. Binary poly(S-b-I)/poly(S-b-2VP) diblock copolymer blend films were prepared by solution casting, varying the volume fraction of the three-block sequences. Morphological results were obtained by transmission and scanning electron microscopy (TEM and SEM). The three-phase separated microdomains formed depended strongly on the volume fraction of binary block sequences and casting conditions.

(Keywords: diblock copolymer; binary copolymer blends; volume fraction; electron microscope; three-phase separated microdomain)

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 extensively studied and found to depend, according to Molau's rule[1], on the volume fraction of the phases. Mesomorphic structures of three-phase systems have also been studied for ABC type triblock copolymers[2–4]. Riess *et al.*[3] indicated schematically some of the structures for ABC type triblock copolymers as a function of their compositions. According to their results, for a given B/A mole ratio, the basic morphologies could be a spherical structure of (A+B) dispersed in a poly C matrix, if the volume fraction of (A+B) is $\leqslant 20\%$, a cylindrical structure of (A+B) dispersed in a poly C matrix, if the volume fraction of (A+B) is 20–40%, or a lamellar structure.

Blending of block copolymers with other homopolymers is an industrially useful technique for the production of new polymeric materials. In fundamental studies[5–8] of polymer blends of AB type block copolymer/poly A/poly B, it has been shown that a given homopolymer can be solubilized in the microdomains formed by AB type block copolymer up to a certain amount. The miscibility of homopolymers in the domains is possible as long as the molecular weight of the homopolymers does not greatly exceed that of the block sequence of composition[7].

Most studies of polymeric surfactants, typically block copolymers, focus on single component systems. More recently, Halperin[9] has published a theoretical analysis of microphase separation in binary micelles. He focused on intermicellar segregation occurring after a quench, yielding complete intramicellar microphase separation. In this paper we discuss experimental aspects of multi-component systems. The problem of mesomorphic structures of binary AB/BC type diblock copolymer blends is very interesting, because the A, B and C three-block sequences can exhibit a variety of functional chemical species. If we can fabricate the three-phase separated microdomains from binary diblock copolymer blend, then it is possible to avoid the complicated process on synthesis of the ABC type triblock copolymers.

In this paper, the aim is to reveal the bulk morphology of binary poly(styrene(S)-b-isoprene(I))/poly(S-b-2-vinylpyridine(2VP)) diblock copolymer blend films by solution casting, varying the volume fraction of the three-block sequences and casting conditions.

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, the method used in References 10 and 11. The monodisperse poly(S-b-I) diblock copolymers were prepared by anionic addition, with sec-butyllithium (sec-BuLi) as initiator in benzene at 5°C. The microstructure of polyisoprene (PI) blocks obtained by the above method contained 50%, 3,4- and 50% 1,4-structures (60% *cis*, 40% *trans*)[12].

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 the polystyrene (PS) prepolymers was determined with a Toyo Soda high speed liquid chromatograph 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. *Tables 1* and *2* list the characteristics and domain sizes of the well defined poly(S-b-I) and poly(S-b-2VP) diblock copolymers, respectively.

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

Specimen code	$10^{-4} \times \bar{M}_n$		Content of PS block		Shape[e]	Domain size (nm)[f]			
	PS[a]	Block[b] copolymer	(mol%)[c]	(vol%)[d]		$\bar{D}_{PS}$	$\bar{D}_{PI}$	$\bar{R}_{PS}$	$\bar{R}_{PI}$
SI1	4.1	4.7	81.3	85.4	S_{PI}				4.8
SI2	1.1	2.1	43.2	50.6	L	7.8	8.3		
SI3	1.7	10.9	15.7	20.0	S_{PS}			7.6	

[a] Determined by g.p.c.
[b] Determined by osmometry
[c] Determined by ^{1}H-n.m.r. spectra
[d] Estimated from following densities (ρ): $\rho_{PS} = 1.01 \times 10^4$; $\rho_{PI} = 1.36 \times 10^4$ mol m^{-3} (Reference 13)
[e] $S_{PS}(S_{PI})$, PS(PI) sphere; L, lamella
[f] $\bar{D}_{PS}(\bar{D}_{PI})$, average domain distance of PS(PI) lamellae; $\bar{R}_{PS}(\bar{R}_{PI})$, average radius of PS(PI) spheres

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

Specimen code	$10^{-4} \times \bar{M}_n$		Content of PS block		Shape[e]	Domain size (nm)[f]			
	PS[a]	Block[b] copolymer	(mol%)[c]	(vol%)[d]		$\bar{D}_{PS}$	$\bar{D}_{P2VP}$	$\bar{R}_{PS}$	$\bar{R}_{P2VP}$
SV1	18	23	78.0	75.9	S_{P2VP}				23.9
SV2	1.0	2.0	51.3	54.3	L	9.2	10.3		
SV3	0.3	1.6	18.1	20.0	S_{PS}			8.2	

[a] Determined by g.p.c.
[b] Determined by osmometry
[c] Determined by $\bar{M}_n$ of PS precursor and diblock copolymer
[d] Estimated from following density: $\rho_{P2VP} = 1.14 \times 10^4$ mol m^{-3} (Reference 11)
[e] $S_{PS}(S_{P2VP})$, PS(P2VP) sphere; L, lamella
[f] $\bar{D}_{PS}(\bar{D}_{P2VP})$, average domain distance of PS(P2VP) lamellae; $\bar{R}_{PS}(\bar{R}_{P2VP})$, average radius of PS(P2VP) spheres

Morphology of binary diblock copolymer blend films

Poly(S–b-I) or poly(S–b-2VP) diblock copolymer films (40 μm thick) were cast from a 0.03 g ml^{-1} 1,1,2-trichloroethane (TCE) or $CHCl_3$/1,4-dioxane (6/4 v/v) mixture on a Teflon sheet (0.11 ml cm^{-2}), evaporating the solvent as gradually as possible under saturated vapour of casting solvents. Most of the films were annealed at 86°C for 24 h in high vacuum. Next, the films were embedded in an epoxy resin and cut perpendicularly to the film interfaces into ultra-thin sections ($\approx$70–100 nm thick) using an Hitachi UM-3 ultramicrotome. Another method was adopted for poly(S–b-I) diblock copolymer exhibiting a high content of PI blocks (SI3). An ultra-thin film specimen was prepared for electron microscopy by placing one drop of 1.0 wt% $CHCl_3$/dioxane (6/4 v/v) mixture of SI3 on a microscopy mesh coated with a carbon film, and evaporating the solvent as gradually as possible at room temperature. The film was annealed under the conditions described above.

The binary poly(S–b-I)/poly(S–b-2VP) diblock copolymer blend films (1/1 (wt/wt), 40 μm thick) were also cast from TCE or $CHCl_3$/dioxane (6/4 v/v) mixture on a Teflon sheet, evaporating the solvent as gradually as possible in the saturated vapour of casting solvents. Most of the blend films were annealed under the conditions described above. The ultra-thin sections were also obtained by means of an ultramicrotome. The specimens were exposed to the vapour of methyl iodide (MeI) or osmium tetraoxide (OsO_4) for 24 h at room temperature. The MeI selectively stained poly(2-vinylpyridine) (P2VP) phases. OsO_4 stained both P2VP and PI phases. Morphological results were obtained with an Hitachi H-600A transmission electron microscope (TEM).

The binary SI3/SV3 copolymer blend film was dry-etched. For this, the blend film was broken in liquid nitrogen to obtain the vertical section and the PI domains were dry-etched by Samco Plasma Deposition system Model BP-1 (15 w, 0.2 Torr ($\approx$30 Pa)) with argon (flow rate: 14 ml min^{-1}) for 30 min. The morphological results were obtained with a JEOL-T220 (SEM) electron microscope.

RESULTS AND DISCUSSION

Figure 1a shows typical sets of gel permeation chromatography (g.p.c.) profiles of PS precursor and poly(S–b-I) diblock copolymer SI2. The conversions are almost 100% within experimental error, in all cases. 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 SI2 is shifted to higher molecular weight, compared with its precursor. The g.p.c. profiles show that PS precursor and SI2 diblock copolymer have a single narrow molecular weight distribution. *Figure 1b* shows typical sets of g.p.c. profiles of PS precursor and poly(S–b-2VP) diblock copolymer SV2. The g.p.c. profiles poly(S–b-2VP) diblock copolymers prepared by anionic addition also have a single narrow molecular weight distribution.

Figure 2 shows TEM micrographs of poly(S–b-I) diblock copolymers. *Figures 2a* and *b* show the cross sections of the films formed by casting the TCE solution of SI1 and the $CHCl_3$/dioxane mixture of SI2, respectively. *Figure 2c* shows an ultra-thin film specimen formed on the carbon support by casting the $CHCl_3$/dioxane mixture of SI3. The dark portions correspond to the PI phases selectively stained with OsO_4. The microdomain structure in the SI1 specimen (81.3 mol% PS) shows the texture of discrete PI spheres in a PS matrix. The absolute value of the radius of the PI spheres, $\bar{R}_{PI}$, is well below the theoretical value (8.0 nm)[14]. The domain size of the SI1 specimen indicates a non-equilibrium value (see *Table 1*). It is found from *Figure 2b* that the thermal equilibrium morphology of SI2 (43.2 mol% PS) is a structure of alternating PI/PS lamellar microdomains. The domain identity period is almost the same size as the theoretical value[14]. On the other hand, the microdomain structure in the SI3 specimen (15.7 mol% PS) shows the texture of discrete PS spheres in a PI matrix.

Figure 3 shows TEM micrographs of poly(S-b-2VP) diblock copolymer films. *Figure 3a* shows the cross section of film formed by casting the TCE solution of SV1. *Figures 3b* and *c* show cross sections of the films formed by casting the $CHCl_3$/dioxane mixture of SV2 and SV3, respectively. The TCE used is a good solvent

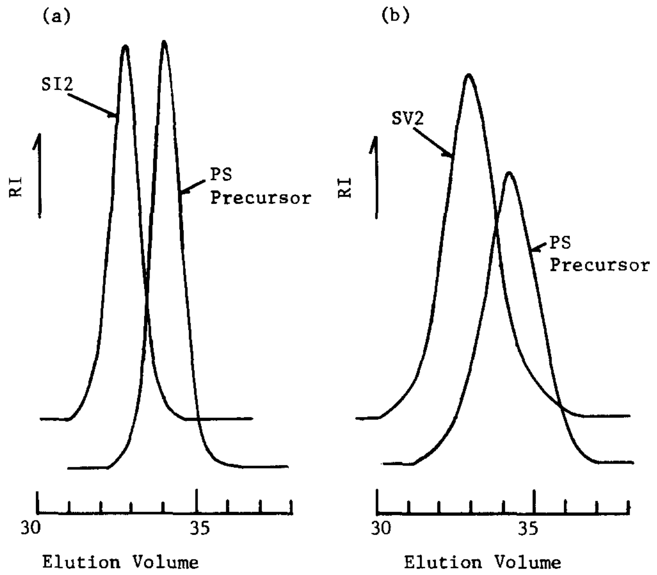


Figure 1 G.p.c. profiles of poly(S-b-I) and poly(S-b-2VP) diblock copolymers: (a) SI2; (b) SV2

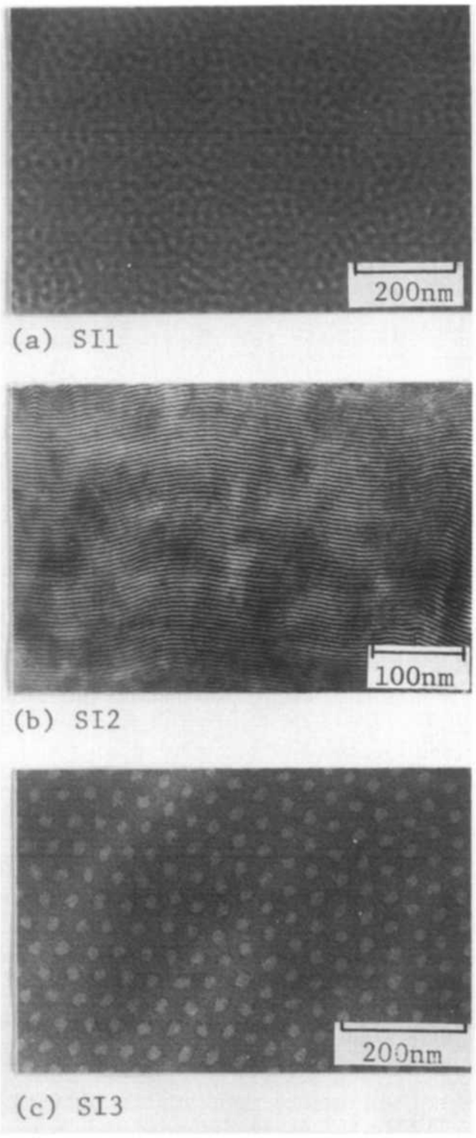


Figure 2 TEM micrographs of poly(S-b-I) diblock copolymers stained with OsO_4: (a) cross section of SI1 film cast from TEC solution; (b) cross section of SI2 film cast from $CHCl_3$/dioxane (6/4 v/v) mixture; (c) ultra-thin film SI3 cast from $CHCl_3$/dioxane (6/4 v/v) mixture

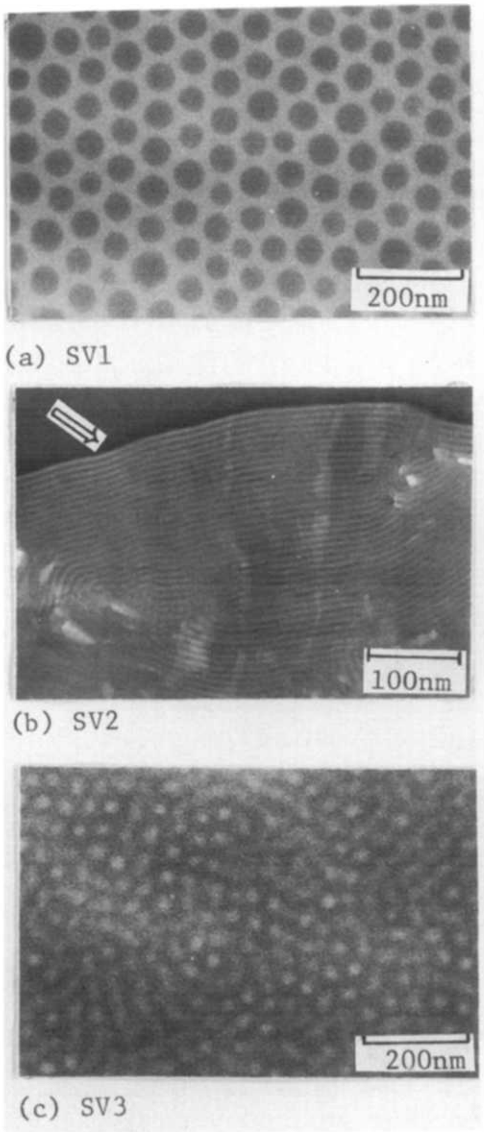
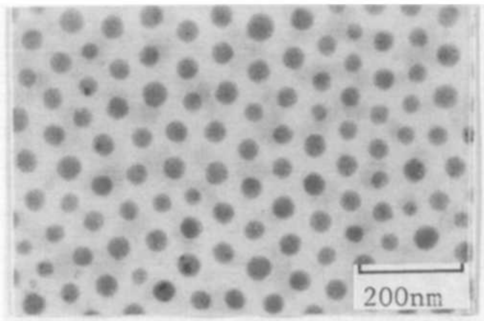


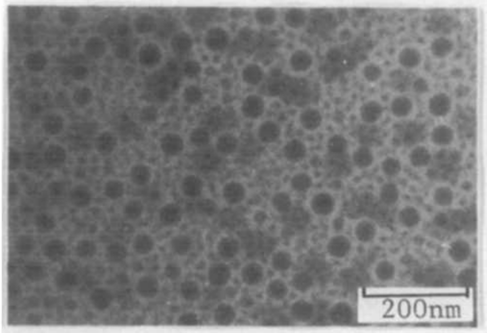
Figure 3 TEM micrographs of poly(S-b-2VP) diblock copolymers stained with OsO_4: (a) cross section of SV1 film cast from TCE solution; (b) cross section of SV2 film cast from $CHCl_3$/dioxane (6/4 v/v) mixture; (c) cross section of SV3 film cast from $CHCl_3$/dioxane (6/4 v/v) mixture

for PS, and a poor one for P2VP blocks, judging from the Hildebrand parameter. In fact, the TCE solution of SV2 or SV3 exhibiting relatively rich contents of P2VP blocks is cloudy. The dark portions correspond to the P2VP phases selectively stained with OsO_4. The microdomain structure in the SV1 specimen (78.0 mol% PS) shows the texture of discrete P2VP spheres in a PS matrix. The absolute value of the radius of P2VP spheres, $\bar{R}_{P2VP}$, is also far below the theoretical value (32 nm) as well as the morphological results of the SI1 film. The domain size of the SV1 specimen indicates a non-equilibrium value. In *Figure 3b*, the arrow shows the free surface. The thermal equilibrium morphology of SV2 (51.3 mol% PS) is a structure of alternating PS/P2VP lamellar microdomains. Moreover, it seems that the PS domains with lower solid-state surface tension accumulate at the air interface. Subsequently, alternating lamellar structures of P2VP/PS microphases are oriented parallel near the air–polymer interface. On the other hand, it is found from *Figure 3c* that the microdomain structure in the SV3 specimen (18.1 mol% PS) is the texture of discrete PS spheres in a P2VP matrix.

The glass transition temperatures (T_g) of PS, PI and P2VP are: 373; 200 (*cis*)–215 (*trans*); and 377 K[15], respectively. It is therefore difficult to judge the miscibility behaviour of binary SI/SV diblock copolymer blends by means of thermal analysis. In this work, we rely on electron microscope observations to elucidate the phase separation behaviour of binary copolymer blends. *Figure 4* shows cross-sectional micrographs of the film formed by casting the TCE solution of SI1/SV1 (1/1 wt/wt) binary diblock copolymer blend (BB1) under annealing treatment. The ultra-thin sections of this blend film are independently stained with MeI (*Figure 4a*) or with OsO_4 vapour (*Figure 4b*). The ultra-thin section of the blend film stained with MeI alone should show P2VP phases as the dark portions. On the other hand, if PI and P2VP phases are simultaneously stained with OsO_4, there must be a definite contrast between the two because OsO_4 stains double bonds darker than pyridine groups[2,4]. It is found from *Figure 4a* that P2VP spherical microdomains disperse randomly in a white matrix. This white portion corresponds to PI and PS phases. The average radius of P2VP spheres after blending decreases compared with that in *Figure 3a*. The number density of P2VP spherical domains in *Figure 4a* is about one half that in *Figure 3a*. In *Figure 4b*, the two components of P2VP and PI cannot be distinguished precisely from the electron density contrast only. However, the radius of PI spheres (SI1) is smaller than that of P2VP (SV1) used in binary copolymer blend. So the P2VP and PI spheres can be distinguished by the difference in sphere sizes. As a result, the blend film BB1 cast from TCE solution shows the three-phase separated structure of dispersed P2VP and PI spheres in a PS matrix. Thus we have found an exact result that the binary blend of SI1/SV1 diblock copolymers (BB1) is compatible with PS phases, which are common block components in the binary blend system.



(a) BB1 stained with MeI



(b) BB1 stained with OsO_4

Figure 4 Cross-sectional TEM micrographs of the film formed by casting TCE solution of SI1/SV1 (1/1 wt/wt) binary diblock copolymer blend (BB1): (a) BB1 stained with OsO_4; (b) BB1 stained with MeI

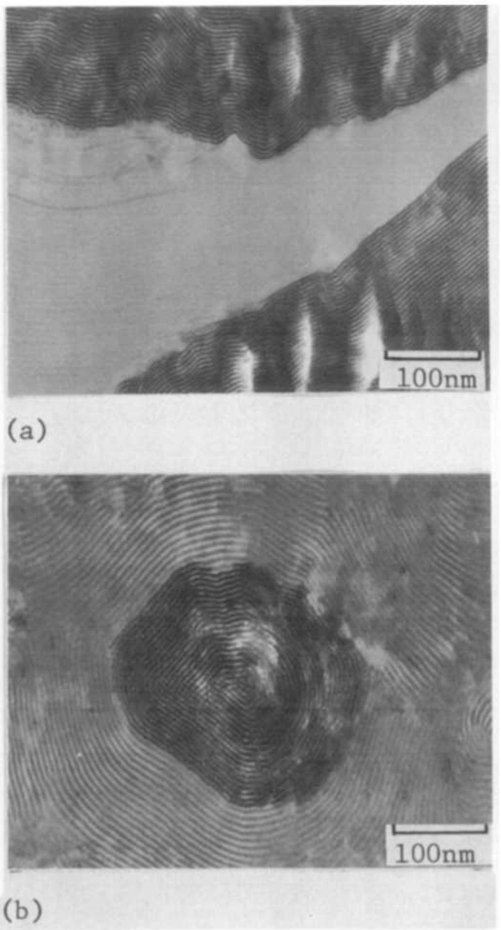
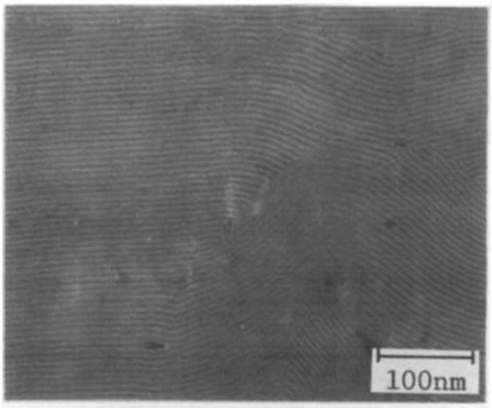


Figure 5 Cross-sectional TEM micrographs of the film formed by casting $CHCl_3$/dioxane (6/4 v/v) mixture of SI2/SV2 (1/1 v/v) binary diblock copolymer blend (BB2-1) and evaporating the solvent at 30°C, with no annealing treatment

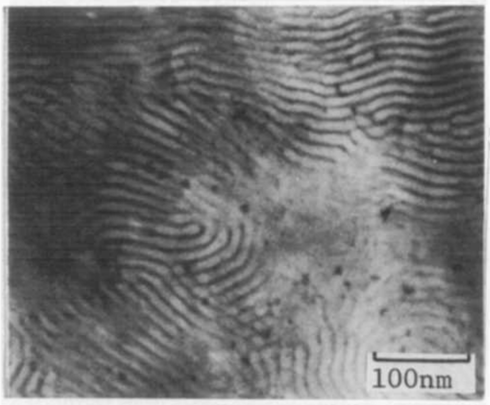
The $\bar{M}_n$ of SI2 diblock copolymer is almost equal to that of SV2. Then the domain identity periods are almost the same size in both diblock copolymer films (see *Tables 1* and *2*). *Figures 5a* and *b* show typical cross-sectional micrographs of the film formed by casting $CHCl_3$/dioxane

(6/4 v/v) mixture of SI2/SV2 (1/1 wt/wt) binary diblock copolymer blend (BB2-1) and evaporating the solvent at 30°C. The ultra-thin section of this blend film is stained with OsO_4 vapour. In this BB2-1 film specimen, there is a definite contrast between PI and P2VP phases because OsO_4 stains double bonds darker than pyridine groups. That is, the black, grey and white portions correspond to PI, P2VP and PS phases, respectively. It is found from these micrographs that SI2 and SV2 are macroscopically phase separated and that each diblock copolymer forms the lamellar structure individually. In particular, the 'onion-skin morphology' of SI2 diblock copolymer is observed in part of the ultra-thin section such as that in *Figure 5b*.

Next, the SI2/SV2 (1/1 wt/wt) binary diblock copolymer blend film (BB2-2) was cast from $CHCl_3$/dioxane (6/4 v/v) mixture, under different casting conditions. Briefly, the solvent was evaporated as gradually as possible in the saturated vapour of the casting solvent and the blend film was annealed at 86°C. *Figure 6a* shows a cross section of blend film BB2-2 stained with OsO_4. It shows clear -white-dark-lamellar structures. This morphology is observed in large areas of the ultra-thin section. The white phase corresponds to the PS layer. However, the two components of PI and P2VP cannot be distinguished precisely from the contrast in *Figure 6a*. It may be that the lamellar structure in *Figure 6a* is neither pure SI2 lamellae nor pure SV2 lamellae, nor lamellae of PS layer and PI + P2VP mixed layers. *Figure 6b* shows a cross section of blend film BB2-2 stained with MeI alone. It is found from this micrograph that the white layer is three times as large as the pure block copolymer. From the above results, the lamellar structure in *Figure 6a* is speculated to be three-layer lamellar -S-I-S-2VP-S- structure with three components in the same order. The binary blend BB2-2 is compatible with PS phases, which are common block components in the binary diblock copolymer blend. Thus the microdomain morphology strongly depends on the thermal history. Further investigation will be necessary to enhance electron density contrast by controlling the staining conditions with OsO_4.



(a) BB2-2 stained with OsO_4



(b) BB2-2 stained with MeI

Figure 6 Cross-sectional TEM micrographs of the film formed by casting $CHCl_3$/dioxane (6/4 v/v) mixture of SI2/SV2 (1/1 v/v) binary copolymer blend (BB2-2), evaporating the solvent as gradually as possible in saturated vapour and annealing: (a) BB2-2 stained with OsO_4; (b) BB2-2 stained with MeI

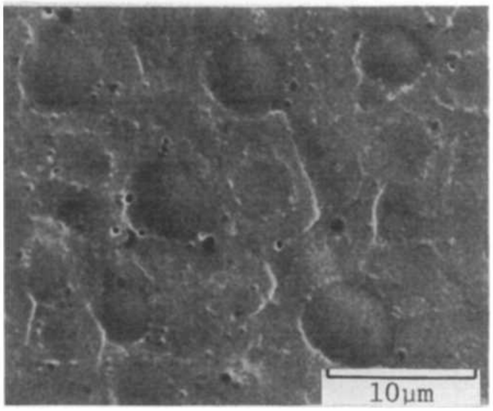


Figure 7 Cross-sectional SEM micrograph of the film formed by casting $CHCl_3$/dioxane (6/4 v/v) mixture of SI3/SV3 (1/1 wt/wt) diblock copolymer blend (BB3) after dry-etching

Figure 7 shows a cross-sectional SEM micrograph of the film formed by casting $CHCl_3$/dioxane mixture of SI3/SV3 (1/1 wt/wt) binary diblock copolymer blend (BB3) after dry-etching. This film was prepared by evaporating the solvent as gradually as possible in the saturated vapour and by subsequent annealing treatment. The dark etched holes (average diameter, $\approx 5\,\mu m$) correspond to PI domains. This micrograph indicates that SI3 and SV3 are macroscopically phase separated. As a result, the miscibility of PS blocks in the domains is possible as long as the molecular weight of PI and P2VP blocks does not greatly exceed that of the PS block sequence of composition.

The possible molecular arrangements within the domains are illustrated schematically in *Figure 8*. There must be a critical concentration at which each block segment of binary copolymer chains undergoes phase separation and aggregates into characteristic molecular micelles. In binary blend BB1, the core-shell type micelles with PI and P2VP spherical cores are formed at a critical concentration (*Figure 8a*). The micelle structures thus formed may be maintained intact until the solid structures are formed. The common PS block chains in shell portions are mutually compatible and form the continuous matrix. The two modes of molecular arrangement within the micelles, i.e. the intermicellar and intramicellar arrangements, are taken into consideration for the core-shell type micelles. The molecular arrangements within the micelles are illustrated with intermicellar arrangements in these figures. For alternating lamellar micelles such as binary blend BB2-1, the common PS block chains are mutually compatible and each end of the block chains

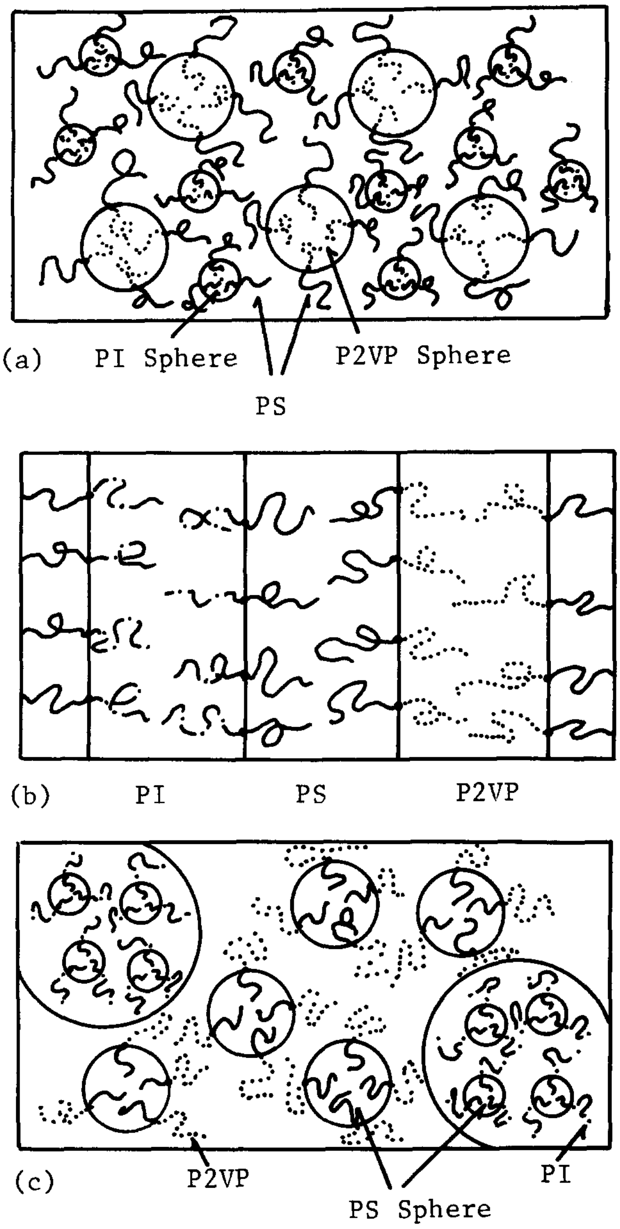


Figure 8 Schematic representations of molecular arrangement within the domains: (a) BB1 binary blend system; (b) BB2-2 binary blend system; (c) BB3 binary blend system

is at the middle layer of respective lamellae lying on a line perpendicular to the interface (*Figure 8b*). In binary blend BB3, the two core–shell type micelles with PS spherical cores are formed at a critical concentration in the opposite of binary blend BB1. The PS chains in cores are not able to interpenetrate each other. On the other hand, the PI chains in one shell portion can be incompatible with P2VP chains in other shell portions due to a repulsion effect. Therefore, SI and SV are macroscopically phase separated and each diblock copolymer forms the cluster structure of PS spheres/PI matrix or PS spheres/P2VP matrix individually (*Figure 8c*). The bulk morphology of AB/BC type binary diblock copolymer blends depends strongly on the volume fraction of three block components and casting conditions. The morphologies of binary diblock copolymer blends as a parameter ratio and of SI/SV/PS ternary blend systems are of interest. Information obtained from these results will be reported soon.

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