

polymer papers

Free surface morphology of block copolymers: 1. Styrene–butadiene diblock copolymers***Antonio Turturrot, Ercole Gattiglia and Paolo Vacca***Istituto di Chimica Industriale, Università-Centro Studi Chimico Fisici Macromolecole Sintetiche e Naturali, CNR – Corso Europa, 30-16132 Genova, Italy***and Gian Tommaso Viola***Enichem Elastomeri, Centro Ricerche e Sviluppo – Via Baiona, 107-48100 Ravenna, Italy
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The topology and morphology of the free surface of styrene–butadiene diblock copolymers were investigated by transmission electron microscopy as functions of molecular weight, composition, diene configuration, casting solvent and solvent evaporation rate. It was found that in solvent-cast thick films the formation of equilibrium free surface depends on a delicate balance of kinetic and thermodynamic parameters. Fast evaporation rates induce orientation of lamellar and cylindrical microdomains perpendicular to the free surface, while slow rates produce equilibrium-like domain orientation, parallel to the free surface. Molecular mechanisms of such arrangements are discussed, and it is concluded that to rapidly obtain an equilibrium free surface, the difference between critical surface tensions of polystyrene (PS) and polybutadiene blocks must be the greater the higher the affinity between the casting solvent and the block (PS) with the higher critical surface tension.

(Keywords: block copolymers; free surface; morphology)

INTRODUCTION

In recent times the surface characterization of block copolymers and polymer blends has been the subject of numerous papers^{1–28}. In general, it was found that in multicomponent polymer systems the composition of the surface is different from that of the bulk. Namely, the free surface or, in other words, the polymer–air interface is usually enriched in the component with the lower surface tension, as may be expected to satisfy the thermodynamic requirements for a minimal surface free energy. The extent of such a preferential surface segregation depends on the nature of the systems and on the conditions of sample preparation.

In this respect block copolymers represent a very interesting case. The chain connectivity imposes limitations on the degree of freedom of molecules. In the bulk, the incompatible blocks self-assemble in microdomains with well defined geometry and spatial organization^{29–31}. Now, questions arise about whether the microphase separation in the bulk affects the surface organization and which relationships exist between surface and bulk morphologies.

To date, there is still a limited, although growing, number of studies on the surface characteristics of phase-

separated block copolymers and a comprehensive understanding is still to be gained. In this context, it is worth mentioning the large body of works by Russell and coworkers^{9–18} on very thin films of polystyrene–poly(methyl methacrylate) diblock copolymers. This research has clarified the relationships between surface composition, surface morphology and molecular characteristics such as chain length and block constitution.

Among block copolymers, poly(styrene-*b*-butadiene), (SB) and poly(styrene-*b*-isoprene) (SI) systems are the most widely studied examples and the knowledge of their bulk characteristics is very extensive^{29–31}. Given their practical importance in applications such as adhesives, their surface characteristics are being studied by several research groups.

It has been reported that the free surface of as-cast^{6,21} or annealed^{7,8} films of SI diblock copolymers obey the thermodynamic requirements: the component block with the lower critical surface tension covers the external surface, independently of copolymer composition, molecular weight and casting solvent, at fixed temperature (30°C), evaporation time (1–2 weeks) and film thickness (100–500 µm). Moreover, Hasegawa and Hashimoto²¹ showed that, in a mixture of SI and SB diblock copolymers, the SB diblock copolymer preferentially covers the free surface, and suggested that the critical surface tension should increase in this order: 1,4-polybutadiene (PB) < 3,4-polyisoprene (PI) < polystyrene (PS).

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Thomas and co-workers^{20,22,23} examined the free surface of SB diblock copolymer films, prepared by slowly casting from toluene solutions and annealing at 115°C for 1 week under vacuum to get an equilibrium morphology. Independently of bulk morphology, PB lamellae or spherical microdomains in a PS matrix, they still observed an outermost layer of PB at the air/polymer interface.

These results are very interesting, but a complete and convincing description and explanation about the roles played by physical and molecular parameters during the formation of the free surface of the above block copolymers are missing. Many factors are still open to question as regards the morphology and topology of the free surface of as-cast films, particularly: (1) the influence of the bulk morphology on the arrangements of surface microdomains; (2) the effect of the block surface tension; (3) the effects of casting solvents and evaporation rate; (4) the influence of chain architecture; (5) the effects of substrate or strains.

We have carried out a systematic study of the surface morphology of SI and SB block copolymer thick films with the intent of investigating the effects of the copolymer constitution and composition (number and molecular weight of the blocks, diene configuration, linear and star shaped chains), as well as non-equilibrium conditions in the formation of the external surface, relative to the role of the casting solvent and its evaporation rate. This is a very important aspect since solvent casting represents a preparation method of practical importance, even in many industrial applications. Since non-equilibrium states can be reproducible and very long-life metastable states, they are worthy of investigation.

In this first paper we will present the surface morphologies of as-cast and annealed films of SB diblock copolymers and discuss them on the basis of copolymer molecular characteristics, critical surface tension of the blocks, casting solvent and its evaporation time.

EXPERIMENTAL

Materials

Poly(styrene-*b*-butadiene) (SB) diblock copolymers were synthesized by sequential living anionic polymerization, using *n*-butyllithium as initiator and cyclohexane or tetrahydrofuran as the solvent, to obtain a high percentage of 1,4- or 1,2-linkages in the PB block chain.

The copolymers were characterized via size exclusion chromatography, light scattering and infra-red spectroscopy; these data are collected in Table 1.

Critical surface tension

Few literature data exist on the critical surface tension γ_c of pure PB, PI and PS homopolymers. Due to some uncertainties which characterize the reported values^{32–35} we determined γ_c for two PB samples with about 92% 1,4-*cis* linkages and about 83% 1,2-vinyl units and PI with 65% 1,4-*cis*, 25% 1,4-*trans* and 10% 3,4-linkages.

The critical surface tension was derived by measuring the contact angles (θ) for a series of pure homologous liquids on the film surface. Before θ measurements, the homopolymers were purified by dissolution in toluene (2% w/v) and slow precipitation with ethanol.

The samples were completely dried under vacuum at 25°C. Films of $\sim 300 \mu\text{m}$ thick were cast from 7% w/v solutions in toluene at $22 \pm 2^\circ\text{C}$ in Teflon dishes, for about 3 days. Teflon dishes were used to permit easy detachment of the film from the substrate. To avoid contamination, the Teflon dishes were previously extracted in a Soxhlet apparatus for 2 days with toluene and cyclohexane, the solvents used to prepare the films for morphological observations.

Film strips ($20 \times 5 \text{ mm}^2$) on glass slides were used for contact angle measurements at 25°C and 55% relative humidity. Measurements were performed with the G-1 angrometer by Krüss, following the advancing and static drop methods. The θ value considered was the average value of 10 readings, the reproducibility of which was $\pm 2^\circ$. The liquids were ethylene glycol, 1,4-butanediol, methylformamide, dimethylsulfoxide, Pluronic 10R5, Pluronic 17R1 and poly(propylene glycol), the surface tensions of which were measured at 25°C with a tensiometer apparatus by Krüss.

Film preparation

The copolymers were dissolved into selected solvents, toluene and cyclohexane, at a 7% w/v concentration. These two solvents were chosen on the grounds of their different interactions with PB and PS blocks. Films $\sim 300 \mu\text{m}$ thick were cast by evaporation in Teflon Petri dishes, as explained above. The solvent evaporation rate was controlled by placing the dishes in an ampoule closed with an adjustable stopcock. In such a way, two evaporation times, τ_{ev} , were chosen: about 3 days (65–70 h) and almost 20 days (480–500 h). In all cases, the residual solvent (3–5% by weight) was removed under vacuum, at room temperature.

Annealing treatment

Films of SB-292 and SB-293, cast from both the solvents ($\tau_{\text{ev}} = 3$ days), were sealed in a glass ampoule under 10^{-3} torr pressure and put into an oven at 85°C for 30 days or 120°C for 45 h. The samples contained Irganox 1520 as antioxidant; however, they were also

Table 1 Characteristics of the SB diblock copolymers investigated

Sample code	PS (wt%)	M_n ($\times 10^{-3}$)	M_w/M_n	Diene configuration (1,4 <i>cis-trans</i> , %)	Morphology of microdomain ^a by TEM
SB-293	25	58.7	1.05	92	PS cylinders
SB-292	50	20.7	1.30	92	lamellae
SB-407	50	122.1	1.22	92	lamellae
SB-625	51	25.1	1.04	17	lamellae

^a Film cast from toluene solution

protected from the light by suitably covering the ampoules. After annealing the films were still soluble, proving that no crosslinking took place under these conditions.

Morphological observations

The films were exposed to aqueous solution vapours of osmium tetroxide for 1 h. The stained films were then embedded in Araldite epoxy resin, partially prepolymerized at 50°C for about 2 h to prevent eventual swelling and damage to the external surface of the film; the curing temperature and time were 70°C and about 20 h, respectively. The embedded specimens were carefully trimmed, removing the film surface in contact with the casting substrate, according to the procedure reported in the literature⁶. Ultramicrotoming was performed at -110°C in a Reichert ultramicrotome with a diamond knife at -80°C. The ultrathin sections (60–90 nm), recovered on copper grids with open mesh, were further stained with osmium tetroxide vapours for 10 min to enhance phase contrast. Morphological observations were carried out with a transmission electron microscope (Elmiskop 102 by Siemens) at 100 kV accelerating voltage.

RESULTS AND DISCUSSION

Critical surface tension

Figure 1 shows the Zisman plot ($\cos \bar{\theta}$ versus surface tension γ_{LV} , of the test liquids) for 1,2-PB, 1,4-PB and PS from θ measurements according to the advancing drop method; θ data for 1,4-PI were obtained following the static drop method because of the great difficulty in carrying out dynamic θ measurements on this sample. All the results were obtained on films that were merely well dried, since measurements done on the same films, but after some time (about 1 month), gave rise to higher surface tension values, probably due to surface oxidation phenomena. We observe a good fitting of the experimental data in linear trends which, when extrapolated to $\cos \bar{\theta} = 1$, give the γ_c values listed in Table 2 together with the solubility parameter values, δ , taken from the literature^{32,33,35}; similar data of γ_c from the literature^{32–36} are reported for comparison. No data exist for 3,4-PI homopolymer. Generally, it is deemed that

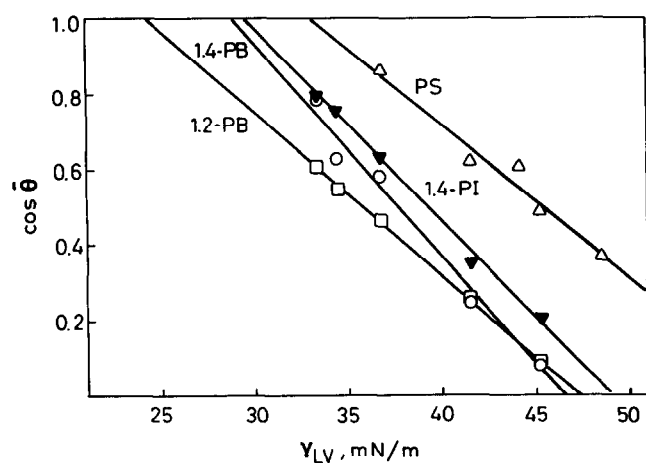


Figure 1 Zisman plots from advancing (PS, 1,4-PB, 1,2-PB) and static (1,4-PI) measurements of θ

Table 2 Critical surface tensions (γ_c) and solubility parameters (δ) for the materials used

Sample	δ^a (MPa) ^{1/2}	γ_c (mN m ⁻¹)	
		measured	literature ^b
1,2-PB	14.2*	24.5	25 (33)
1,4-PB	17.3	28.5	31–32 (33)
3,4-PI	—	—	—
1,4-PI	16.3	29.5	30–31 (33)
PS	18.6	33.5	30–36 (32,35)
Toluene	18.2	—	—
Cyclohexane	16.8	—	—

^a Data for δ from refs 32 and 35, except for * which is from ref.33

^b Ref. given in parentheses

1,2-PB and 3,4-PI homopolymers have the same critical surface tension. The γ_c value of 1,4-PI is a little higher than that measured for 1,4-PB; this difference is probably due to the different methods, as we observed that the static method gives rise to higher values than the advancing drop method. Our γ_c values for 1,4-PB and 1,4-PI are a little lower than those reported, while for 1,2-PB our γ_c value is in good agreement with the reported one. Several literature values of γ_c exist for PS, ranging from 30 to 36 mN m⁻¹^{32–36}. Our γ_c value of 33.5 mN m⁻¹ is equal to that (33 mN m⁻¹) we more frequently find and is suggested by Wu³⁶. Therefore, a difference is derived

$$\gamma_c(\text{PS}) - \gamma_c(1,4\text{-PB or } 1,4\text{-PI}) \simeq 4 \text{ mN m}^{-1}$$

which is about twice that obtainable from literature values.

Moreover, our data also confirm that γ_c for 1,2-PB is lower than that for 1,4-PB. Generally speaking, the methyl group on the side vinyl group of 3,4-PI tends in itself to lower the γ_c value³⁵; however, it slightly enhances the polarity of the side isopropenyl group, with respect to that of the vinyl group, and then contributes to raise γ_c . We feel that γ_c for 3,4-PI should be practically the same as for 1,2-PB and, in any case should not be higher than γ_c for 1,4-PB or 1,4-PI, as otherwise suggested on the basis of the surface composition of the 3,4-SI/1,4-SB diblock copolymers mixture²¹. If this were the case γ_c of 3,4-PI should be almost the same as that of PS and then it would be difficult to explain the high tendency of that block to concentrate on the surface and form the outermost layer, as clearly shown by the same authors. We believe that the presence of the SB copolymer on the film surface of the aforementioned 50/50 mixture can be caused by the higher solubility of the SB copolymer, the molecular weight of which is about five times smaller than that of the SI copolymer blended.

Unfortunately, contact angle measurements on these styrene–diene block copolymers do not allow us to obtain reliable information about the surface composition, because the γ_c values of the blocks do not differ too much with respect to the extent of experimental uncertainty of the technique used.

Surface morphology

In the following pictures representative of predominant features of the samples, the free surface of the film will be evidenced by an arrow pointing downwards to the film bulk; moreover, as is well known, due to osmium staining, the polybutadiene microdomains appear black while the polystyrene ones are white.

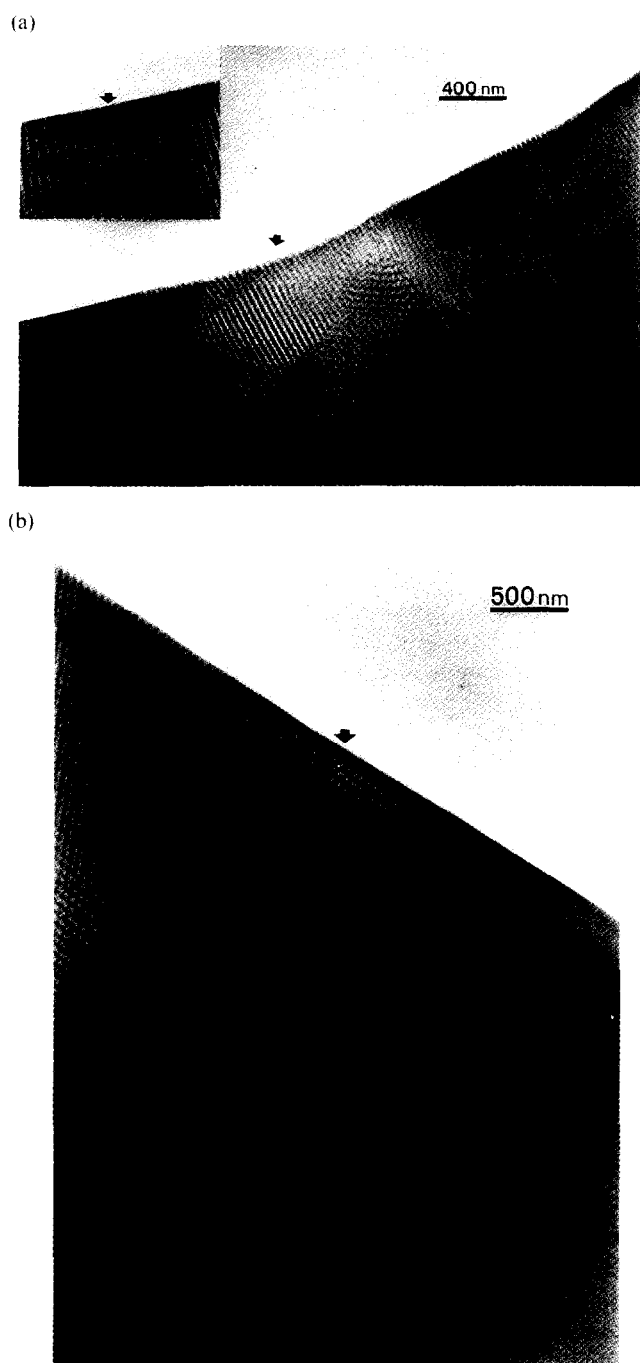


Figure 2 TEM micrographs of ultrathin sections near the free surface of SB-293 film cast from toluene solution. $\tau_{ev} = 3$ days (a) and 20 days (b)

Toluene-cast films. (a) Effect of evaporation rate. The micrographs of *Figures 2a* and *b* show the morphologies of SB-293 (25% by weight of PS, $M_n = 58\,700$) film near the external surface. For $\tau_{ev} = 3$ days, the molecular organization exhibits mainly cylinders with the main axis perpendicular to the surface (*Figure 2a*). We have always observed that, near the free surface, zones with well defined block segregation are present together with zones with a confused morphology. However, in all clearly defined areas the outermost ends of the domains are well separated from each other, and no bundles of PB chains connecting them are visible, as is more clearly shown by the higher magnification inset.

On increasing the evaporation time to 3 weeks,

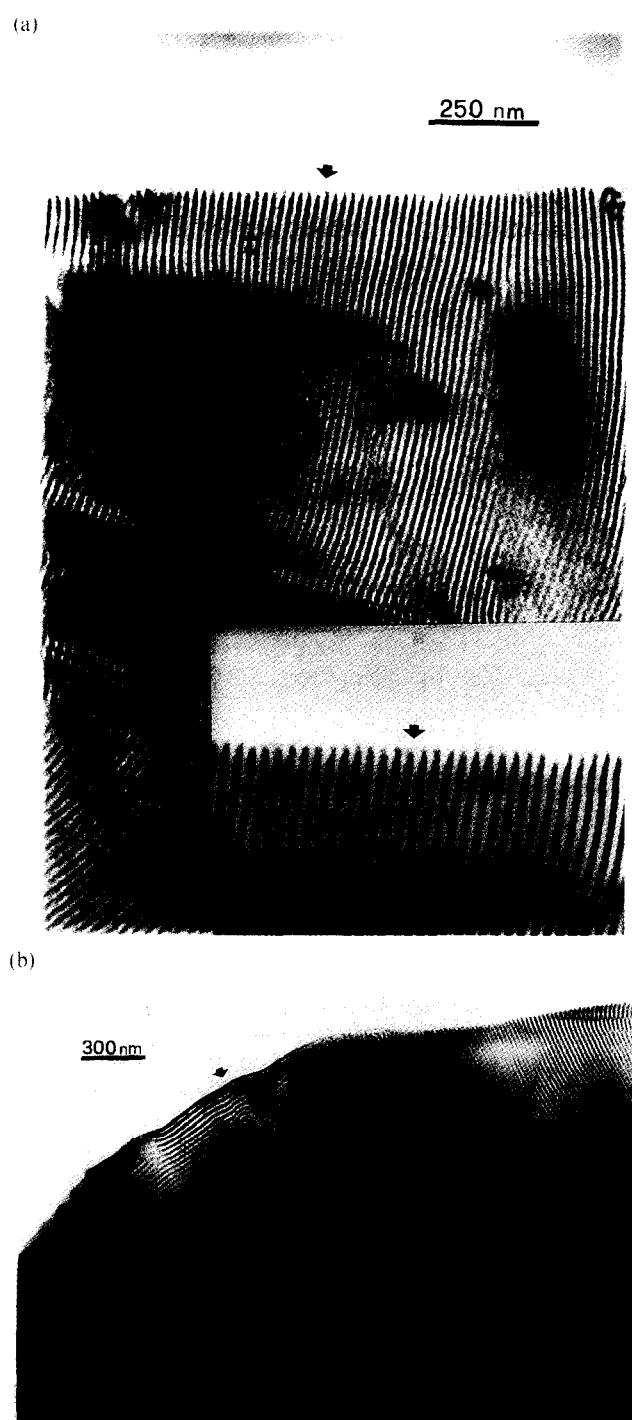


Figure 3 TEM micrographs of ultrathin sections near the free surface of SB-292 film cast from toluene solution: $\tau_{ev} = 3$ days (a) and 20 days (b)

cylinders with the main axis parallel to the free surface with the well known hexagonal packing structure are observed (*Figure 2b*). In this case we can see surface regions covered with a PB layer.

Figures 3a and *b* present the morphologies of the surface and neighbouring areas of SB-292 copolymer (50 wt% of PS, $M_n = 20\,700$) at different evaporation rates. As expected, the morphology is lamellar both in the bulk and at the surface, but the orientation of the lamellae depends on the evaporation rate. For 3 days' evaporation time, in most of the surveyed free surface the lamellae are oriented perpendicularly to the film free surface (*Figure 3a*): PB lamellae ends appear less black

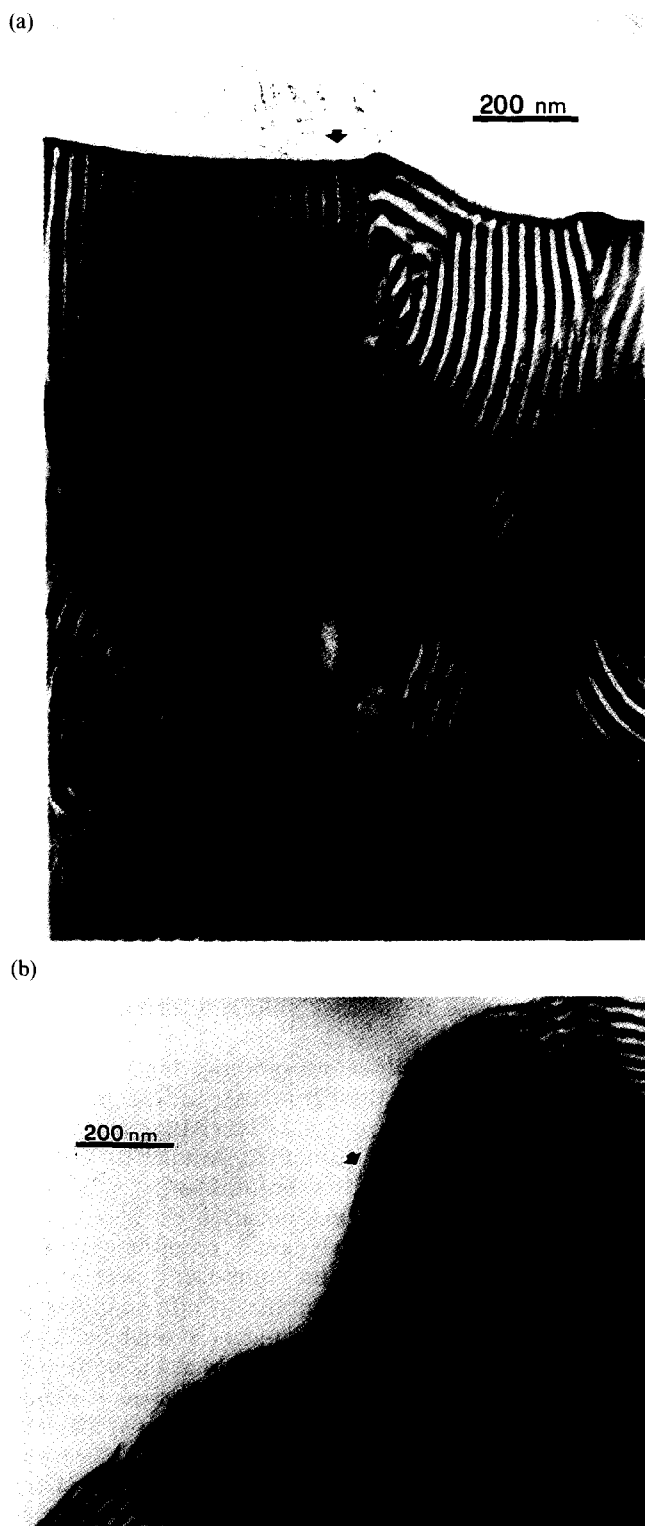


Figure 4 TEM micrographs of ultrathin sections near the free surface after annealing at 120°C for 45 h: (a) SB-293 film of Figure 2a; (b) SB-292 film of Figure 3a

than the inner parts of them, suggesting an initial spreading on the free surface of PB blocks; however, no connection between the ends of these lamellae is visible (see inset).

If the solvent evaporation is slowed down to about 3 weeks, a significant change in the surface morphology is observed as shown in Figure 3b: together with areas presenting lamellae prevalently perpendicular, regions with lamellae parallel to the free surface are also visible.

The outermost ends of the perpendicular lamellae (right part of the micrograph) are well defined and, in this case also, no material connecting them is observed. A further increase of evaporation time up to about 30 days results in a morphology consisting of surface parallel lamellae, closely resembling what is considered to be the equilibrium morphology shown for SI block copolymer films cast from solutions in toluene, but in a shorter time of 1–2 weeks²¹.

A surface topography with both domains perpendicular to the free surface has been suggested by Thomas and O'Malley¹ for polystyrene–poly(ethylene oxide) (PEO) diblock copolymer thin films. By X-ray photoelectron spectroscopy (XPS) analysis they observed surface excesses of PS, but all results were not consistent with the continuous overlayer model. So they suggested the presence of perpendicular domains, with PS ones raised above the PEO component. Schmitt *et al.*⁴ reached the same conclusions when studying bisphenol-A polycarbonate–poly(dimethylsiloxane)diblock copolymer films by XPS and IIS (ion scattering spectroscopy) techniques. In both cases no thin overlayer of the lower surface tension component residing at the surface was shown, in contrast to the findings of Clark *et al.*⁵ for poly(dimethylsiloxane)–polystyrene diblock copolymer cast films, of Hasegawa and Hashimoto²¹ for SI and of Thomas and co-workers²³ for SB diblock copolymer films annealed at a temperature greater than the glass transition temperature of polystyrene.

To gain more insight into the equilibrium state for our specimens annealing experiments were performed. The annealing at 85°C for 30 days did not induce any variation in the film morphology; instead, the annealing at 120°C ($>T_g$ of PS) for about 2 days significantly modified the surface organization. Figure 4a shows the morphology of the free surface of the SB-293 film of Figure 2a, after annealing: a well defined PB top layer always covers the underlying microdomains. In the case of SB-292, starting from the morphology with normal orientation of lamellae of Figure 3a, the annealing tends to reorient the lamellae parallel to the free surface (Figure 4b).

This experiment confirms that the equilibrium surface topology is characterized by a thin layer of PB, the lower critical surface tension component.

Figure 5 shows a micrograph of the cross-section of the

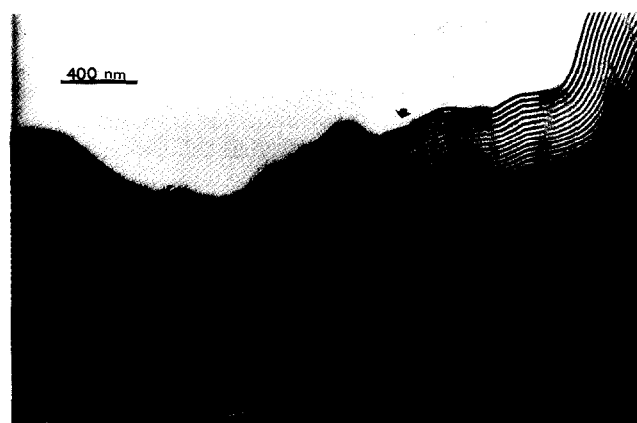


Figure 5 TEM micrograph of ultrathin sections near the free surface of SB-625 film cast from toluene solution: $\tau_{ev} = 3$ days

free surface of the SB-625 film (51% by weight of PS, $M_n = 25\,700$, and PB with 83% vinyl 1,2-linkages). As can be seen, the surface of this copolymer reaches an equilibrium overlayer morphology in a shorter time (about 3 days) than that required for the copolymer with the 1,4-PB block and almost the same molar mass (see SB-292). This suggests that the difference between the critical surface tension values of PS and 1,2-PB is great enough for it to become the main parameter controlling the formation and topology of the film surface.

A possible explanation of the coexistence of both PS and PB block microdomains on the non-equilibrium surface, cylinders or lamellae normal to the free surface, despite the unfavourable PS surface tension, can be put forward. It is known that, during film casting, the surface layer is formed first and if ordered structures are created, these propagate from the top inwards^{10,19}. It was also shown¹² that selective solvents do cause surface enrichment of the most soluble species. In general, toluene is considered to be a mutual solvent for PS, PB and PI. However, a careful analysis of several Hildebrand solubility parameter (δ) values reported in the literature^{32,35} shows that the most reliable values are those listed in Table 2 (17.3, 18.6 and 18.2 (MPa)^{1/2} for 1,4-PB, PS and toluene, respectively). No data exist for 3,4-PI while only one value (14.2 (MPa)^{1/2}) has been reported for 1,2-PB by Lee³³. This critical selection indicates that toluene should not be considered a mutual solvent for both PS and PB, but it is more selective towards PS than PB. This conclusion is also supported by the fact that solvents with higher δ (such as methyl ethyl ketone and dioxane) are very good for PS and very poor for PB, while, on the other hand, solvents with lower δ (such as cyclohexane) have the opposite characteristics. Hence, we deem that the PS block is slightly more soluble in toluene than the PB block. Then, during the formation of the solid surface the preferential affinity of the PS block causes the earlier precipitation of the PB blocks while the PS ones are pushed towards the free surface: the tendency of the PB block to occupy the film-air interface, due to its lower surface tension, is hindered by the higher affinity of the PS block chains for the solvent. For a given range of evaporation rate, these PS-toluene preferential interactions can control the chemical composition of the free surface of SB cast films, so both microdomains contribute to form the top layer. The fact that such a coexistence of PS and PB microdomains on the external surface was not observed by other authors is perhaps due to the lower evaporation rates generally used, or annulment of the solvent effect owing to annealing treatments.

However, as has been suggested by Thomas³⁷, other phenomena can also be involved in the arrangements of the block chains, such as the different diffusion speeds of solvent molecules through the segregated phases and the rate at which the SB copolymer chains in solution may add to the segregated microdomains. To discuss this point we have to consider when, during the evaporation, microphase segregation occurs.

Mori *et al.*³⁸ showed that cylindrical or lamellar microphase segregation of SI diblock copolymers in a toluene solution, at room temperature, takes place at a copolymer concentration of about 25% w/v, and the T_g of the PS block reaches room temperature at a copolymer concentration of about 75% w/v. If this is

the case, the diffusive process of the solvent molecules must play an important role in the organization of the copolymer blocks as a function of thermodynamic properties and the evaporation rate of the solvent. We note here that the glass transition temperatures of PS and PB homopolymers are very different ($T_g(\text{PS}) \simeq 100^\circ\text{C}$, $T_g(\text{PB, 1,4-cis}) \simeq -80^\circ\text{C}$); in other words, PB microdomains have a free volume content typical of a rubber and then much higher than glassy PS. Therefore, diffusivity of toluene molecules will be faster through PB than through PS microdomains, also because of the slightly more preferential interactions between toluene and PS blocks, as just discussed. This means that the solvent molecules can escape more rapidly when the lamellae are perpendicular to the free surface because they spread mainly through PB phase only, in the case of lamellae parallel to the external surface, solvent diffusion is slowed down since the transport path now involves a sequence of slow (PS layer) and fast (PB layer) alternate steps. Figures 6a and b show schematic representations of these two mechanisms.

In addition to the above phenomenon, one should consider the rate at which the SB copolymer chains still in solution can add to the already segregated microdomains. As sketched in Figure 6a, it seems relatively easier for the dissolved copolymer chains to add to lamellae in a direction normal to the free surface than to contribute to the growth of parallel lamellae. In fact, owing to the presence of the solvent molecules, and mainly due to the fast aggregation process, the newly created microdomains are not in equilibrium; therefore, the growth of the parallel lamellae is hindered because a copolymer chain, moving from the disordered solution to the microphase, must cross a more or less rich layer of PS (Figure 6b).

In the case of cylindrical morphology the solvent can always move through the PB matrix, independently of the orientation of PS cylinders. The change of orientation of the latter, from normal to parallel to the free surface on decreasing the evaporation rate, should be induced by the PB block organization on the surface, according to the thermodynamic requirements (the lowest critical surface tension component) and by the aggregation process. That is, in the cylindrical morphology, the growth of normal cylinders should be faster because PS block chains can easily add at the bottom of each growing cylinder as for normal lamellae in Figure 6a. On the contrary, when the cylinder is parallel, the aggregation of a new block chain becomes more and more difficult, increasing the PB chains emanating from the lateral surface of the cylinder, just as shown in Figure 6b for parallel lamellae.

For a given evaporation rate of the solvent or thermal treatment, perpendicular lamellae with an outermost layer of the component with the lowest critical surface tension have been observed^{21,23}. Notwithstanding this surface layer, however, the normal orientation is not the real equilibrium one. In fact, very low evaporation rates or annealings at $T > T_g$ of PS, for a sufficient time, always give rise to cylinders or lamellae parallel to the external surface. This suggests a non-equilibrium surface organization of the outermost layer chains, probably because of stretching and packing of the chains, which would negatively affect their conformational entropy and the configurational entropy of the surface, respectively.

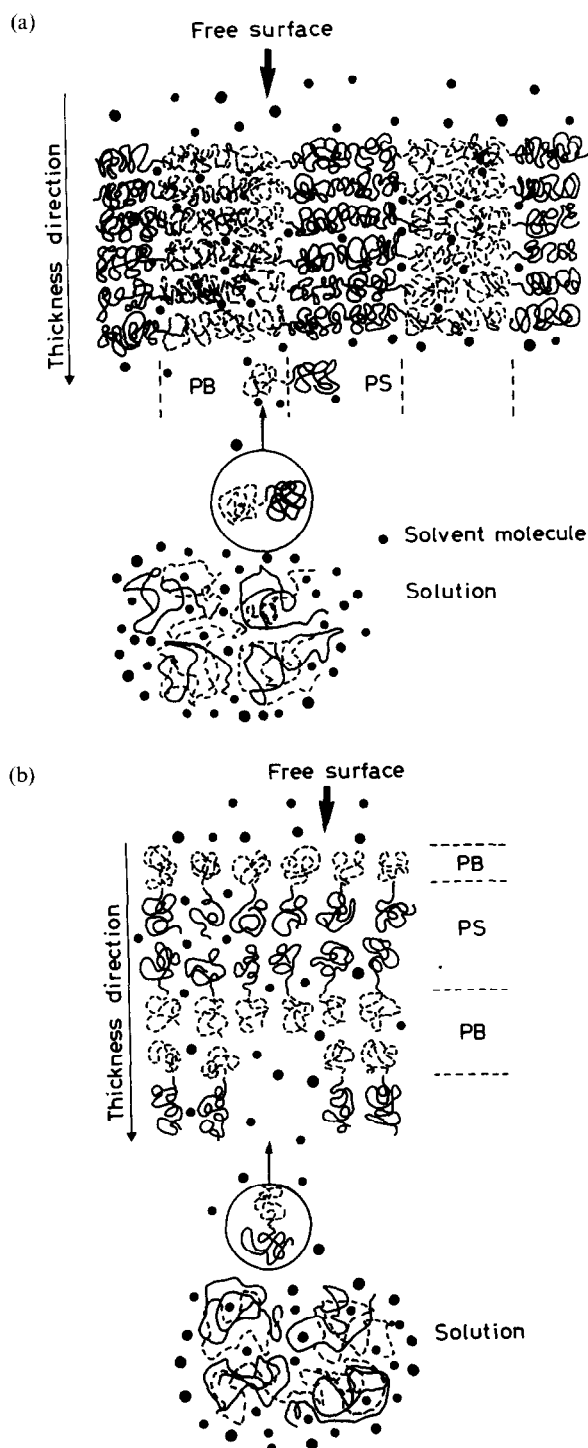


Figure 6 Sketches of molecular mechanism of growth of the lamellae perpendicular (a) and parallel (b) to the free surface

If the chains arrange on the surface according to the thermodynamic requirements, the block junction points of all copolymer chains should be in a same plane, parallel to the surface; the PS blocks of the second molecular layer would aggregate to the PS blocks of the first layer, and so on: all chains should be perpendicularly oriented to the free surface, as shown in *Figure 6b* for a lamellar morphology. In the case of horizontal cylinders only a part of the copolymer chains is arranged normally to the free surface; however, it is enough to induce an equilibrium arrangement to other chains and then an equilibrium surface morphology.

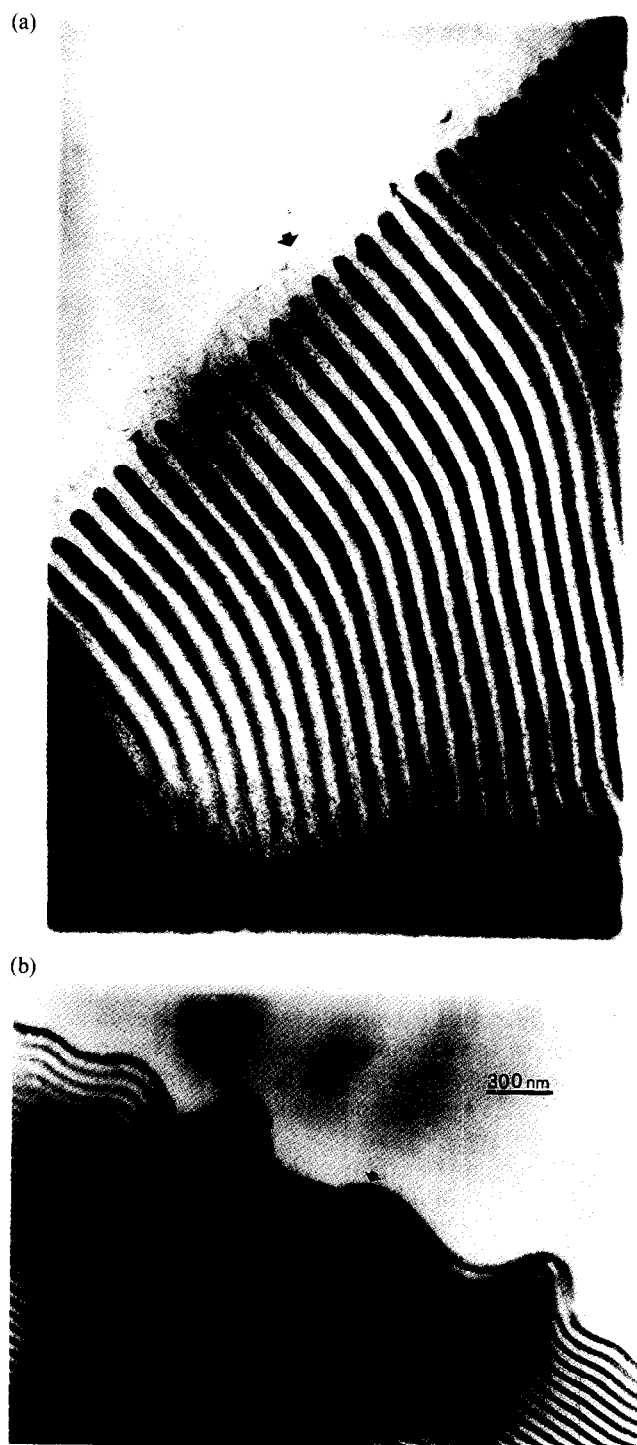


Figure 7 TEM micrographs of ultrathin sections near the free surface of SB-407 film cast from toluene solution: $\tau_{ev} = 3$ days (a) and 20 days (b)

(b) Effect of molecular weight. It is well known that increasing the molecular weight of the blocks increases the phase segregation as well: the size of block microdomains increases while the volume of total interface decreases. It is interesting to study whether M_n of the blocks may have an influence on the formation of the surface morphology. *Figures 7a* and *b* show two electron micrographs of SB-407 copolymer (PS/PB 50/50 by weight and $M_n = 122\,100$) cast from toluene at fast and slow evaporation rates. General aspects observed for low molecular weight are confirmed: fast evaporation in 3 days favours the coexistence of PS and PB domains on

the surface (Figure 7a) while at slower evaporation kinetics (20 days) a top layer of elastomer block is formed with a consequent rearrangement of lamellae parallel to the external surface (Figure 7b). We underline, however, that the outermost ends of the PB lamellae at the air interface have the shape of a match head (Figure 7a), suggesting that PB tends to concentrate on the surface. Moreover, one observes that, in some areas, the ends of PB lamellae are thinner and seem to be connected by PB chains (this aspect is difficult to realize on micrographs, but is well evident in the microscope). This suggests that the higher molecular weight sample has a major tendency to form an equilibrium surface morphology.

Again, annealing the fast evaporated film at 120°C for 45 h produces a top layer of PB covering the surface, but no global rearrangement of the lamellae is realized, probably because of the reduced mobility of high molecular weight chains.

Cyclohexane-cast films. If, as previously hypothesized, the presence of both microdomains on the surface is due to preferential solvent-block interactions, one expects significant variation on changing the casting solvent.

We cast films from cyclohexane ($\tau_{ev} \simeq 3$ days), a notoriously good solvent for PB blocks and a poor solvent for PS; thus it should not favour PS blocks on the surface. Figure 8 shows an electron micrograph of the cross-section of the free surface of the SB-292 film cast from cyclohexane. In this case, in contrast to the toluene-cast film, the microphase segregation is not so well defined. However, a trend of parallel organization of lamellae with an outermost PB lamella is visible: this organization is nearer to the equilibrium one than that with normal lamellae shown in Figure 3a, obtained from toluene-cast film of the same copolymer and after the same evaporation time.

This result can be explained by considering that, in this case, the more soluble block (PB) has the lower critical surface tension (see Table 2); therefore, both the conditions – lower value of γ_c and higher solubility of 1,4-PB in cyclohexane – drive the process in the same direction, increasing the speed of formation of the elastomer top layer.

The case of SB-407 sample is more complex. For this high molar mass copolymer the change from toluene to cyclohexane induces an overall morphology variation (Figure 9): the lamellar morphology, predicted according to the copolymer composition (50% by weight of PS) and observed in toluene-cast films, is transformed into PS cylinders in a PB matrix, oriented orthogonally (zone Y) and longitudinally (zone X) to the film thickness, that is always parallel to the free surface. Such a change is clearly related to the volume concentration of PS chains in the poor solvent cyclohexane, with the subsequent apparent increase of the PB/PS volume ratio to typical values which permit cylindrical arrangement of PS block chains.

Such a solvent influence on the morphology is well known²¹. Nevertheless, it is interesting that this phenomenon did not happen in SB-292 copolymer, which maintains lamellar morphology in films cast from both toluene and cyclohexane solutions. A combination of solvent and molar mass influences is clearly present, but



Figure 8 TEM micrograph of ultrathin sections near the free surface of SB-292 film cast from cyclohexane solution: $\tau_{ev} = 3$ days

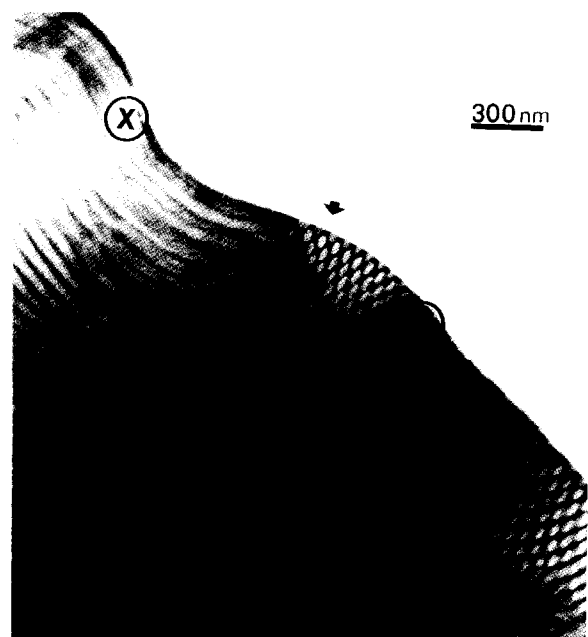


Figure 9 TEM micrograph of ultrathin sections near the free surface of SB-407 film cast from cyclohexane solution: $\tau_{ev} = 3$ days

no detailed information on such associated effects is available in the literature.

As concerns the surface, the interpretation of the TEM micrograph is not straightforward. In region X a top layer of PB seems to be present on the surface, although in the bulk the contrast and the resolution are poor; in

region Y, cylindrical PS domains are seen very close to the surface. For many such cylinders it is very hard to see the PB layer which should cover them, as observed by ourselves and other authors²¹ in other cases for similar morphologies.

As shown for SI diblock copolymers²¹ with 31% by weight of PS, in our cases also the cross-sections of the parallel PS cylinders (Figure 9) exhibit oval, not circular, shapes, with their long axes perpendicular to the external surface. Considering that no mechanical strain related to the adhesion to the casting dishes (which were purposely in Teflon) was present, we agree with Hasegawa and Hashimoto's suggestion²¹ that this deformation may be driven by a surface effect, which pushes the elastomer block chains to the surface and the PS ones away from the surface.

CONCLUDING REMARKS

The present results show that the formation of equilibrium surfaces in styrene-butadiene diblock copolymers depends on a delicate balance of many variables. As expected from thermodynamic requirements, and confirmed by annealing experiments, the equilibrium surface morphology of styrene-butadiene diblock copolymers requires the formation of an external elastomer layer, because of its lower critical surface tension than that of PS. This equilibrium surface is, however, often not achieved during the casting process, clearly pointing out the presence of kinetic and thermodynamic effects related to the characteristics and evaporation conditions of the solvent. Using toluene, a casting solvent more similar to the PS block than to the PB one, the solvent evaporation rate plays a very important role, and the formation of a 1,4-PB outermost layer occurs only for long evaporation times (>1–2 weeks), sufficient in the case of SI 3,4 diblock copolymers, even if the critical surface tensions of both the elastomer blocks are lower than that of PS.

For a given evaporation rate range, microdomains of 1,4-PB and PS blocks are present together on the free surface, independently of copolymer composition and molecular weight.

The relative slowness of the 1,4-PB block to concentrate on the surface during SB film formation, with respect to both predictions and the 3,4-PI behaviour, we believe to be due to its lower solubility in such a solvent than PS and a higher critical surface tension than 3,4-PI. In fact, 1,2-PB block, which has a γ_c probably equal to that of 3,4-PI but lower than that of 1,4-PB, shows a higher affinity for the surface and more rapidly tends to form the topmost layer. On the other hand, films cast from cyclohexane solution, a well known good solvent for PB but poor solvent for PS, exhibit equilibrium surface morphology more rapidly than the above cases. Here the preferential affinity for the surface of PB is driven by both the higher solubility in cyclohexane and the lowest critical surface tension of the 1,4-PB block.

All these findings suggest that the difference between the values of critical surface tension of blocks like PB or PI and PS, needed to permit a surface enrichment of one component, must be the greater the higher the affinity between the solvent and the block with the highest critical surface tension.

The annealing of SB cast films, at a temperature higher

than T_g of PS, cancels the effects of evaporation rate and an equilibrium organization takes place in decreasing time upon increasing the annealing temperature up to the microsegregation temperature.

As regards the dependence of microdomain organization on the solvent evaporation rate, with respect to the free surface, some mechanisms are suggested. The organization of normal lamellae should be caused by the faster diffusion of the solvent molecules through the PB phase and the easier addition of dissolved copolymer chains to the growing microdomains.

In the cylindrical morphology, the growth of parallel cylinders becomes more and more difficult, increasing the PB chains emanating from the lateral surface of the cylinder; on the contrary, the development of normal cylinders should be faster because of the easier addition of PS block chains at the bottom of each growing cylinder, as for normal lamellae.

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