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TEM study of block copolymers confined in thin films

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The behaviour of thin films of symmetric block copolymers of styrene and methyl methacrylate in contact with other polymers or with air is studied by transmission electron microscopy. The characteristic layer formation of the block copolymer in contact with vacuum or with a different, completely immiscible polymer can be observed. If one of the blocks is miscible with a contacting polymer, competitive mechanisms of swelling and diffusion are observed.

(Keywords: block copolymers; transmission electron microscopy; thin film)

Introduction

First evidence for the formation of a layer structure near to the surface of block copolymers with a lamellar morphology was obtained by Hasegawa and Hashimoto[1]. They showed the layer formation of polystyrene-*block*-polyisoprene by transmission electron microscopy (TEM) where the surface was completely covered with a polyisoprene layer. The same behaviour was found in thin films of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) and studied by neutron reflectivity[2–4], X-ray reflectivity[4], dynamic secondary ion mass spectroscopy[5,6] and TEM[7]. The layer formation of block copolymers near to the surface is similar to the phenomenon of surface enrichment of one component in miscible polymer blends[8]. The thermodynamic driving force for these processes is the difference in surface tensions of the respective neat polymers. The component with the lower surface tension is enriched on the surface, whereas for block copolymers with a composition not far from symmetry, layer formation results. In the case of thin films (thickness of several lamellae), where the overall film thickness is not a multiple of the thickness of the lamellar microdomains, holes at the surface might be formed[9–11]. Usually, the block copolymer films are prepared by spin coating on silicon wafers. Here, an additional effect can be observed in the case of PS-*b*-PMMA. Because the PMMA has favourable interactions with the silicon dioxide, which is always formed on a silicon wafer after contact with air, a PMMA layer covers the wafer. This can lead to a layer pattern of the PS and PMMA blocks with a thickness which is not alternating[4].

In this study, the inorganic substrate is replaced by random copolymers of styrene and acrylonitrile containing 25 and 35 wt% acrylonitrile, respectively (SAN-25 and SAN-35). It is known that PMMA is miscible with SAN-25 but immiscible with SAN-35[12,13] and that miscibility can also be achieved between the PMMA block in the block copolymer and SAN-25[14]. Furthermore, it is known that the PS microdomains in block copolymers are, under certain circumstances, miscible with poly(2,6-dimethyl-1,4-phenylene ether) (PPE)[15,16]. Therefore multilayer specimens are also prepared with a thin layer of the block copolymer between two thick substrates of SAN and PPE. The structure formation is then studied by TEM of ultrathin sections after RuO_4 staining.

Experimental

Materials. The molecular weight data and sources of the polymers are given in *Table 1*. The molecular weights were determined by size exclusion chromatography at room temperature using PS standards. The solvent was *N,N*-dimethylformamide for SAN and PS-*b*-PMMA and toluene for PPE. A refractive index detector was used.

Table 1 Characterization of the polymers used

Polymer	Source	M_w (g mol^{-1})	M_w (g mol^{-1})[a]	M_w/M_n
PS-*b*-PMMA(1)	[b]	81 000	47 000	1.1
PS-*b*-PMMA(2)	[b]	94 000	53 000	1.1
SAN-25	BASF	176 000	–	2·0
SAN-35	BASF	174 000	–	1.7
PPE	Aldrich	31 000	–	1.8

[a] M_w of the PS block
[b] Prepared anionically by standard procedure[23]

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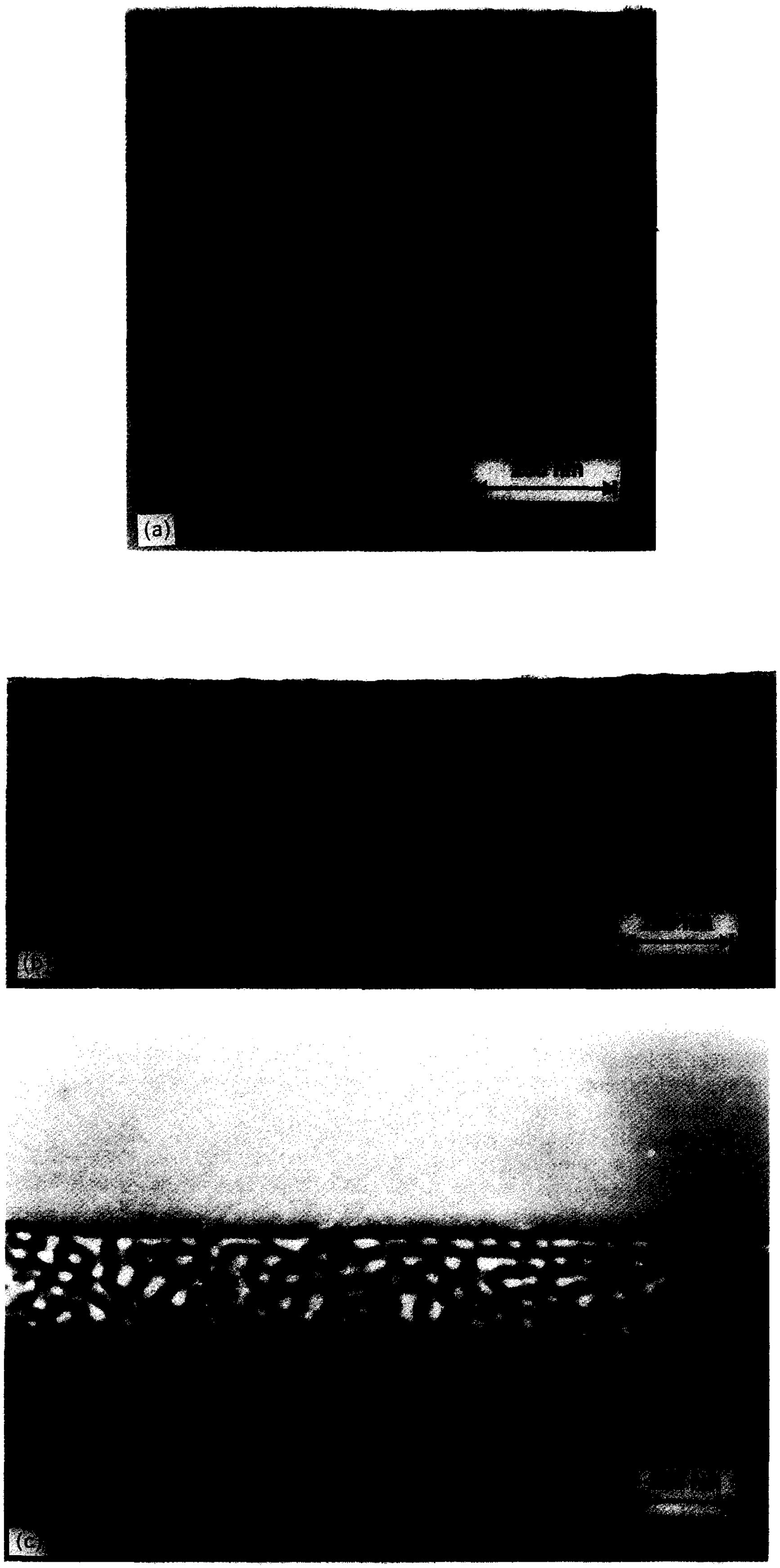

Figure 1 TEM micrographs of multilayer specimens (bottom/intermediate/top). (a) SAN-35/PS-*b*-PMMA(1); vacuum annealed at 150°C for 36 h. (b) SAN-35/PS-*b*-PMMA(1); vacuum annealed at 150°C for 72 h. (c) PPE/PS-*b*-PMMA(2)/SAN-35; annealed at 175°C for 120 h

Sample preparation. The multilayer specimens were prepared by mounting a thin PS-*b*-PMMA block copolymer film on top of a thick SAN substrate. The 1 mm thick substrate was prepared in a hot press between two polished metal plates. The thin PS-*b*-PMMA film was prepared by spin coating a 5 wt% solution of the block copolymer in toluene onto a glass slide. The film was then floated off onto a water surface and picked up with the SAN substrates. These samples were dried in a vacuum oven for 24 h and then annealed at different temperatures and for different periods of time under argon. Some of the specimens, which were not annealed, were covered with another thick layer of PPE or SAN-25 (1 mm thickness). After this procedure the samples were isothermally annealed for different times. The PPE layer was also prepared in a hot press between two highly glossy metal plates.

Transmission electron microscopy (TEM). The TEM measurements were carried out with a Zeiss EM 902 microscope with an acceleration voltage of 80 keV. The ultrathin sections were prepared with an ultramicrotome (Ultracut S of Reichert-Jung) in a direction normal to the film surface at room temperature[17]. The ultrathin sections were stained with RuO_4 in the gas phase[18].

Results and discussion

Figure 1a shows a TEM micrograph of a thin film of PS-*b*-PMMA block copolymer on a substrate of SAN-35 after isothermal annealing at 150°C for 36 h. It is known that RuO_4 is a good staining agent for the phenyl ring of styrene units in polymers[19]. In the case under consideration it is possible to stain a ternary system selectively by RuO_4. Microphase separation takes place in PS-*b*-PMMA block copolymers in the case of sufficiently high molecular weight (more than 30 000 g mol^{-1}). If the composition of the block copolymers is not too far from symmetry, a lamellar structure is formed[20]. The dark areas of the top layer in *Figure 1a* are the PS microdomains and the bright areas are the PMMA microdomains. The SAN-35 copolymer has an intermediate grey value. The early stage of layer formation can be observed at both sides of the block copolymer film. *Figure 1b* was obtained after the sample was annealed for 72 h. It can clearly be seen that the layer formation is much more perfect after a longer annealing time. Only in the middle of the block copolymer film is the layer formation partially incomplete, but there are already areas where the layer formation is finished over the whole film. As already mentioned, layer formation starts at both sides of the block copolymer film. The driving force at the surface is the lower surface tension of PS compared to PMMA[21,22]. The thickness of the upper lamella is about one-half of the PS lamella dimension in the bulk. This is reasonable because the outermost PS layer consists only of PS block chains emerging from one interface with the PMMA layer. The lamellae in the bulk always contain two layers of blocks emerging from the opposite interfaces. This result is in agreement with measurements of block copolymers of PS and polyisoprene[1]. At the interface between block and random copolymers, the lower interfacial tension between SAN-35 and PMMA compared to SAN-35 and PS should be the driving force for the layer formation. Thus one layer of PMMA blocks is arranged towards the SAN-35 surface. The next layer must then be formed by PS blocks emerging from two interfaces with PMMA. This phenomenon can be seen better in *Figure 1c*. Here, the bottom phase is PPE and the top phase contains SAN-35. At the interface between random and block copolymer, the formation of a PS stripe is most characteristic. But careful inspection shows that a diffuse bright stripe is on top of the PS stripe. The diffuse layer belongs definitively to PMMA blocks arranged towards the SAN-35 phase. At the other side of the block copolymer film PPE is mounted. Here the layer formation cannot be observed. Obviously, PS blocks could penetrate the PPE even when the annealing temperature is below the glass transition temperature of PPE. An annealing temperature of 175°C was chosen in order to make sure that thermal degradation of the PMMA block is avoided for very long annealing times.

The situation is different in the case where the substrate is SAN-25. SAN-25 is miscible with PMMA. Thus *Figure 2a* demonstrates that two competitive processes take place. At the surface the layer formation can be observed but most of the lamellae are arranged perpendicular to the interface with SAN-25. It is obvious that at the interface between random and block copolymer, an interdiffusion process occurs. A similar behaviour is observed when the thin block copolymer film is confined between two thick SAN-25 layers (*Figure 2b*). The lamellae are also extended towards the SAN-25 layers caused by the interdiffusion process. At the outermost parts of the block copolymer film, PMMA domains are swollen by an excess of SAN-25 resulting in the collapse of PS lamellae to cylindrical or spherical domains. Finally, *Figure 2c* shows PS-*b*-PMMA in contact with SAN-25 and PPE. The interface between the block copolymer and PPE becomes very rough. This is caused by PS domains attached to the interface with PPE. The spherical domains at the interface are deformed, indicating that a wetting process has occurred. The excess of block copolymer is again swollen by SAN-25.

Conclusions

TEM is a suitable tool for the study of block copolymer morphologies near to interfaces. Staining with RuO_4 gives the possibility to distinguish between PS and PMMA microdomains as well as PPE or SAN having an acrylonitrile content of 25 or 35 wt%. The layer formation can be well observed in PS-*b*-PMMA near to the surface or interface with other polymers in the case when none of the blocks is miscible with the contacting polymers. The driving force for the layer formation at the surface is the difference in the surface tension of blocks or the difference in the interfacial tensions between the blocks and the contacting polymer. In the case that one of the blocks is miscible with the contacting polymer, diffusion processes can be observed.

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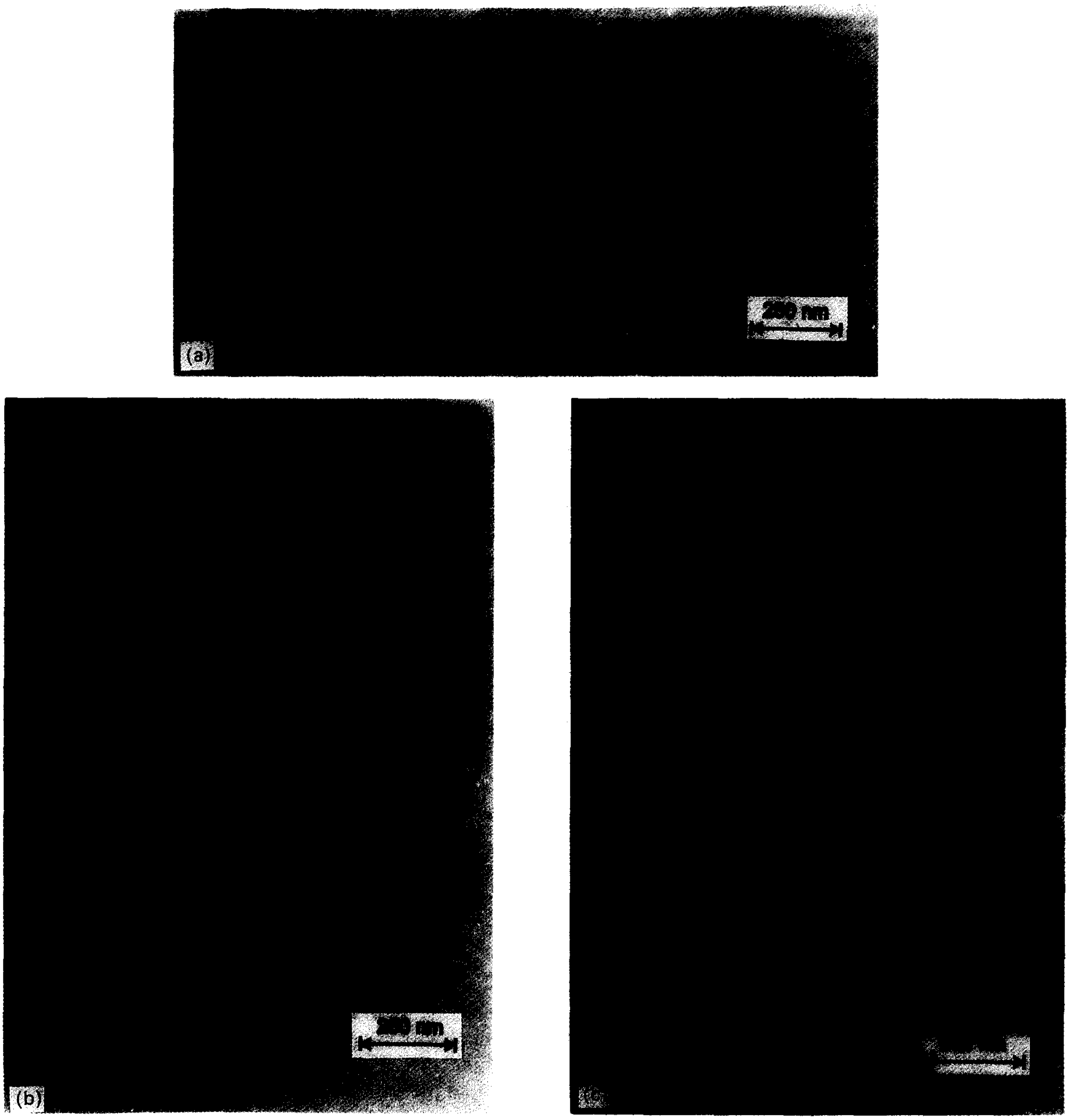

Figure 2 TEM micrographs of multilayer specimens (bottom/intermediate/top). (a) SAN-25/PS-*b*-PMMA(1); vacuum annealed at 150°C for 36 h. (b) SAN-25/PS-*b*-PMMA(2)/SAN-25; annealed at 150°C for 48 h. (c) PPE/PS-*b*-PMMA(2)/SAN-25; annealed at 175°C for 120 h

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