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TEM- AND NEUTRON REFLECTION STUDIES ON SURFACES AND INTERFACES WITH BLOCK COPOLYMERS

Bernhard Stark[+], Jonas Scherble, Markus Ganter, Jörg Kressler*, Bernd Stühn[+] und Jochen Lauter[++]

Institut für Makromolekulare Chemie und Freiburger Materialforschungszentrum, Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Str. 21, D-79104 Freiburg i.Br., Germany

[+]Fakultät für Physik, [++]ILL Grenoble, F-38042 Grenoble Cedex 9, France

Abstract: The behavior of block copolymers at various interfaces is studied by transmission electron microscopy and neutron reflection. A thin film of a symmetric diblock copolymer of styrene and methyl methacrylate forms layer structures when in contact with air and a random copolymer of styrene and acrylonitrile containing 35 wt% acrylonitrile. When the random copolymer has an acrylonitrile content of 25 wt%, a competition between layer formation and diffusion of disordered micelles takes place. Driving force for these processes are different interfacial tensions and a changing miscibility behavior as a function of acrylonitrile contents of the random copolymers. The ordering behavior of a symmetric diblock copolymer of deuterated styrene and isoprene in contact with poly(3,5-dimethyl phenylene ether) is studied by neutron reflection. Polystyrene-block-poly(ethene-co-but-1-ene)-block-polystyrene with cylindrical PS microdomains shows an interfacial phase transition to lamellae near to the interface with different polymers. The morphological studies are in agreement with adhesion data obtained by peel tests on different bilayer specimens.

INTRODUCTION

It has been known that symmetric diblock copolymers form lamellae in the bulk phase and ordered layers near to surfaces in thin films (see Ref. 1 and references therein). The difference in the surface tensions of the respective blocks is the driving force for the layer formation. The polymer block with the lower surface tension will always cover the surface after thermal annealing inducing a cooperative ordering process. This ordering process has been studied extensively by various methods in recent years (Refs. 2,3). There are only a few results on the ordering process of asymmetric block copolymers. It could be shown that triblock copolymers of polystyrene and poly(vinylpyridine) with cylindrical microdomains show a faster ordering of cylinders parallel to the surface of silicon wafers compared to the respective diblock

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copolymers with the same morphology (Ref. 4). Also a surface induced phase transition from cylindrical to lamellar morphology could be observed as theoretically predicted (Ref. 5).

This contribution deals with transmission electron microscopy (TEM) and neutron reflection (NR) studies on the behavior of di- and triblock copolymers of the type ABA at free surfaces and interfaces. Thin films of a symmetric diblock copolymer of styrene and methyl methacrylate (PS-b-PMMA) are studied near to free surfaces and in contact with different random copolymers of styrene and acrylonitrile (P(S-ran-AN)). Also the complex behavior of a PS-b-PMMA film between P(S-ran-AN) and poly(3,5-dimethyl phenylene ether) (PPE) is studied by TEM. Furthermore, it is demonstrated that neutron reflection (NR) is a powerful tool to observe the behavior of an ordered diblock copolymer of deuterated styrene and isoprene (d-PS-b-PI) in contact with PPE. Finally, the triblock copolymer polystyrene-block-poly-(ethene-co-but-1-ene)-block-polystyrene (SEBS) with cylindrical PS microdomains is studied at various interfaces. The adhesion of this block copolymer with different polymers is investigated by a peel test.

EXPERIMENTAL PART

Samples: Two random copolymers P(S-ran-AN)-25 and P(S-ran-AN)-35, respectively, (index means wt% acrylonitrile) were supplied by BASF AG. The weight average molar masses were about 170 000 g/mol and the polydispersity was about 2. The PPE sample (Aldrich) had a weight average molar mass of 31 000 g/mol and a polydispersity of 1.8. A symmetric PS-b-PMMA was prepared anionically with a weight average molar mass of 81 000 g/mol and a polydispersity of 1.1. The SEBS sample (Kraton® G1652, Shell) had a styrene content of 29 wt%. The symmetric d-PS-b-PI polymer had a weight average molar mass of 17 000 g/mol and a polydispersity of 1.04. The layer samples containing diblock copolymers were prepared by spincoating. The thin films were floated off onto the water surface and picked up with a different substrate. The bilayer samples containing SEBS were prepared by mounting two bars of the respective polymers together in a hot press.

TEM: TEM measurements were carried out with a Zeiss CEM 902 apparatus applying an acceleration voltage of 80 keV. All samples were cut perpendicular to the interface by an ultramicrotome (Ultracut E, Reichert & Jung) equipped with a diamond knife. Samples containing SEBS were cut at low temperatures. Ultrathin sections of approximately 50 nm thickness were stained with RuO_4 in the gas phase, i.e. the PS blocks appear always dark.

Neutron reflection: The NR measurements were performed at the Institut-Laue-Langevin, Grenoble using the D17 small angle reflectometer. The neutron wavelength, λ, was 11 Å and the beam collimation was achieved by a slit width of 1 mm at a distance of 260 cm. The reflected beam was detected with an area BF_3-detector at a distance of 288 cm. The sample was in upright position and the reflected intensity was measured in a Θ-2Θ-scan as a function of neutron momentum transfer $q = 4\pi/\lambda \sin \Theta$, where Θ is the angle of incidence.

Peel test: Two bars of the respective polymers were mounted together in a hot press for different times. The SEBS layer was bent and fixed in the Instron machine. The average delamination force was normalized by the width of the specimen to calculate the peel strength (Ref. 6).

RESULTS AND DISCUSSION

Fig. 1 shows three TEM micrographs of PS-b-PMMA located in thin films. The microphase separated but not very ordered block copolymer film obtained by spincoating without any thermal treatment can be seen in Fig. 1a. The same film on a substrate of P(S-ran-AN)-35 and after an isothermal annealing at 150°C for 72 h is shown in Fig. 1b. The ordering into a layer structure induced at both sides of the film is clearly seen. There is half of a lamella of PS which covers the surface to air and half of a lamella of PMMA is located at the interface to P(S-ran-AN)-35. These ordering processes are driven by the smaller surface tension of PS in comparison to PMMA and by the smaller interfacial tension of P(S-ran-AN)-35 / PMMA compared to P(S-ran-AN)-35 / PS. The situation is different when the PS-b-PMMA film is placed on P(S-ran-AN)-25 and isothermally annealed for 26 h at 150°C (Fig. 1c). In this case the PMMA block is miscible with P(S-co-AN)-25 (Ref. 7). This leads to a competition between layer formation and diffusion of disordered micelles into the P(S-ran-AN)-25 bulk phase.

A complex behavior is observed when a PS-b-PMMA film is placed between P(S-ran-AN)-25 and PPE (see Fig. 2). Fig. 2a shows that the block copolymer film forms disordered micelles during diffusion into the P(S-ran-AN)-25 bulk phase. Because the annealing temperature of 175°C is below the glass transition temperature of PPE, there is not any diffusion into the PPE bulk phase. The interface is smooth and covered with a PS lamella (dark stripe). After an annealing time of 5 days at 175°C the surface roughness

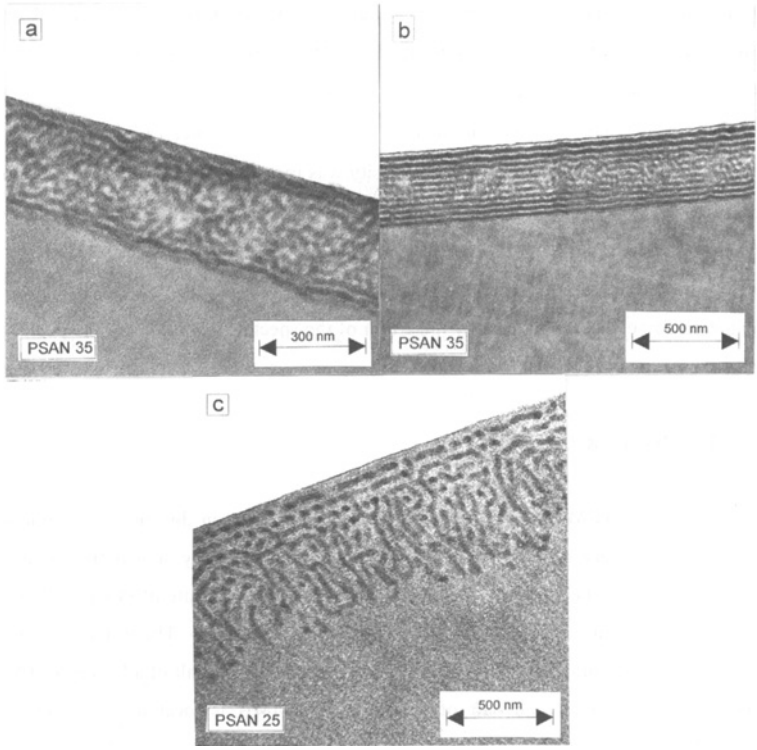


Fig. 1: PS-b-PMMA in thin films. (a) as-prepared by spincoating and mounting on P(S-ran-AN)-35, (b) as (a) but after isothermal annealing for 72 h at 150°C, (c) the substrate is P(S-ran-AN)-25 after isothermal annealing for 36 h at 150°C.

increases tremendously (Fig. 2b). Also after an annealing time of 10 days at 175°C a wavy interface can be observed (Fig. 2c). The situation changes when the sample is isothermally annealed for additional 5 days at 220°C as can be seen in Fig. 2d. The surface becomes smooth again but new domains covered with block copolymer are formed. Obviously the interface is not stable when densely covered with block copolymer. Both blocks have enthalpic favorable interactions, i.e. the PMMA block with P(S-co-AN)-25 (Ref. 6) and the PS block with PPE (Ref. 8). Thus the blocks form a dry brush on both sides of the original interfaces (Ref. 9). This means that the blocks located in the interface are not penetrated by PPE and P(S-ran-AN)-25, respectively. Thus there does not exist any interfacial tension between PPE and P(S-ran-AN)-25. Therefore, new interfacial area is created by the increase of the interface roughness and finally by the formation of new domains. Thus the amount of block copolymer in the interface is decreased leading to a wet brush. The interface is then stabilized by the

interfacial tension between PPE and P(S-ran-AN)-25. This behavior may be amplified by the fact that the attractive interactions between PS and PPE are much stronger compared to the attractive interactions in the system PMMA / P(S-ran-AN)-25 leading to an osmotic pressure at the interface.

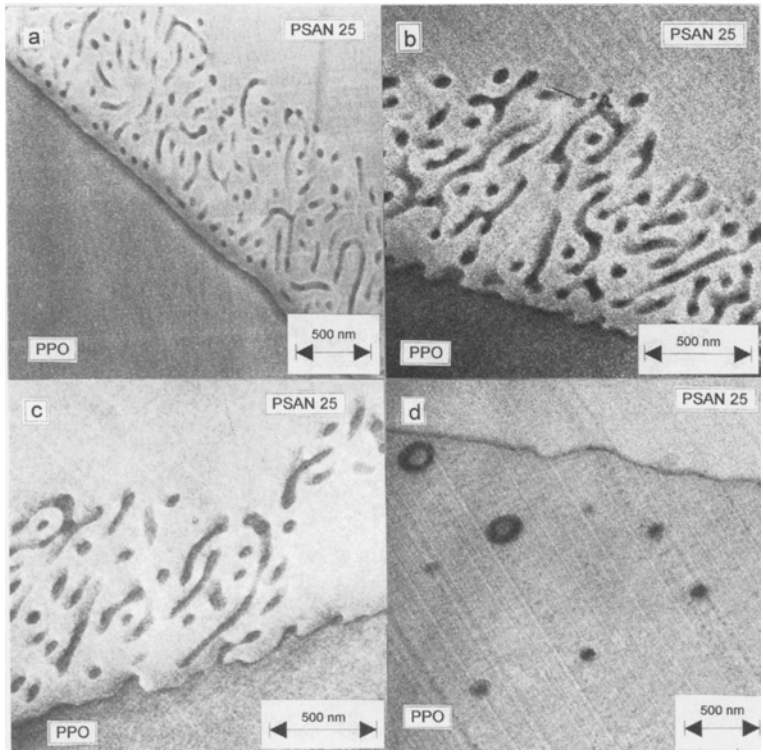
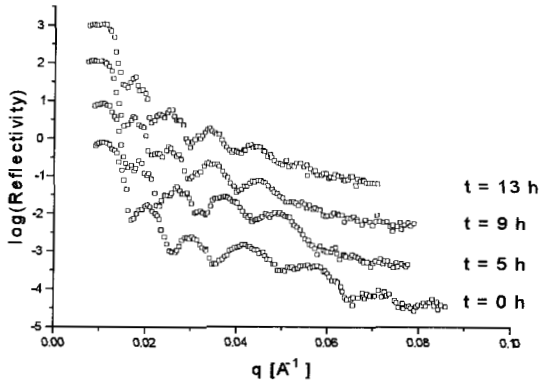


Fig. 2: PS-b-PMMA film between PPE and P(S-ran-AN)-25. (a) annealed for 3 days at 175°C, (b) annealed for 5 days at 175°C, (c) annealed for 10 days at 175°C, (d) as (c) but additionally annealed for 5 days at 220°C.

Fig. 3 shows NR measurements of d-PS-b-PI in contact with PPE. The curves are shifted on logarithmic scale. In a first step, a thin film of the symmetric d-PS-b-PI block copolymer on an Si wafer is thermally annealed leading to a layer structure where the surface is covered with PI (Ref. 10). The surface layer may contain holes in the case that the film thickness is not a multiple of the lamella thickness (Ref. 11). Then a PPE film is placed on top of the ordered d-PS-b-PI film. The NR data in Fig. 3a show Kiessig fringes which allow the

a)



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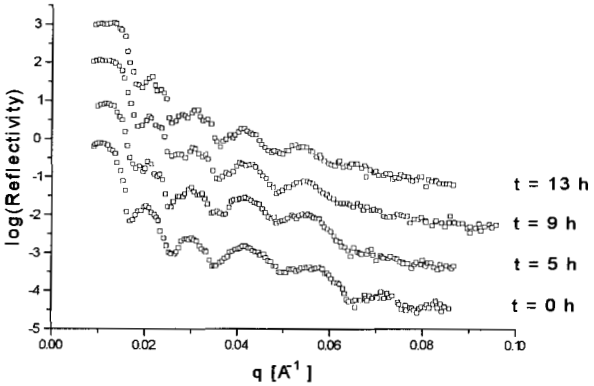

Fig. 3: NR traces of a thin d-PS-b-PI film covered with a PPE layer. (a) taken after different annealing times at 130°C, (b) the traces at 5h, 9h and 23 h are stretched by a factor of 1.1186, 1.2162 and 1.2215 in x-direction.

determination of the thickness of the block copolymer film. They are modulated by the interference from the internal structure of this film. It can be seen that the distance between the large maxima decreases with increasing annealing time. This means that the thickness of the block copolymer film (deuterated layer) increases. But the increase levels off with time. This can also be seen in more detail in Figure 3b. The NR traces of the annealed samples are

stretched by constant factors in x direction. This leads to NR traces which are then widely identical with the sample at t = 0 h. Thus it seems possible that only the first d-PS lamellae is mixed with PPE but the layer structure of d-PS-b-PI is widely unaffected. That means a PI lamella is in contact with PPE and prevents a further diffusion of d-PS lamellae into the PPE phase.

The situation is different for SEBS which forms in the bulk phase hexagonally packed PS cylinders in an EB matrix (Ref. 12). Fig. 4a shows an example for SEBS in contact with PPE after an isothermal annealing time of 15.25 h at 225°C. The explanation of this behavior is schematically shown in Fig. 4b. The PS cylinders start to rearrange parallel to the interface driven by favorable interactions between PS and PPE. Near to the interface occurs an interfacial phase transition, i.e. lamellae can be observed. This provides the possibility that the interface is completely covered with PS and simultaneously it prevents unfavorable contacts between PPE and EB blocks. It can be seen that this process is cooperative and a second lamella is formed parallel to the interface.

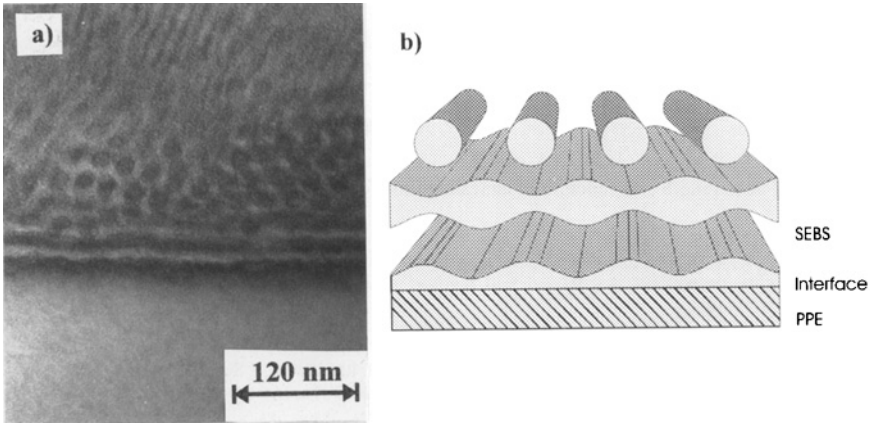

Fig. 4: (a) TEM micrograph of SEBS at the interface to PPE after isothermal annealing for 15.25 h at 225°C. (b) Schematic drawing of the interfacial phase transition.

Finally, Fig. 5 shows peel test results for SEBS in interfacial contact with different polymers. It can be seen that the peel strength depends strongly on the polymer species which is in contact with SEBS. There is only a weak peel strength between SEBS and the PS

homopolymer. Because the PS homopolymer has a much higher molecular weight compared to the PS blocks in SEBS, there does not exist any miscibility caused by entropic restrictions. Furthermore, the molecular weight of the PS blocks is below the entanglement molecular weight. On the other hand, there is a strong adhesion between SEBS and PPE as well as isotactic polypropylene (i-PP). Again this correlates with the observed morphologies and it is a direct result of strong favorable interactions between the systems PS / PPE and i-PP / EB, respectively.

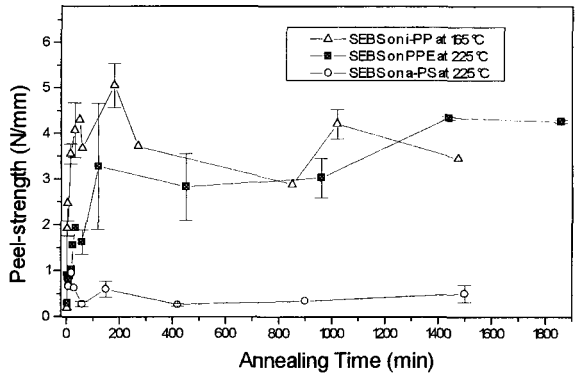

Fig. 5: Peel strength as a function of annealing time for SEBS on three different polymers.

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