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Polymer 49 (2008) 2153–2159

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Phase separation of polystyrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS) deposited on polystyrene thin films

Li Wang [a,b], Jiang Zhao [a,*], Charles C. Han [a,*]

[a] *Beijing National Laboratory of Molecular Science, Joint Laboratory of Polymer Science and Materials,*
State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry,
Chinese Academy of Sciences, 2 Zhongguancun Bei Yi Jie, Beijing 100080, China
[b] *The Graduate School of the Chinese Academy of Sciences, Beijing 100080, China*

Received 23 October 2007; received in revised form 9 February 2008; accepted 16 February 2008
Available online 4 March 2008

Abstract

Phase separation of a triblock copolymer, polystyrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS) on the thin films of a homopolymer, polystyrene (PS), was studied by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The final morphology after phase separation was found to be greatly dependent on the relation between the molecular weight of the PS block and homo-PS. Dispersed spherical and worm-like micelles of SEBS were observed when the molecular weight of homo-PS is smaller than the PS block in SEBS, while large structures with inner micro-phase separation of SEBS was found when the molecular weight of homo-PS was much higher than that of the PS block. The origin of such a change in morphology is attributed to the difference of structure and interfacial tension at the interface between the matrix homo-PS and the PS block in SEBS triblock copolymer assembly.

Keywords: Block copolymer; Phase separation; Interface

1. Introduction

Surface patterning by the micro-phase separation of block copolymers has been receiving considerable research attention. Compared with the micro-phase separation in three dimensions, surface patterning with thin films of block copolymers is largely affected by the interfacial effect, such as the surface segregation of block segments and the surface confinement effect, in which the match and mismatch of the film thickness and the periods of the ordered structure matters. Extensive efforts have been put to achieve ordered surface patterning via block copolymers by surface modification in order to tune the surface interaction as well as to adjust the film thickness to match the repeating periods of the ordered structures [1–6].

Blending homopolymers with block copolymers has been proved to be another interesting approach to modify the morphology of the block copolymer self-assembly. By blending homopolymer of identical chemical structure with one block in the copolymer, the dimension of the domains in the final phase separation has been adjusted, by changing either the volume fraction or the molecular weight of the homopolymer [7–12]. At low volume fraction of the block copolymers, the structure formation is analogous to micelle formation of surfactant molecules in solutions, and the interfacial tension between the copolymer and the homopolymer is a critical factor. A number of works were conducted two decades ago, both experimentally and theoretically [12–21]. However, they mainly focused on the situation of blending the homopolymer with diblock copolymers, for example, the well studied systems of polystyrene-*b*-polybutadiene and polystyrene-*b*-polyisoprene [7,8,17–19]. Compared with diblock copolymers, micro-phase separation of triblock copolymers has been found to generate much richer morphology, and the

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* Corresponding authors. Tel./fax: +86 10 82619847.
E-mail addresses: jzhao@iccas.ac.cn (J. Zhao), c.c.han@iccas.ac.cn (C.C. Han).

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doi:10.1016/j.polymer.2008.02.037

morphological novelty of triblock copolymer drove us to explore the system of their blends with homopolymers. Also, the phase separation of these systems in thin films is another motivation of this study because it may provide a new route for thin film and surface patterning. Because the interfacial effect can affect the morphology of thin polymer films to a large extent, it is important to explore an effective way to screen the interfacial effect and maintain the morphology by phase separation of triblock polymer and the homopolymers. Such a study on this phenomenon in thin films is also important for the thin film applications, for example, in the coating technology.

In this paper, we report our studies of the phase separation of a triblock copolymer, polystyrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS) in the thin film of a homopolymer, polystyrene (PS). By studying the morphology as a result of such a mixing process in the annealing of solvent, the effect of the molecular weight difference between the homopolymer PS and the PS block in the SEBS triblock copolymer was investigated. The phase separation exhibits drastic differences in morphology when the molecular weight of the homopolymer is varied with respect to the molecular weight of the PS block in SEBS copolymer.

2. Experimental section

The sample preparation was conducted in two steps. Firstly, a thin film of PS was prepared on silicon wafer by spin-coating. Afterwards, mixing SEBS triblock copolymer with this PS film was conducted by applying SEBS solution on top of this PS film, by either spin-coating or droplet deposition method. The purpose of the pre-coated PS film is to screen the possible interfacial effect of the substrates because it was found, in our previous study, that the PS block interacts stronger to the silicon oxide surface than the PEB block [22]. The surface morphology of the surface and the inner structure of the film were characterized by an atomic force microscope (AFM) and a transmission electron microscope (TEM).

2.1. Materials

The triblock copolymer, polystyrene-*b*-(ethylene-*co*-butylene)-*b*-styrene (SEBS) was purchased from Kraton Co. (Catalog Number: G-1651). It is a linear triblock copolymer with two PS end blocks, each with a molecular weight of 29×10^3 g mol^{-1}, and a poly(ethylene-*co*-butylene) (PEB) mid-block with a molecular weight of 116×10^3 g mol^{-1}. The homopolymer, polystyrene, was purchased from Aldrich ($M_n = 4 \times 10^3$ g mol^{-1}, $M_n/M_w = 1.01$; $M_n = 29 \times 10^3$ g mol^{-1}, $M_n/M_w = 1.01$) and National Standard Material Center of China ($M_n = 635 \times 10^3$ g mol^{-1}, $M_n/M_w = 1.26$).

2.2. Film preparation

Silicon wafers with $\langle 110 \rangle$ orientation were purchased from General Research Institute for Nonferrous Metals (Beijing, China). As substrates, they were cut into 10 × 10 mm pieces. PS films on substrates were prepared by spin-coating technique at the rate of 2500 rpm using its 4.0 wt% toluene solution. The samples were dried in vacuum at room temperature for 24 h to remove residual solvent and the thickness of the PS films ranged from 100 nm to 500 nm depending on the molecular weight of the polymer. Afterwards, SEBS solutions of toluene with different concentrations ranging from 0.02 wt% to 2.0 wt% were spun onto polystyrene film at 2500 rpm for 60 s. Samples were also prepared by droplet deposition method, in which a droplet of SEBS solution (~40 μl) was deposited onto the PS film and considerable time was allowed to let the solvent evaporate. All of the samples were kept in vacuum overnight for solvent removal. The thickness of the films was measured by an F20 Thin-Film Analyzer (Filmetrics).

2.3. Atomic force microscopy (AFM) and transmission electron microscopy (TEM)

The surface morphology of the sample was characterized by an AFM in its tapping mode. The measurements were conducted at ambient conditions by a NanoScope III Multimode AFM (Digital Instruments), using a silicon tip with a scan rate of 1.0 Hz. The inner morphology of the sample was observed by a TEM (JEM-2200FS, JEOL). The samples were stained by RuO_4.

3. Results and discussions

Fig. 1 shows the AFM images of the surface morphology for the film after SEBS spin-coated from its 0.1 wt% toluene solution on the film of PS with different molecular weights, 4×10^3 g mol^{-1}, 29×10^3 g mol^{-1} and 635×10^3 g mol^{-1} at different magnifications. In the images, the structures formed by the micro-phase separation are clearly seen with the dark parts correspond to domains formed by PEB blocks, and the light parts indicate PS.

Drastic differences in surface morphology are discovered for SEBS in homo-PS film with different molecular weights. In the PS film of 4×10^3 g mol^{-1}, the morphology appears to be scattered PEB dots of ~40 nm in diameter inside the PS matrix (Fig. 1A and a). In the PS film of 29×10^3 g mol^{-1}, a dendritic and branch-like morphology is discovered (Fig. 1B and b). The width of the individual branch is approximately 40 nm. In the PS film of even higher molecular weight (635×10^3 g mol^{-1}), the surface appears to consist of features of much bigger dimensions inside PS matrix (the formation of "coin-like" objects in Fig. 1C and c). Judging from the phase images and the mutual ratio between the two polymers, the large object with fine structures inside is the segregation of the SEBS block copolymer in the matrix of PS. Inside such objects, the nanometer-sized (~40 nm wide) structure by micro-phase separation is clearly observed.

The stability of such morphologies was investigated by annealing the sample under elevated temperature. The morphology created on homo-PS of 635×10^3 g mol^{-1} was stable, as proved by the fact that no change was observed after annealing for 15 h at 120 °C. This temperature was much higher than the

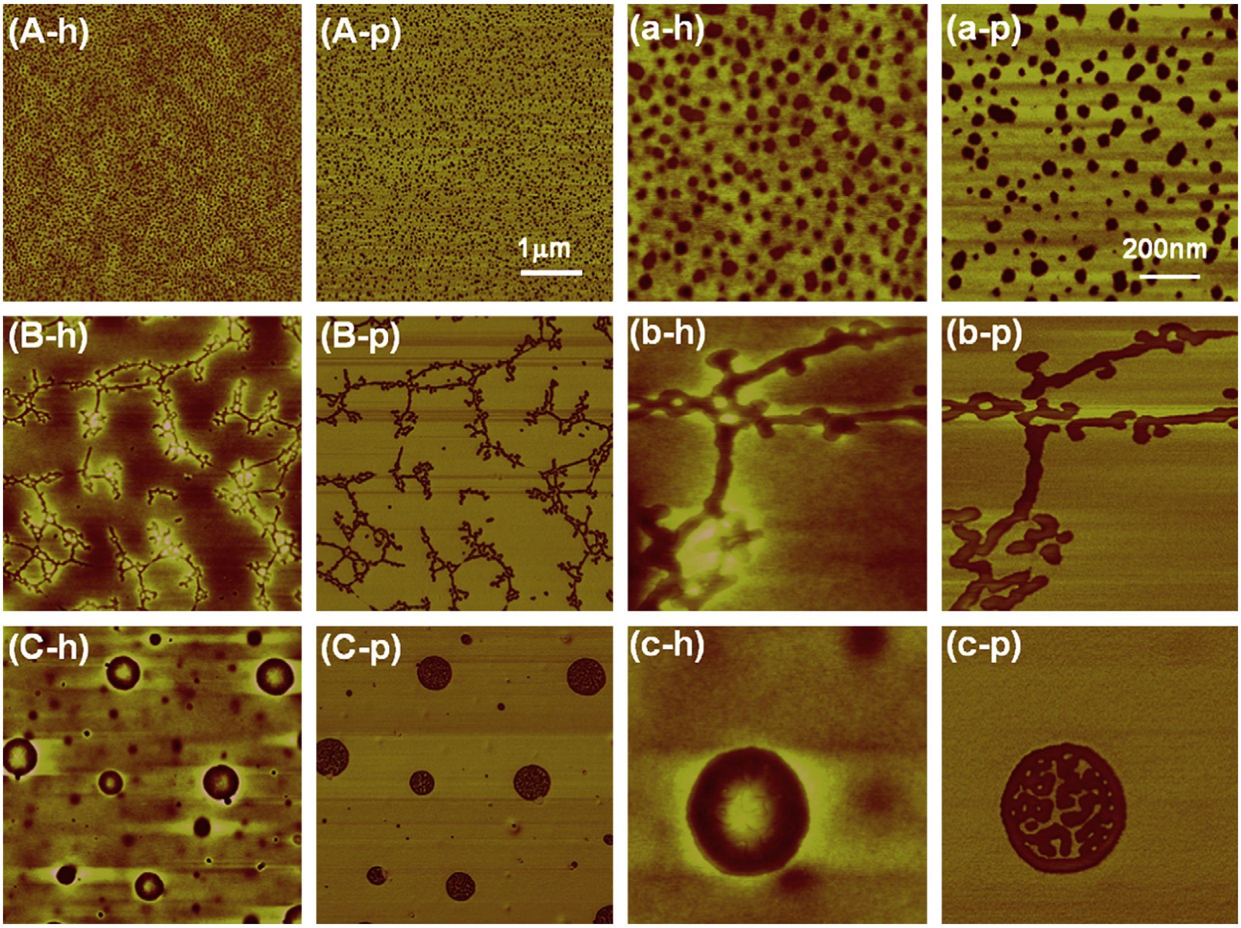

Fig. 1. AFM images of SEBS spin-coated on thin films of PS with the molecular weight of (A) 4×10^3 g mol^{-1}; (B) 29×10^3 g mol^{-1}; (C) 635×10^3 g mol^{-1}. (a)–(c) are magnified images of (A)–(C), respectively, and h and p stand for height and phase images, respectively. The concentration of SEBS solution is 0.1 wt%.

glass transition temperature of PS and PEB (100 °C for PS and −50 °C for PEB). The stability of the morphologies on 4×10^3 g mol^{-1} and 29×10^3 g mol^{-1} PS films failed to be checked because the samples de-wetted during annealing process. Please refer to Supplementary data for images.

In the range of film thickness 100–500 nm, no thickness dependence of the morphology was observed. However, the experiments on thinner films found that the morphology was greatly affected by the effect of substrate's surface. This is the result of the stronger affinity of the PS block in SEBS with the silicon oxide surface, as evidenced in our previous observation [22]. Another control experiment was conducted with SEBS spin-coated on PS-grafted surface. In this case, SEBS was deposited on silicon substrates grafted with PS brush with a molecular weight of 30×10^3 g mol^{-1}. When the concentration of SEBS solution was kept low, discontinuous film was formed with large objects of aggregations, in which the micro-phase separation of SEBS was discovered (please refer to Supplementary data). Such a phenomenon demonstrates that the thickness does have an effect on film's morphology when the film gets thinner. However, as the thickness control with respect to substrate's effect appear to be difficult in the current study, we are exploring new ways to address this issue.

As a comparison, samples were also prepared by droplet deposition method. A tiny droplet (∼40 μl) of SEBS–toluene solution with the concentration 0.04 wt% was applied on the PS film. Immediately, the droplet spread on the surface, and afterwards, the solvent evaporated gradually. Characterization of the surface morphology was conducted after the solvent has completely evaporated. The surface morphologies are displayed in Fig. 2, and similar surface morphology to that for spin-coating preparation was observed.

When SEBS solution with different concentrations was used in the spin-coating, the resulted surface morphology is displayed in Fig. 3, in which the molecular weight of homo-PS is 4×10^3 g mol^{-1} (a); 29×10^3 g mol^{-1} (b); and 635×10^3 g mol^{-1} (c). For SEBS in PS film with the molecular weight of 4×10^3 g mol^{-1}, the surface morphology was dispersed dots in PS matrix at very low concentration (0.02 wt%). As the concentration increased, elongated "bar-like" structures began to appear (for example at the SEBS concentration of 0.4 wt%). At even higher concentrations, such elongated structures developed into even longer structures, and also branch-like structures formed. For SEBS deposited on PS film with the molecular weight of 29×10^3 g mol^{-1}, the morphology was similar to that of the molecular weight of 4×10^3 g mol^{-1}: scattered spherical dots in PS matrix but

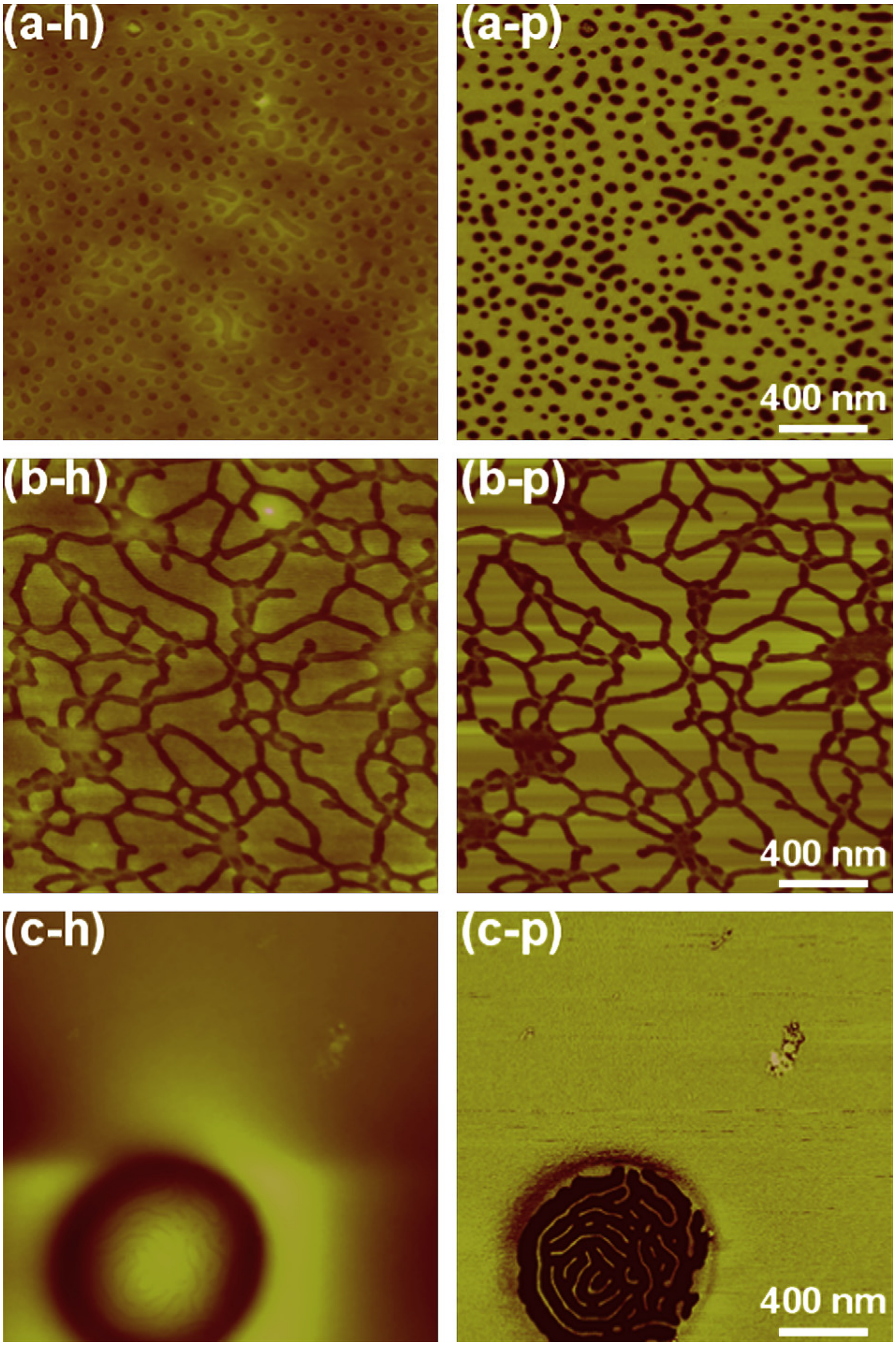

Fig. 2. AFM images of SEBS deposited on PS film by droplet deposition method. The images (a)–(c) correspond to SEBS on PS film of molecular weight of 4×10^3 g mol^{-1}, 29×10^3 g mol^{-1}, and 635×10^3 g mol^{-1}, respectively, and h and p denote height and phase images, respectively.

the elongated bar-like structures formed at much lower concentrations (0.02 wt%). As the concentration of SEBS solution increased slightly (0.06 wt%), the morphology evolved into much longer structures and continuous structures were observed. When the concentration of the SEBS solution was increased further (>0.12 wt%), the formation of branch-like and continuous structures was discovered. The most different morphology was observed for SEBS deposited on PS film with the molecular weight of 635×10^3 g mol^{-1}: even at very dilute concentration of SEBS solution (0.02 wt%), the "coin-like" structures formed, and the further increase of the concentration (~0.3 wt%) enlarged the dimension of the "coin-like" structure. When the concentration increased further (>0.4 wt%), the surface exhibits an inversed morphology: the matrix is the SEBS polymer with microstructures and the homogeneous circular structures made of PS resided inside SEBS matrix.

The data above show the evolution of the surface morphology when the volume fraction of these two polymers was varied. Although the volume fraction of each case is hard to determine as the film thickness changed when SEBS solution

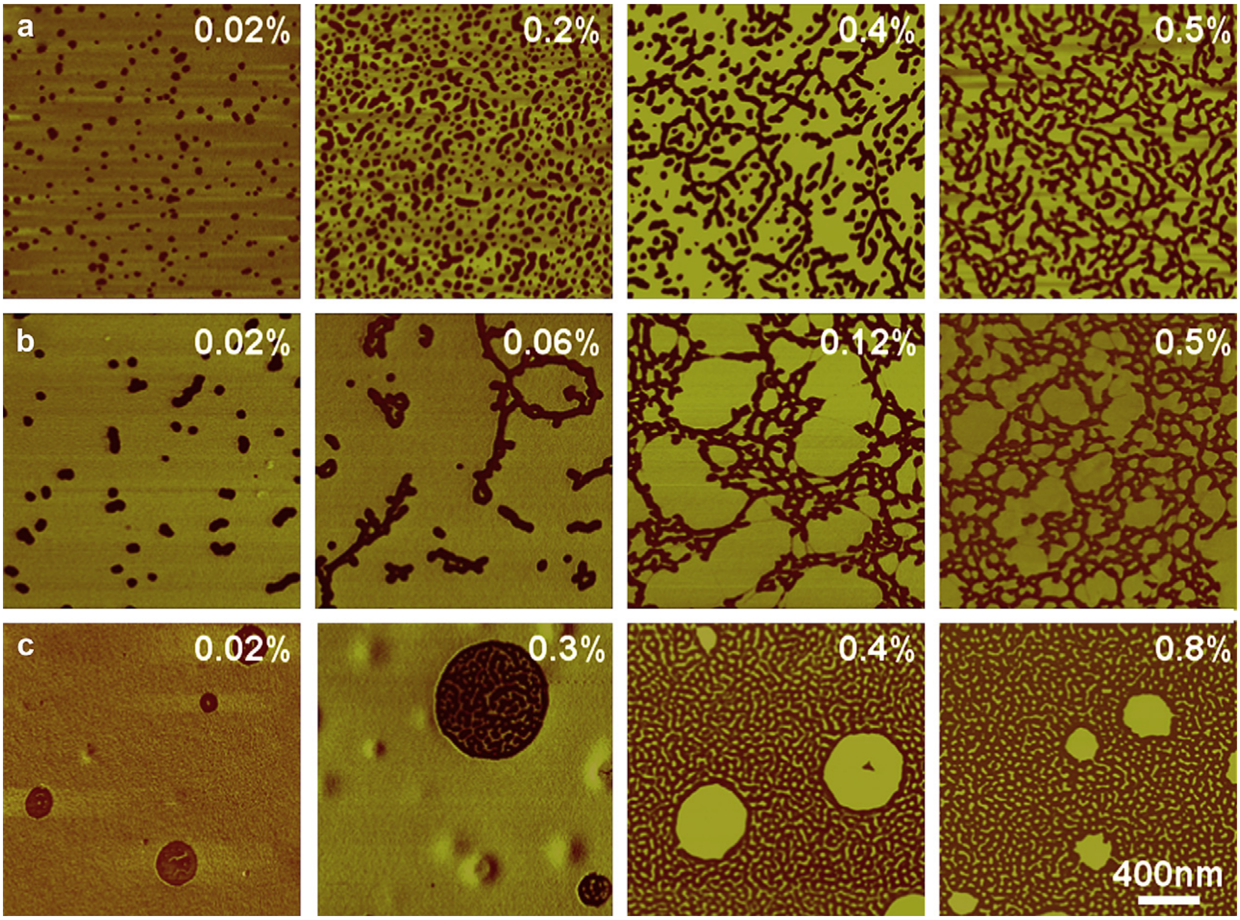

Fig. 3. The AFM images of SEBS spin-coated on the films of PS with molecular weight of (a) 4×10^3 g mol^{-1}; (b) 29×10^3 g mol^{-1}; (c) 635×10^3 g mol^{-1}. The concentration of the SEBS solution during the spin-coating preparation is indicated in each image. In order to provide better image contrast, only phase images are displayed.

with different concentrations were applied (data of thickness characterization are presented in Supplementary data), the data show that the morphology of SEBS on PS film of each molecular weight exhibits its own morphological feature and the evolution as the volume fraction changes. The morphological evolution is well distinguished between each other, especially for the film of SEBS deposited on PS film of 635×10^3 g mol^{-1}. This proves that the mere molecular weight dependence of the morphology, instead of the effect of the volume fraction is due to the change of film thickness. Also, taking into account that the initial thickness of the PS film was constant for each molecular weight, the effect of volume fraction change by thickness variation is considered to be ignored.

Phase separation occurs after SEBS solution was added to the PS film. When SEBS–toluene solution is applied to the PS films, the solvent (toluene) dissolves PS quickly, and the SEBS triblock copolymer mixes with homo-PS. Afterwards, phase separation takes place during the evaporation of the solvent. The volume fraction of the triblock copolymer and the homopolymer during the phase separation is varied by the concentration of the SEBS copolymer. The observation of the inner structures by TEM shows that similar morphology exists inside the film. Fig. 4 shows the TEM images of SEBS deposited on PS film with the molecular weight of 4×10^3 g mol^{-1} and 635×10^3 g mol^{-1}. In these images, the dark features correspond to structures formed by PS (stained by RuO_4), while the bright features stand for those by PEB. For SEBS in homo-PS of 4×10^3 g mol^{-1} (Fig. 4a), PEB domains are dispersed inside the matrix of PS, and their shapes are semi-spherical and elongated with their smallest dimension of ~20 nm to 40 nm. For SEBS in PS of 635×10^3 g mol^{-1}, large structural features are observed inside the PS matrix (Fig. 4b). The dimension of such large features ranges from 100 nm to 500 nm, and they have their own fine structures, as indicated by the regulated brightness modulation inside the structures. The boundary between these large features and PS matrix is very sharp, as indicated by the double thin dark lines at the edge of the structure and a single thicker bright line between the dark double lines. This is in a big contrast with the diffusive boundaries in Fig. 4a (SEBS in 4×10^3 g mol^{-1} homo-PS). Besides these large structures, there also exist a number of small aggregation of SEBS chains (30–50 nm in size) dispersed in PS matrix (the light-colored dots in Fig. 4b).

The drastic difference in morphology for SEBS deposited on PS film of different molecular weights is attributed to the interplay of micro-phase separation of SEBS and the

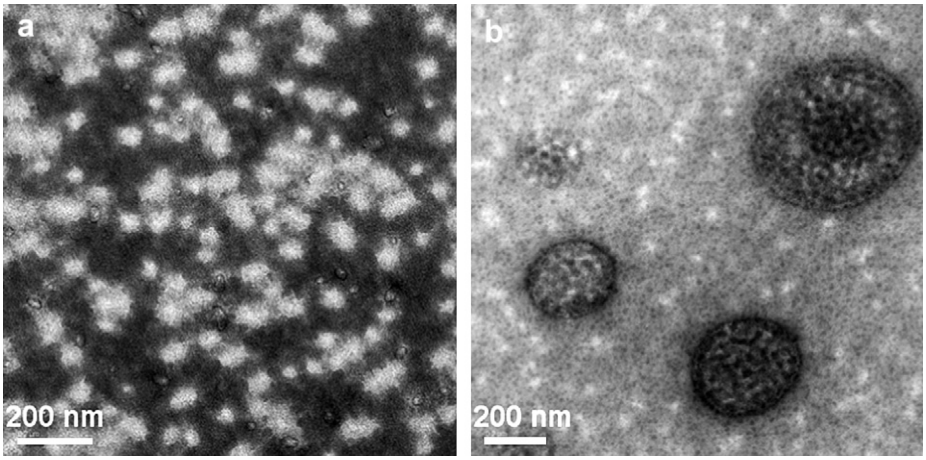

Fig. 4. The TEM images of SEBS spin-coated on PS film with the molecular weight of (a) $4 \times 10^3\ \mathrm{g\,mol^{-1}}$ and (b) $635 \times 10^3\ \mathrm{g\,mol^{-1}}$.

macro-phase separation between them. The interfacial interaction between the triblock SEBS and homo-PS plays the critical role. The increase of the molecular weight of homo-PS increases its repulsion with the SEBS copolymer, scaled as $\sim \chi N$. Because of their chemical difference, the segments of PEB blocks are repulsive to PS homopolymer, while the PS blocks are more attractive to the homopolymers, and therefore the PS blocks form the brush-like PS layer facing the homo-PS matrix. The change of interfacial tension is related to the change of morphology. For SEBS triblock copolymer in $4 \times 10^3\ \mathrm{g\,mol^{-1}}$ PS homopolymer, the molecular weight of homopolymer is less than 1/7 of the PS block. The short homo-PS chains can penetrate into the PS block in SEBS and make it swelled as if it behaves like the solvent for the PS block of $29 \times 10^3\ \mathrm{g\,mol^{-1}}$ molecular weight (please see Fig. 5a). The interface consists of the corona layer of the long PS block chains and the incorporated homo-PS chains. In this case, the surface tension is low and it favors the increase of the interfacial area. This is consistent with the dispersed morphology, corresponding to the micelle-like structure made by SEBS inside the matrix of PS homopolymer. The interface with lower energy can also be evidenced by the diffusive interfacial structure, as demonstrated in the TEM image shown in Fig. 4a. Such a low surface tension also allows the existence of considerable interfacial area and this leads to the formation of elongated objects, which are worm-like micelles at higher volume fraction of SEBS (Fig. 3a). Similar situation exists when SEBS was mixed with $29 \times 10^3\ \mathrm{g\,mol^{-1}}$ PS homopolymer, in which the interfacial energy between the PS block and the PS matrix is tuned to be higher than the case with $4 \times 10^3\ \mathrm{g\,mol^{-1}}$ PS, and therefore, the worm-like micelles formed at much lower volume fraction (at the concentration of 0.02 wt%), shown in Fig. 3b.

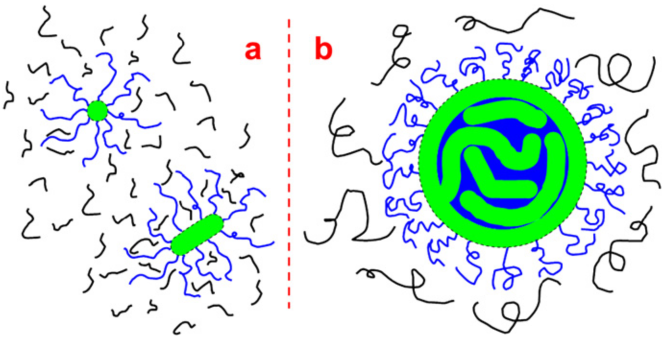

Fig. 5. Schematic illustration of the phase separation of the mixture of SEBS and PS. The green and blue color represent PEB and PS in SEBS triblock copolymer, respectively. Lines in black color denote the PS chain in the matrix. (a) The formation of spherical micelles and worm-like micelles by SEBS in PS matrix of $4 \times 10^3\ \mathrm{g\,mol^{-1}}$; (b) big structural features in PS matrix of $635 \times 10^3\ \mathrm{g\,mol^{-1}}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In order to demonstrate the effect of the interfacial tension, a control experiment was conducted on the morphology of pure homopolymer PEB mixed with PS ($29 \times 10^3\ \mathrm{g\,mol^{-1}}$). The molecular weight of PEB is $118 \times 10^3\ \mathrm{g\,mol^{-1}}$, which is close to the molecular weight of the PEB block in SEBS block copolymer adopted. In this case, no spherical or worm-like micelles were observed and large spherical structures (with the dimension of 150–220 nm at the PEB solution concentration of 0.02 wt%) made by PEB were found in the matrix of homo-PS (please refer to Supplementary data for details). This experiment demonstrates the great effect of the reduction of interfacial tension by the interaction of the PS block chains and the homo-PS.

When the molecular weight of the homo-PS of the matrix increased further to $635 \times 10^3\ \mathrm{g\,mol^{-1}}$ (more than 10 times higher than that of the PS block), it is difficult for the large PS chain to penetrate into the much shorter PS block chains. In this case, the PS block chains are no longer swelled by the homo-PS and they take a "collapsed" conformation. Such an entropy-unfavored situation results in a much higher interfacial tension between the PS block and the PS matrix. This kind of entropy-driven leveling of interfacial tension has been observed in the de-wetting process of polymer melt on the brush of identical chemical architecture [23,24]. In order to minimize the interfacial area, the cylinders formed by the micro-phase separation of SEBS segregate together and form these large structures (Figs. 1c, 2c and 3c). The higher interfacial energy is also clearly reflected by the smooth and sharp nature of the boundaries. TEM observations indicate that this interface is of shell-like structure: the exterior and interior of the shell (out-layer) are made of PS blocks (the double dark lines at the edge of the SEBS segregation in Fig. 4b) and the inner layer of the shell is made of PEB blocks (the bright wider line in Fig. 4b). From the discussion above, there exists an increase of the interfacial tension between the brush-like PS and the homo-PS when the molecular weight of the homo-PS increases. However, it was rather hard to determine the interfacial tension, as the ordinary methods such as pendant drop method will not be applicable. As a trail, the contact angle measurement was conducted for homo-PS adopted in this study on PS-grafted surface (fabricated by grafting hydroxyl-terminated PS of molecular weight 30×10^3 g mol^{-1}). No de-wetting was observed for PS film on the PS brush surface; experiments to quantify the interfacial tension by contact angle measurement appeared to be difficult.

The physical model was illustrated by a schematic illustration shown in Fig. 5. Fig. 5a demonstrates the case when the molecular weight of homo-PS is smaller than that of the PS block in SEBS, where the mutual interpenetration is very good and the spherical and worm-like micelles are formed. Fig. 5b denotes the case when the molecular weight of homo-PS is much higher than that of the PS block, in which the poor interpenetration occurs and the higher interfacial tension brings about the segregation of the SEBS copolymer. Such an interfacial tension variation via molecular weight adjustment in the current situation of triblock copolymer in the matrix of homopolymer shows great similarity to the case of diblock copolymer in homopolymer, in which the regions of “wet brush” (Fig. 5a) or “dry brush” (Fig. 5b) are defined for the case when the molecular weight of the PS block is bigger or smaller than that of homopolymer, respectively [19].

4. Conclusion

When triblock copolymer SEBS is phase-separated in homo-PS with the presence of the solvent, the interfacial energy between PS block and homo-PS is adjusted when the molecular weight of the PS homopolymer is tuned with respect to that of the PS block in SEBS triblock copolymer. When the molecular weight of PS matrix is lower than that of the PS block, the thorough interpenetration of the PS block chain and the homo-PS chain results in a low surface tension, allowing a large interfacial area and therefore the formation of micelle-like structures of SEBS in PS matrix. When the molecular weight of PS matrix is much higher than that of the PS block, a higher interfacial tension is resulted because of little penetration of the PS block and homo-PS chain and the triblock copolymer self-organizes into a structure with segregation of the micro-phase separation.

Acknowledgement

This work is supported by the Natural Science foundation of China (NSFC) under the contract no. 20490225, and by the Ministry of Science and Technology of China (MSTC) under the project contract no. 2003CB615602.

Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.02.037.

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