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Morphology control of PS-*b*-PB-*b*-PMMA/PMMA blends by silica nanoparticles

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Abstract The effect of the silica nanoparticles on the morphology of a blend consisting of poly(methyl methacrylate) (PMMA) and the poly(styrene)-*b*-poly(butadiene)-*b*-poly(methyl methacrylate) (SBM) triblock copolymer was studied. Upon blending PMMA with SBM, macrophase separation between the block copolymer and homopolymer occurred, in which the higher molar mass chains of homopolymer separate into homopolymer-rich domains due to the ‘dry-brush’ regime, whereas the lower molar mass chains of homopolymer tend to be selectively solubilized in the block copolymer-rich domains due to the ‘wet-brush’ regime. Upon adding the hydrophilic silica nanoparticles to the PMMA/SBM blend, a significant suppression effect on the extent of macrophase separation between the homopolymer and block copolymer can be observed. It was shown that the silica particles are preferentially localized in the PMMA phase due to the strong hydrogen bonding interaction between the hydroxyl groups on the surface of silica nanoparticles with the carbonyl groups of the PMMA. The suppression effect of the silica particles may be related to the selective adsorption of the high molar mass PMMA on the surface of the silica particles, which may force the system into the ‘wet-brush’ regime, but this was only observed for the systems with a low silica content. For the systems with a high silica content, both the homopolymer PMMA and the PMMA block of the SBM block copolymer interact with the silica surface, which becomes the connecting part between both polymers, thereby suppressing the extent of macrophase separation.

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Introduction

The preparation of a tough, heterogeneous system based on brittle amorphous polymers such as poly(methyl methacrylate) (PMMA) and poly(styrene) (PS) has been the subject of numerous studies [1, 2]. The toughness of a brittle polymer can be improved by the introduction of a second (rubber) phase as impact modifier [3–7]. The need for heterogeneities is universal and its role is to prevent the first cavity of the first craze to start to grow [2].

A possible route to prepare these systems is through the use of self-organizing block copolymers, which are able to form a morphology of nanosized core–shell particles in the amorphous matrix. The size of the dispersed rubber phase should be decreased to nanometer scale to combine the ductile mechanical behavior with a minimum loss in modulus and strength. In contrast to conventional rubber impact modifiers that phase separate during mixing, amphiphilic block copolymers, containing a block that is miscible with the matrix and a block that is immiscible with the matrix, could microphase separate into ordered or disordered microstructures. The morphology of the system can be controlled by optimizing the block copolymer constituents, architecture, and composition.

For ABC triblock copolymers, unique morphologies have been observed and reported over the past decades, which can offer an increased potential to create systems with tailored chemical, physical and mechanical properties [8–12]. Compared to mixing a diblock copolymer BC with a homopolymer A, microphase separation of triblock copolymers ABC has been found to generate much finer and richer morphologies, which might lead to a morphology containing a nanosized rubber shell with an easy-cavitating core, as was already demonstrated in earlier work [8, 13, 14].

Recently, researchers found that nanoparticles can be used as a compatibilizer to reduce domain coarsening during macrophase separation of polymer blends [15]. Depending on the physical interaction between the surface of the nanoparticles and the polymer components, the nanoparticles can migrate to the interface and thereby affect the coalescence process or can be selectively incorporated in one of the polymer phases [16]. Other studies showed that the incorporation of nanoparticles into self-assembled block copolymers can lead to alteration of the morphology by selective distribution of nanoparticles in one of the phases or at the interface [17–20]. The cooperative self-organization of nanoparticles and block copolymers could yield a wide variety of structures with well-controlled particle arrangements. Experiments imply that the spatial distribution of nanoparticles in the microphase-separated morphologies can be controlled by tailoring the nanoparticle surface and the size of the nanoparticles relative to the radius of gyration of the polymer [21–23]. However, the introduction of nanoparticles in block copolymer/homopolymer systems and the effect on the macrophase separation was not explored. In this paper,

the effect of silica nanoparticles on the micro/macrophase separation was studied with PMMA as matrix material with poly(styrene)-*b*-poly(butadiene)-*b*-poly(methyl methacrylate) (PS-PB-PMMA) as the triblock copolymer.

Materials and methods

Materials

PMMA was provided by Arkema (France), with a number-averaged molar mass (M_n) of 42 kg/mol and a polydispersity index (PDI) of 2.1. The poly(styrene)-*b*-poly(butadiene)-*b*-poly(methyl methacrylate) (SBM) ($M_n = 55$ kg/mol) was supplied by Arkema (France), coded as S₂₀B₂₅M₅₅, where the subscripts represent the weight fractions of the respective blocks. The as-received triblock copolymer contained 29 wt% SB diblock and was used without any further purification, while the S and B blocks had the same molar mass in the triblock and the diblock copolymer. Two monodisperse PMMAs were provided by Polymer Source (Canada), one with a M_n of 15 kg/mol and a PDI of 1.06, another with a M_n of 75 kg/mol and a PDI of 1.05. These two monodisperse PMMAs will be referred to as PMMA15k and PMMA75k, respectively. MMA and methyl ethyl ketone (MEK) were obtained from Sigma Aldrich and were used as received. Pre-made colloidal silica nanoparticles (MEK-ST) with a diameter of 10–15 nm, dispersed in MEK with approx. 30 wt% silica, were purchased from Nissan Chemical (USA) and the surface was covered with methyl and hydroxyl groups.

Sample preparation and characterization techniques

Solvent casting

The MEK-ST nanoparticles dispersions were diluted with MEK and the two polymers were dissolved separately to obtain two separate silica-filled solutions. Next, the two obtained solutions were mixed followed by solvent casting on a glass substrate. The solvent-cast samples were dried in a fume hood at room temperature for 2 days followed by a final drying step at 100 °C under reduced pressure with a low nitrogen flow for 1 more day to ensure complete solvent removal. The dried films were annealed at 135 °C for 7 days under a nitrogen atmosphere. The samples were subsequently cooled to room temperature.

Solvent casting using high-throughput experimentation setup (HTE)

A convenient approach to study the miscibility of polymer blends is based on the preparation of composition (ϕ) gradient films, where one single film can provide extensive information on the phase-separated morphology of the mixture. Here, we used a high-throughput experimentation (HTE) setup for the preparation of ϕ gradient film libraries developed in our group, which can rapidly screen the phase behavior of polymer blends. The procedure for the preparation and the calibration of

ϕ -gradient film libraries was described in the paper of l’Abee et al. [16, 24] using blends of PMMA and SAN.

Two silica-filled solutions were prepared from the as-received MEK-ST nanoparticle dispersions, which were diluted with MEK to the required concentration. Subsequently, the two polymers were separately dissolved in the silica-filled solutions. Next, the two obtained solutions were mixed and solvent cast on a glass substrate with a size of 70×70 mm using the HTE setup. For a detailed description of the film gradient preparation and the HTE settings, see Ref. [24]. The drying procedure of the thin film with the ϕ -gradient is the same as for the samples prepared via solvent casting.

Size-exclusion chromatography (SEC)

SEC was carried out using a Waters GPC equipped with a 510 pump and a Waters WISP 712 autoinjector, using a PL-gel guard precolumn (5 mm, 50×7.5 mm), followed by two PL-gel mixed-C columns (10 mm, 300×7.5 mm, Polymer Laboratories) at 40 °C. THF was used as the eluent (1.0 mL/min and 50 μ L of the polymer solution was injected). The column was calibrated by PS standards (Polymer laboratories).

Atomic force microscopy (AFM)

The AFM investigations were performed using a Smena P47H microscope (NT-MDT Ltd, Moscow, Russia). The AFM was operated in semi-contact mode under an air atmosphere using a silicon cantilever (NSG 11 NT-MDT), which was coated with a gold layer for a higher laser beam reflectivity. The resonance frequencies applied were 115–190 kHz.

Results and discussion

The morphology of PMMA/S₂₀B₂₅M₅₅ blends and the effect of the molar mass distribution of the PMMA

The improvement of properties of the amorphous polymers modified with di- or triblock copolymers depends strongly on the morphology of the blend. To obtain good mechanical properties, a high molar mass amorphous polymer as the matrix is needed. Therefore, the main problem with dispersing block copolymers in homopolymers is the occurrence of macrophase separation.

First, the morphology of the neat block copolymer/homopolymer blend PMMA/S₂₀B₂₅M₅₅ was investigated. The HTE setup is helpful to get insight in this complex phase behavior due to its fast screening. Commercial polymers like PMMA usually have a relatively high polydispersity index. The PMMA used in this blend has a M_n of 42 kg/mol and a PDI of 2.1. PMMA/S₂₀B₂₅M₅₅ films with a ϕ -gradient were prepared using the HTE setup.

The morphology was investigated with AFM and the measurements were performed from one side of the film on the glass substrate to the other (from low concentration of $S_{20}B_{25}M_{55}$ to high concentration of $S_{20}B_{25}M_{55}$), at six different positions separated by a distance of 10 mm. The obtained contrast is based on the relatively low stiffness of the butadiene block of SBM relative to PMMA. Figure 1a shows the morphology with $S_{20}B_{25}M_{55}$ domains dispersed in the PMMA matrix. It is evident that with increasing $S_{20}B_{25}M_{55}$ concentration, the domain size of $S_{20}B_{25}M_{55}$ increases (Fig. 1b). Furthermore, a co-continuous morphology is observed in Fig. 1c. Moving to position d, phase inversion occurs and $S_{20}B_{25}M_{55}$ becomes the matrix with PMMA as the dispersed phase and the extent of macrophase separation grows to larger length scales at positions e and f.

The polydispersity of the matrix is a key factor on the length scale of the macrophase separation. Thus, the phase separation behavior based on the polydispersity of the PMMA homopolymer is explored first. The homopolymer PMMA of the previous blend has a M_n of 42 kg/mol and a PDI of 2.1 and the majority of polymer chains have a molar mass which is higher than that of the PMMA block of the $S_{20}B_{25}M_{55}$ (the M_n of PMMA block is 30 kg/mol). The higher molar mass chains separate into homopolymer-rich domains, whereas the lower molar mass chains tend to be selectively solubilized in the block copolymer-rich domains. To study the influence of the molar mass (distribution), two monodisperse PMMAs with different molar masses and their mixture were chosen. One has a M_n of 15 kg/mol ('wet-brush' regime), while the other has a M_n of 75 kg/mol ('dry-brush' regime).

Fig. 1 AFM phase angle images of neat PMMA(broad PDI = 2.1)/ $S_{20}B_{25}M_{55}$ blend prepared with the HTE setup

The PMMA/S₂₀B₂₅M₅₅ blend with a fixed composition of 50/50 is used in the polydispersity study and the same annealing condition was applied as before. In Fig. 2, the different length scales of phase separation are observed when blending the S₂₀B₂₅M₅₅ with different PMMAs. Macrophase separation with similar length scales is revealed in the blends of PMMA(broad)/S₂₀B₂₅M₅₅ and PMMA(monodisperse75k)/S₂₀B₂₅M₅₅, in which the molar mass of homopolymer PMMA exceeds the molar mass of the PMMA block of the block copolymer (homopolymer $N_{Ah} > \text{copolymer } N_{Ac}$), in Fig. 2a, c. On the other hand, in Fig. 2b, wetting of the PMMA phase of the block copolymer occurs if the molar mass of the PMMA homopolymer is smaller than the molar mass of the PMMA block ($N_{Ah} < N_{Ac}$) in the blend of PMMA(monodisperse15k)/S₂₀B₂₅M₅₅. The small light domains arise from the SB diblock copolymer, which phase separately from the SBM triblock. The reason is related to the change of the curvature of the lamellar structure of SBM when the PMMA15k is soluble in the PMMA block of S₂₀B₂₅M₅₅, which induces swelling of the PMMA domain. As a result, the SB diblock is easily expelled from the matrix. Furthermore, a bimodal homopolymer PMMA, which contains a mixture of 50/50 PMMA15k/PMMA75k, was used to blend with the S₂₀B₂₅M₅₅. In Fig. 2d, the scale of macrophase separation of the PMMA(bimodal)/S₂₀B₂₅M₅₅ blend is in between of the PMMA(broad PDI)/S₂₀B₂₅M₅₅ and PMMA15k/S₂₀B₂₅M₅₅.

The suppression effect of silica nanoparticles

In Fig. 1, the PMMA(broad)/S₂₀B₂₅M₅₅ homopolymer/triblock copolymer systems showed a combination of macro- and microphase separation for the whole composition range. The occurrence of macrophase separation is the reason that the system is in the ‘dry-brush’ regime. On addition of the PMMA homopolymer with a broad molar mass distribution, either swelling of the PMMA phase of the block copolymer can occur if the molar mass of the PMMA homopolymer is smaller than the molar mass of the PMMA block (‘wet-brush’ regime) or macrophase separation takes place if the molar mass of the PMMA homopolymer is larger than the molar mass of the PMMA block (‘dry-brush’ regime). In this case, the distinction between the ‘dry-brush’ and ‘wet-brush’ regimes becomes less clear. Due to the complex phase behavior of PMMA(broad)/S₂₀B₂₅M₅₅, the effect of nanoparticles is studied for this system first.

Fig. 2 AFM images of the PMMA/S₂₀B₂₅M₅₅ 50/50 blend, of which the homopolymer PMMA is with different polydispersity **a** broad PMMA PDI = 2.1, **b** monodisperse PMMA15k, **c** monodisperse PMMA75k and **d** bimodal PMMA15k:PMMA75k 50:50

For solvent casting the silica-filled blends using the HTE setup, both starting solutions were mixed with MEK-ST silica to a final weight percentage of 2 wt%. Using the same settings as for the blends without silica, films with the required composition gradient were prepared on the glass substrates. The blends were subsequently annealed under the same condition as the neat samples. The morphologies of the silica-filled blend were investigated at the same positions a–f as that of the polymer blend without silica, of which the results are shown in Fig. 3. The hydrogen bonding interaction facilitates the dispersion of the silica nanoparticles in the PMMA-rich phase, as can clearly be distinguished in Fig. 3a, b. On comparing Fig. 1 with Fig. 3, it is evident that the addition of silica particles has a significant impact on the coarsening of the morphology during annealing. After adding 2 wt% silica nanoparticles, the macrophase separation is strongly suppressed. One possible reason is that the strong hydrogen bonding interaction between the silica surface and PMMA makes the homopolymer PMMA binding on the silica surface together with the PMMA block of $S_{20}B_{25}M_{55}$, which disrupts the extent of macrophase separation. Another explanation is similar with the one used by Huang et al. [25], i.e., selective adsorption of the high molar mass PMMA on the surface of the silica particles, by which the addition of the silica nanoparticles may force the system into the ‘wet-brush’ regime. This also leads to a suppression of the extent of macrophase separation. The comparison between Figs. 1a, b and 3a, b reveals that the domain size of the $S_{20}B_{25}M_{55}$ -rich phase is reduced by adding 2 wt% silica. In addition, phase inversion has not occurred at positions d, e and f of

Fig. 3 AFM phase angle images of PMMA (broad PDI = 2.1)/ $S_{20}B_{25}M_{55}$ blends with 2 wt% MEK-ST silica prepared with the HTE setup at six positions separated by a distance of 10 mm from one side of the sample to the other. The *dark spheres* correspond to silica particles

the silica-filled blends, which implies that the PMMA-rich phase is still the matrix as shown in Fig. 3d–f.

The influence of the silica concentration is further studied by two fixed compositions (50/50 and 80/20) of the PMMA(broad)/SBM blends, of which the morphologies correspond to co-continuous and droplet–matrix structures, respectively. Normal solvent casting was used. Figures 4a and 5a show the AFM phase images of the surface morphologies for the films of the neat PMMA/S₂₀B₂₅M₅₅ 50/50 and 80/20 blends, respectively. The morphologies are similar with those of the positions c and a in the HTE sample (Fig. 1c and a). In addition, the worm-like lamellar and cylindrical structures can be found to coexist in the microphase-separated S₂₀B₂₅M₅₅-rich domains in Fig. 4a. The S₂₀B₂₅M₅₅ domains seem to be more than 50 wt% in Fig. 4a, which may be related to the fact that the fraction with a relatively low molar mass of homopolymer PMMA (below the M_n of the PMMA block) swells the PMMA phase of the triblock copolymer domain due to the ‘wet-brush’ condition. The same observation can be seen in the 80/20 blend (Fig. 5a). In Fig. 4b, with addition of 1 wt% silica, no apparent influence on the large length scale macrophase separation can be observed, although the silica particles were well dispersed in the matrix. At higher silica concentrations, a transition occurs from macrophase separation with large length scale to microphase separation with a co-continuous morphology after adding 3 and 5 wt% silica (Figs. 4c, d). In the high-magnification image (Fig. 4e), the worm-like lamellar structure of S₂₀B₂₅M₅₅ can be found isolated in the PMMA matrix and surrounded by silica particles. The microphase-separated morphology does not change after adding more than 5 wt% silica (image is similar to Fig. 4d, not shown here). However, the bright phase that represents the SB diblock copolymer is still present.

In the silica-filled 80/20 blends, the morphology does not change as obvious as for the 50/50 blends. Although increasing the silica content up to 7 wt%, the size of the dispersed SBM domains only slightly decreased.

Based on these results of 50/50 or 80/20 blends, the suppression effect of the silica particles is limited to low silica concentrations. The existence of the strong interaction between the silica surface and PMMA is the key factor, there are no indications that selective adsorption of the high molar mass PMMA on the surface of the silica particles is the reason of the effect of the silica on the extent of macrophase separation. To explore the possibility of this mechanism, the molar

Fig. 4 AFM phase angle images of neat PMMA(broad PDI = 2.1)/S₂₀B₂₅M₅₅ 50/50 blend: **a** neat blend, **b–d** 1, 3, 5 wt% MEK-ST silica-filled blend and **e** high magnification of 3 wt% MEK-ST silica-filled blend

Fig. 5 AFM phase angle images of PMMA/S₂₀B₂₅M₅₅ 80/20 blend: **a** neat blend and **b–d** 2, 5, 7 wt% MEK-ST silica-filled blends

Fig. 6 AFM height images of PMMA(monodisperse PMMA15k)/S₂₀B₂₅M₅₅ 50/50 blend: **a** neat blend and **b, c** 1 and 3 wt% MEK-ST silica-filled blends

mass distribution of the homopolymer PMMA is considered as a way to help understanding the effect of the silica particles on the morphology.

The effect of the molar mass distribution of the homopolymer PMMA

The influence of the silica particles on the morphology the homopolymer/copolymer blends with different molar mass distributions for the PMMA homopolymer is studied and the PMMA/S₂₀B₂₅M₅₅ blend with a fixed composition of 50/50 is used as followed.

Figure 6 shows the AFM images of the (monodisperse)PMMA15k/S₂₀B₂₅M₅₅ 50/50 blend and the blends with silica nanoparticles. The ‘wet-brush’ condition is expected for mixing the monodisperse PMMA15k with S₂₀B₂₅M₅₅ in Fig. 6a. The AFM height images are used here to investigate the coarsening effect, since there is no clear phase contrast in these system, which may be related to the fact that PMMA has a stronger interaction with air and therefore prefers to migrate to the surface. Figure 6a shows that the dispersed light domains mainly arise from the separation of the SB diblock impurity from the matrix, as explained previously. This can be further proved after adding the silica nanoparticles. The AFM images only show a slight decrease of the dispersed domain size with addition of the silica nanoparticles in Figs. 6b, c. The bright domains are still dispersed in the matrix. The silica nanoparticles do not show a strong effect on the phase separation of the (monodisperse) PMMA15k/S₂₀B₂₅M₅₅ 50/50 blend. The main reason is that the

neat PMMA15k/S₂₀B₂₅M₅₅ is already in a ‘wet-brush’ ($N_{Ah} < N_{Ac}$) condition and the migration of silica particles in the hPMMA/cPMMA(of S₂₀B₂₅M₅₅) domain will not influence the microphase separation, as schematically depicted in Fig. 9a, b.

The ‘dry-brush’ regime is applicable to the case of PMMA75k blended with S₂₀B₂₅M₅₅, of which the results are shown in Fig. 7. The effect of the silica particles on the coarsening of the blend is obvious from the observation that the large length scale macrophase separation is substantially suppressed. Comparing the 1 wt% silica-filled PMMA75k/S₂₀B₂₅M₅₅ blend (Fig. 7b) with the 1 wt% silica-filled PMMA(broad PDI)/S₂₀B₂₅M₅₅ blend (Fig. 4b), the effect of the silica is more pronounced for the monodisperse PMMA75k system. Based on this result, the selective adsorption of the high molar mass PMMA on the surface of the silica particles is probably the reason of the disruption effect of the silica on the extent of macrophase separation. To further test this hypothesis, a bimodal homopolymer PMMA containing a mixture of 50/50 PMMA15k/PMMA75k was used.

The scale of macrophase separation of the neat PMMA(bimodal)/S₂₀B₂₅M₅₅ 50/50 blend is smaller than that of the PMMA(broad)/S₂₀B₂₅M₅₅ system and PMMA75k/S₂₀B₂₅M₅₅, since half of the homopolymer PMMA is 15 kg/mol, see Fig. 8a. For the PMMA(bimodal)/S₂₀B₂₅M₅₅ blend, the reduction of the length scale of the macrophase separation by 1 wt% silica is not as large as that of the

Fig. 7 AFM height images of PMMA(monodisperse PMMA75k)/S₂₀B₂₅M₅₅ 50/50 blend: **a** neat and **b**, **c** 1 and 3 wt% MEK-ST silica-filled blends

Fig. 8 AFM phase angle images of PMMA(bimodal PMMA15k:PMMA75k 50:50)/S₂₀B₂₅M₅₅ 50/50 blend: **a** neat and **b**, **c** 1 and 3 wt% MEK-ST silica-filled blends

Fig. 9 The effect of silica on the phase behavior of homopolymer/block copolymer blends in 'dry-brush' or 'wet-brush' conditions. N_{Ah} and N_{Ac} represent the degree of polymerization of the homopolymer and the similar block of the block copolymer, respectively

PMMA75k/S₂₀B₂₅M₅₅ blend; this can be explained by the tendency of the selective adsorption of the high molar mass PMMA on the surface of the silica particles, which provide a possibility to force the low molar mass PMMA to solubilize in the S₂₀B₂₅M₅₅ ('wet-brush': $N_{Ah} < N_{Ac}$). However, after adding more silica, the selective adsorption of high molar mass PMMA is not significant. The hydroxyl groups on the surface of silica nanoparticles can interact with most of the carbonyl groups either of the homopolymer PMMA or the PMMA block of the triblock copolymer, which lead to microphase separation in all systems, as depicted in the scheme of Fig. 9c, d. Therefore, the selective adsorption of the high molar mass PMMA on the silica particles exists in this system, although it is only significant for low silica contents.

Thus, a reducing effect of silica nanoparticles on the macrophase separation is observed for the PMMA/S₂₀B₂₅M₅₅ blends in the 'dry-brush' regime, which can be attributed to the strong hydrogen bonding interaction between the silica surface and the homopolymer PMMA or the PMMA block of S₂₀B₂₅M₅₅. In the system of homopolymer PMMA with the broad molar mass distribution, the selective adsorption of the high molar mass PMMA on the surface of the silica particles, which may force the system into the 'wet-brush' regime, can be observed with low silica content, especially in the PMMA(broad PDI)/S₂₀B₂₅M₅₅. For the system with high silica content, this selective adsorption phenomenon of high molar mass PMMA is not significant. Instead, both the homopolymer PMMA and the PMMA block of S₂₀B₂₅M₅₅ interact with the silica surface, which becomes the connecting part between both polymers and thereby suppresses the extent of macrophase separation.

Conclusions

In this paper, the effect of silica nanoparticles on the morphology of the homopolymer/block copolymer PMMA/SBM blend was studied. It was shown that

the hydrophilic MEK-ST silica particles could suppress the extent of macrophase separation between the block copolymer and homopolymer. This is related to the selective localization of the silica particles in the PMMA phase during phase separation due to the strong hydrogen bonding interaction between the hydroxyl groups on the surface of silica nanoparticles and the carbonyl groups of the PMMA. The observations can be explained by selective adsorption of the high molar mass PMMA on the surface of the silica particles, which may force the system into the ‘wet-brush’ regime, similar to the experimental results as presented by Huang et al. [25]. This hypothesis was tested using PMMA homopolymers with different molar mass distributions. In the system with PMMA with the broad molar mass distribution, the selective adsorption of the high molar mass PMMA on the surface of the silica particles can be observed with low silica content. However, for the systems with a high silica content, where enough specific surface is available for PMMA to interact with, the selective adsorption of the high molar mass PMMA is not significant. Instead, both the homopolymer PMMA and the PMMA block of $S_{20}B_{25}M_{55}$ can interact with the silica surface, which becomes the connecting part between both polymers and thereby suppressing the macrophase separation to a large extent. As a result, the silica nanoparticles provide a larger processing window to obtain a homopolymer/copolymer blend which is only with microphase separation.

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