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# Block Copolymers in Homopolymer Blends: Interface vs Micelles

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ABSTRACT: The location of poly(styrene-*b*-poly(methyl methacrylate)) (PS-*b*-PMMA) block copolymers in PMMA/poly(cyclohexyl methacrylate) (PCHMA) melt mixed blends was determined. Among all these components, only the PS portion of the block copolymer can be stained by ruthenium tetroxide and appears dark in transmission electron micrographs. Then the locations of block copolymer in the blends, i.e., interfaces and micelles, can be easily identified. Morphology and the aggregation of the PS-*b*-PMMA were studied as a function of molecular weight and molecular weight fraction. At low molecular weight PS-*b*-PMMA, a PMMA/PS-*b*-PMMA macrophase formed. At higher $M_n$, small (<1 $\mu$m) minor phase (PMMA) drops coated with copolymer formed, but these drops also contained micelles even at low PS-*b*-PMMA concentration. Increasing the molecular weight of the PMMA first caused the drop size to increase, and then the copolymer micelles to relocated from the PMMA to the PCHMA phase. Increasing block copolymer concentration caused PMMA drop size to decrease roughly in proportion to interfacial coverage. The results are discussed qualitatively in terms of Leibler's wet−dry brush theory.

## Introduction

Many studies have advocated the use of premade block copolymers to compatibilize (or emulsify) immiscible polymer blends.[1] Theoretically the block copolymer should reside in the interface. This will lower interfacial tension (facilitating drop breakup), prevent drop coalescence, and enhance interfacial adhesion. However, very few commercial blends are compatibilized with premade block copolymers; rather, graft copolymers formed in situ by coupling reactions at the interface are employed.[2] Typically much of the premade block copolymer resides in micelles rather than in the interface between the immiscible homopolymers. Since premade copolymers are generally more expensive than commodity polymers, micelle formation by premade block copolymer emulsifier is an inefficient use of the costly copolymer. It should be possible through design of the block copolymer and perhaps the melt mixing conditions to minimize the amount of copolymer that form micelles. However, experimentally it is not easy to directly identify the locations of block copolymers in blends. In the present study we chose a model system composed of poly(methyl methacrylate) and poly(cyclohexyl methacrylate) homopolymers and poly(styrene-*b*-methyl methacrylate) as copolymer. Among all the components, only polystyrene is strongly stained by ruthenium tetroxide and appears dark when imaged with transmission electron microscopy operated in bright field.[3] The block copolymer, then, can be easily identified as dark regions on micrographs. We studied how the molecular weights of poly(methyl methacrylate) and block copolymer affect blend morphology, especially location of the block copolymer.

## Experimental Section

**Materials.** We chose a blend system containing poly(cyclohexyl methacrylate) (PCHMA), poly(methyl methacrylate) (PMMA), and poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymers. PCHMA is immiscible with PMMA[4] but miscible with PS when the molecular weight is not too high. PS and PMMA exhibit LCST behavior with a critical temperature around 230 °C.[4,5] All these polymers were synthesized using an anionic polymerization method in our laboratory, except the PCHMA which was donated by Dr. Jorge Kressler. Nomenclature in this paper is as follows: PMMA11 represents PMMA with a number-average molecular weight of 11 kg/mol, and SM55 represents PS-*b*-PMMA with $M_n$ = 55 kg/mol. Characteristics of these polymers are listed in Table 1. In all the compatibilized blends reported here, the mass fraction of the minor phase (PMMA homopolymer) was maintained at 20 wt % while the major phase (PCHMA) was varied (80 − $x$) wt %, where $x$ is the mass fraction of the block copolymer. Three PS-*b*-PMMA with different molecular weights were used such that the ratio of the molecular weight of the PMMA block in the copolymer to that of the PMMA homopolymer ranged from 0.4 to 7. Compositions of all the blends are given in Table 2.

**Table 1. Characteristics and Acronyms for the Polymers Used**

| polymer | acronym | $M_n$[a] (kg/mol) | $M_w/M_n$ | PS weight fraction |
|---|---|---|---|---|
| PMMA | PMMA11 | 11 | 1.09 | |
| PMMA | PMMA27 | 27 | <1.09 | |
| MMA | PMMA35 | 35 | 1.09 | |
| PMMA | PMMA59 | 59 | 1.38 | |
| PCHMA | PCHMA | 19 | 2.4 | |
| PS-*b*-PMMA | SM55 | 32−23 | 1.05 | 0.58 |
| PS-*b*-PMMA | SM85 | 47−38 | 1.08 | 0.55 |
| PS-*b*-PMMA | SM160 | 80−80 | 1.08 | 0.50 |

[a] Based on poly(methyl methacrylate) standards.

**Blending.** All the components of each blend, total mass about 200 mg, were dry-mixed in powder form and introduced into a 13 mm diameter, preheated cup−rotor mixer (Minimax CS-183MMX, Custom Scientific Instrument, Inc.). The powder was mixed for 20 min at 200 °C and a rotation rate of 300 rpm. The rotor was lifted, pulling up a thread of melt from the center of the mixer every 3 min. Such experimental conditions were found to be sufficient to achieve uniform mixing.[6] The mixed melts were annealed at the processing temperature for 20 min to allow for relaxation of the drop shape to near spheres, followed by cooling to room temperature at about 10 °C/min.

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**Table 2. Morphological Characteristics of Blends (All Contained 20 wt % PMMA)**

| PMMA $M_n$ (kg/mol) | SM $M_n$ (kg/mol) | SM (wt %) | $D_n$ ($\mu$m) | $D_{vs}$ ($\mu$m) | $\Sigma/\Sigma_0{}^a$ | comment |
|---|---|---|---|---|---|---|
| 11 | | 0 | >1 | | | very unstable |
| 11 | 55 | 5 | | | | macro-phase, micelles in PMMA (Figure 2) |
| 11 | 85 | 5 | 0.33 | 0.44 | 1.0 | drops + micelles in PMMA |
| 35 | 85 | 5 | 0.50 | 0.68 | 1.6 | drops + micelles in PMMA |
| 59 | 85 | 5 | 0.3 | 0.4 | 0.9 | drops + micelles in both phases (Figure 3−c) |
| 11 | 160 | 5 | 0.42 | 0.57 | 0.9 | drops + micelles in PMMA |
| 35 | 160 | 5 | 0.64 | 0.76 | 1.2 | drops + micelles in PMMA |
| 59 | 160 | 5 | 0.6 | 1.0 | 1.5 | drops + micelles in PCHMA (Figure 3d−f) |
| 11 | 85 | 2 | 0.52 | 0.71 | 0.7 | drops + micelles in PMMA |
| 11 | 160 | 2 | 1.06 | 1.14 | 0.7 | drops + micelles in PMMA |
| 11 | 160 | 5 | 0.42 | 0.57 | 1.2 | drops + micelles in PMMA |
| 11 | 160 | 10 | 0.37 | 0.48 | 1.5 | drops + micelles in PMMA |
| 11 | 160 | 30 | 0.13 | 0.14 | 1.3 | drops (Figure 4a−d) |

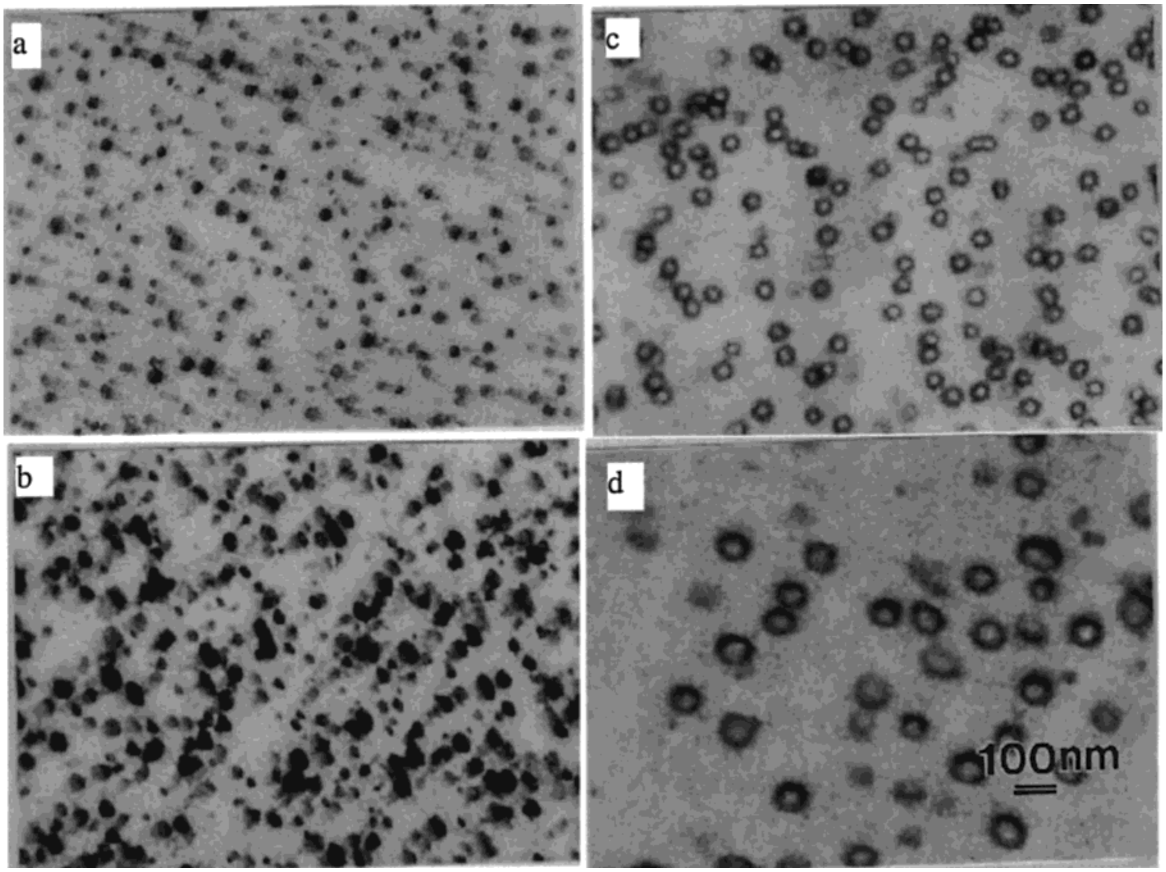

**Figure 1.** Micelles of SM85 (a) and SM160 (b) formed in PMMA27 and inverted micelles formed in PCHMA (c and d for SM85 and 160, respectively). In all blends PS-*b*-PMMA was 5 wt %.

**Transmission Electron Microscopy.** As all the polymers are glassy, the blends were microtomed to about 50 nm thick films at room temperature using a Reichert Ultracut with a diamond knife. These thin films were collected on copper grids (400 mesh) and stained in a vapor of $RuO_4$ by suspending them over its aqueous solution (0.6%) in an enclosed glass chamber for 25−30 min. The stained films were observed using a JEOL 1210 transmission electron microscope (TEM) under an accelerating voltage of 120 kV. It is well-known that $RuO_4$ only oxidizes the PS; thus, only the PS portion of block copolymers appeared darker in bright field images. The magnification of the microscope was calibrated with a germanium-shadowed carbon replica of a ruled diffraction grating having a grating spacing of 882 nm (intermediate magnification). Particle size was determined by scanning several micrographs for each sample using Ultimage software (ver 2.6.1, Graftex). Based on 50−100 drops, number-average and volume-to-surface average diameters were calculated and are given in Table 2.

## Results and Discussion

When we blended PMMA into PCHMA without block copolymer, very large PMMA drops formed. In the annealed samples interfacial adhesion is so low and the particles became so large that microtoming was difficult due to lack of mechanical integrity of the blend. Even when we quenched the melt quickly to prevent coalescence, the PMMA drops were >1 $\mu$m. The PCHMA stained very slightly in $RuO_4$ vapor, but even without staining there was some contrast at the PMMA−PCHMA interfaces.

As expected, when SM85 and SM160 were blended with PMMA27 (95 wt %), these block copolymers formed micelles with the PS portion being the cores. Figure 1a,b shows dispersed dark cores with diameters that increase with block copolymer molecular weight. When the block copolymers were blended with the PCHMA, they still

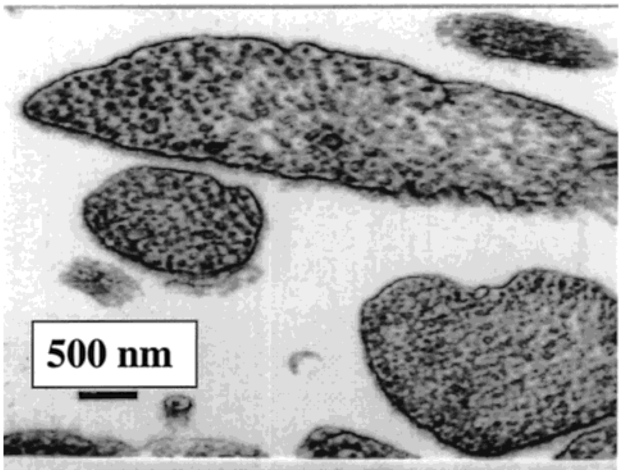

**Figure 2.** SM55 block copolymers stayed at interface and also formed micelles in blends of PCHMA/SM55/PMMA11 (70/10/20 wt %).

formed micelles; however, as expected, they are inverse with the PS portion forming the corona, visible as the dark rings in Figure 1c,d. This micelle inversion indicates the solubility of PS in PCHMA and clearly shows that among the three polymers only PS was strongly stained by $RuO_4$.

When PCHMA, PMMA11, and SM55 (70:20:10 wt) are blended together, PMMA11 and SM55 form irregular macrophases within the PCHMA matrix. The dark spots in Figure 2 are larger than expected for pure micelles of SM55 in PMMA (compare Figure 1a). The dark interfaces in Figure 2 indicate that the SM55 also surrounds each domain.

Before micelles are formed, some block copolymers chains are dissolved in the homopolymer phases as free chains. However, the quantity of these free chains is proportional to $\exp(-\chi N_{b-\mathrm{PMMA}})$.[7,8] Using the Flory−Huggins interaction parameter $\chi = 0.0165$ for PCHMA/PMMA at 200 °C,[3] we calculate that the free chain concentration for SM85 and SM160 is negligible. However, SM55 will be more soluble in PMMA because of its lower value of $\exp(-\chi N_{b-\mathrm{PMMA}})$, which may facilitate formation of the macrophase observed in Figure 2.

All our blends with higher molecular weight block copolymer formed drop-in-matrix morphologies (see Figures 3 and 4). Adding just 2% of SM85 or SM160 gives blends with PMMA drops = 1 μm diameter (see Table 2). These drops and those at higher copolymer concentration are all stable to annealing at 200 °C. Their stability is illustrated by the numerous drop pairs in Figure 3 which are in close contact but have not coalesced.

In all the TEMs images, the drop interfaces are very dark, indicating the presence of block copolymer. Using these dark rings, it would seem possible to measure the block copolymer layer thickness and even estimate interfacial coverage. However, there are many factors that affect the width of the interfaces: staining conditions, the angle between the cutting direction and the interface, film thickness, beam damage, the conditions for imaging. Measurement of the thickness of the block copolymer layer from our TEM images was not reliable. For example, the minimum thickness of the dark ring of SM85 and SM160 in Figures 3 and 4 was almost the same, about 22 nm. This does not agree with theoretical prediction where block copolymer layer thickness is expected to increase with $M_n^{2/3}$ (refs 7 and 8). On the other hand, the micelle diameters of these same copolymers in Figure 1, 28 and 38 ± 5 nm, and ring thicknesses, 14 and 17 nm, do roughly scale with $M_n^{2/3}$. Yet the micelles in Figure 3 do not appear to follow this scaling, perhaps due to swelling with PCHMA or differences in staining conditions.

Even though we cannot determine interfacial coverage quantitatively from the TEM images, using the drop diameters and amount of copolymer we can calculate the maximum possible coverage. If we assume all the added block copolymer lies in the interface (i.e., no micelles), then

$$\Sigma = (\phi_{\mathrm{SM}}/\phi_{\mathrm{PMMA}})(N_A \rho_{\mathrm{SM}} D_{\mathrm{vs}}/6M_{\mathrm{SM}}) \tag{1}$$

where $\Sigma$ = chains/nm$^2$, $\phi_{\mathrm{SM}}$ and $\phi_{\mathrm{PMMA}}$ are the volume fraction of PS-*b*-PMMA block copolymer and PMMA in the blends, and $N_A$ is Avogadro's number. The melt density of the block copolymers, $\rho_{\mathrm{SM}}$, is equal to the average of PS and PMMA, or 1 g/cm$^3$. Using the measured $D_{\mathrm{vs}}$ values, eq 1 gives interfacial coverages of about 0.1−0.2 chain/nm$^2$ (see Table 2). These values can be compared to the maximum surface concentration of block copolymer, $\Sigma_0$, assuming a dense monolayer in the interface. Monolayer thickness has been calculated by rescaling small-angle neutron scattering measurements on a deuterated, symmetric diblock copolymer dPS−PMMA with $M_n$ = 101 kg/mol[9] to give 27 nm for SM160 and 18 nm for SM85.[10] The micelle rings in Figure 1c,d are smaller than these values. However, TEM of pure SM160 gave an average PS layer thickness of 26 nm.

Applying eq 1 and these values of $\Sigma_0$,[10] the ratio $\Sigma/\Sigma_0$ was calculated and is given in Table 2. $\Sigma/\Sigma_0$ is the maximum fractional coverage of the drop surfaces. We see that for both 2% copolymer samples $\Sigma/\Sigma_0 = 0.7$ (i.e., these interfaces cannot be saturated), yet in both samples we observed a significant number of micelles inside the PMMA drops. By counting the number of micelles and knowing the thickness of the microtomed samples, we estimate that their fractional coverage is about 50%. Both 5% samples with PMMA11 gave maximum coverage $\Sigma/\Sigma_0 \sim 1$ (see Table 2), but Figure 3a,d shows micelles, again indicating that the interface is not saturated. In one experiment we changed the mixing protocol. We premixed SM160 in PCHMA for 10 min at 200 °C and then added PMMA27. There was little change in the morphology mixing for 2 min vs 30 min. This independence of morphology on mixing protocol agrees with the recent results of Maríc and Macosko on PS−poly(dimethylsiloxane) blends.[11] Thus, we think that the block copolymer partitioning observed in Figures 3 and 4 represents an energy minimum.

**Effects of PMMA Molecular Weight**. Figure 3a−c shows the microstructure of the SM85 blends as a function of PMMA molecular weight. Increasing PMMA molecular weight to 35 kg/mol increased drop size and the number of micelles in PMMA. However, going to 59 kg/mol shows no micelles in the PMMA59 drops but many inverted micelles in the PCHMA phase (Figure 3c). These micelles appear to be swollen to various degrees such that it is difficult to distinguish them from the smaller PMMA drops. This makes it difficult to get an accurate drop size, but the value appears to decrease and thus the calculated maximum fractional coverage decreases.

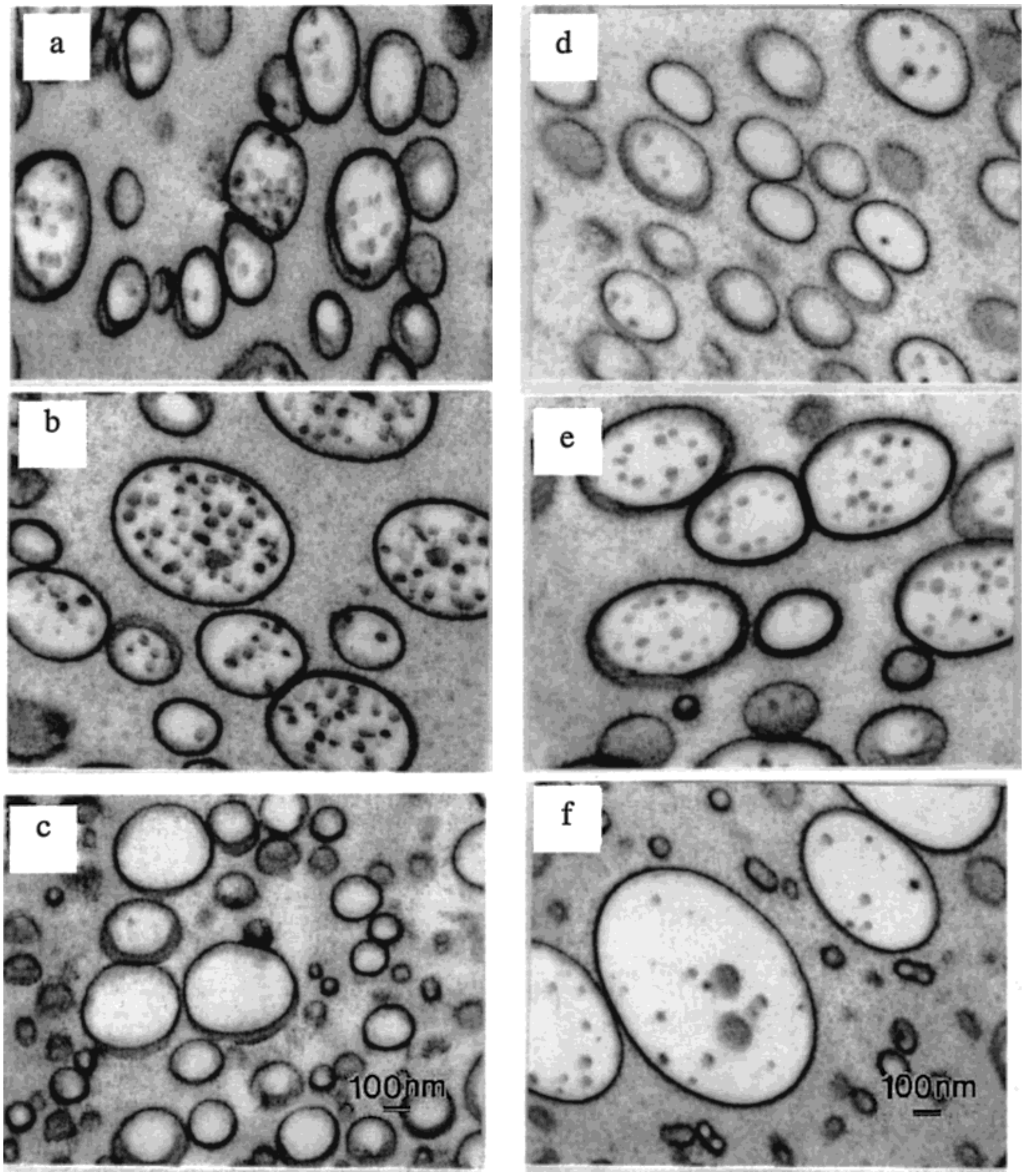

**Figure 3.** Morphologies of blends containing 75 wt % PCHMA, 5 wt % SM85, and 20% PMMA with molecular weight of 11 (a), 35 (b), and 59 kg/mol (c). (d), (e), and (f) correspond to blends of the same composition, but SM160 is substituted for SM85.

Similar trends are observed with the SM160 blends. Changing from PMMA11 to PMMA35 results in an increase in drop size and the number of micelles in the PMMA. Increasing PMMA molecular weight to 59 kg/mol also results in inverted micelles in the PCHMA matrix, but micelles also remain in PMMA59. Again it is more difficult to get an accurate diameter due to the inverted micelles, but here diameter seems to increase over the PMMA35 blend.

Increasing molecular weight of the PMMA phase also increases its viscosity significantly and slows down diffusion. Yet in Figure 3 we see no major difference in drop size, and the block copolymer appears to be well distributed. As discussed above, we believe that thermodynamics rather than rheology is dominant in our experiments. Thus, we compare results to Leibler's brush theory.[7,8] The theory predicts that the ratio of the molecular weight of homopolymer, H, to that of the miscible block, B, in the copolymer, $\lambda = H/B$, controls the interfacial activity of the block copolymers. When $\lambda < 1$, or the homopolymer has lower molecular weight than the block copolymer, it swells the block copolymer chains at interfaces. The block copolymer brush is called a wet brush. On the other hand, when $\lambda > 1$, homopolymer chains cannot efficiently swell the block copolymers, and the block copolymer layer at the interface is called a dry brush.

Table 3 gives $\lambda_{\mathrm{PMMA}}$, the ratio of homopolymer to block PMMA molecular weight for our blends. Since $M_{\mathrm{n}} = 19$ kg/mol for PCHMA, $\lambda_{\mathrm{PS}} < 1$ for all the block copolymers. Furthermore, $\chi < 0$ for PS in PCHMA.[3] Thus, we expect the PS blocks on the surface of the PMMA particles to be wet in all the samples. However, as Table 3 indicates, the PMMA blocks in SM85 are calculated to go from wet to dry as the PMMA homopolymer molecular weight is increased to 59 kg/mol. This should cause the PMMA corona of the SM85 micelles to collapse and make them unstable in PMMA59. However, PS corona should be stable in PCHMA. This agrees with the micelle relocation from PMMA to PCHMA observed from Figure 3b,c. SM160 shows some micelle relocation from PMMA59 (Figure 3f), but in this case $\lambda_{\mathrm{PMMA}} = 0.74$ and we expect the micelles of SM160 to be stable in PMMA59. Their migration to PCHMA may be due to strong swelling of

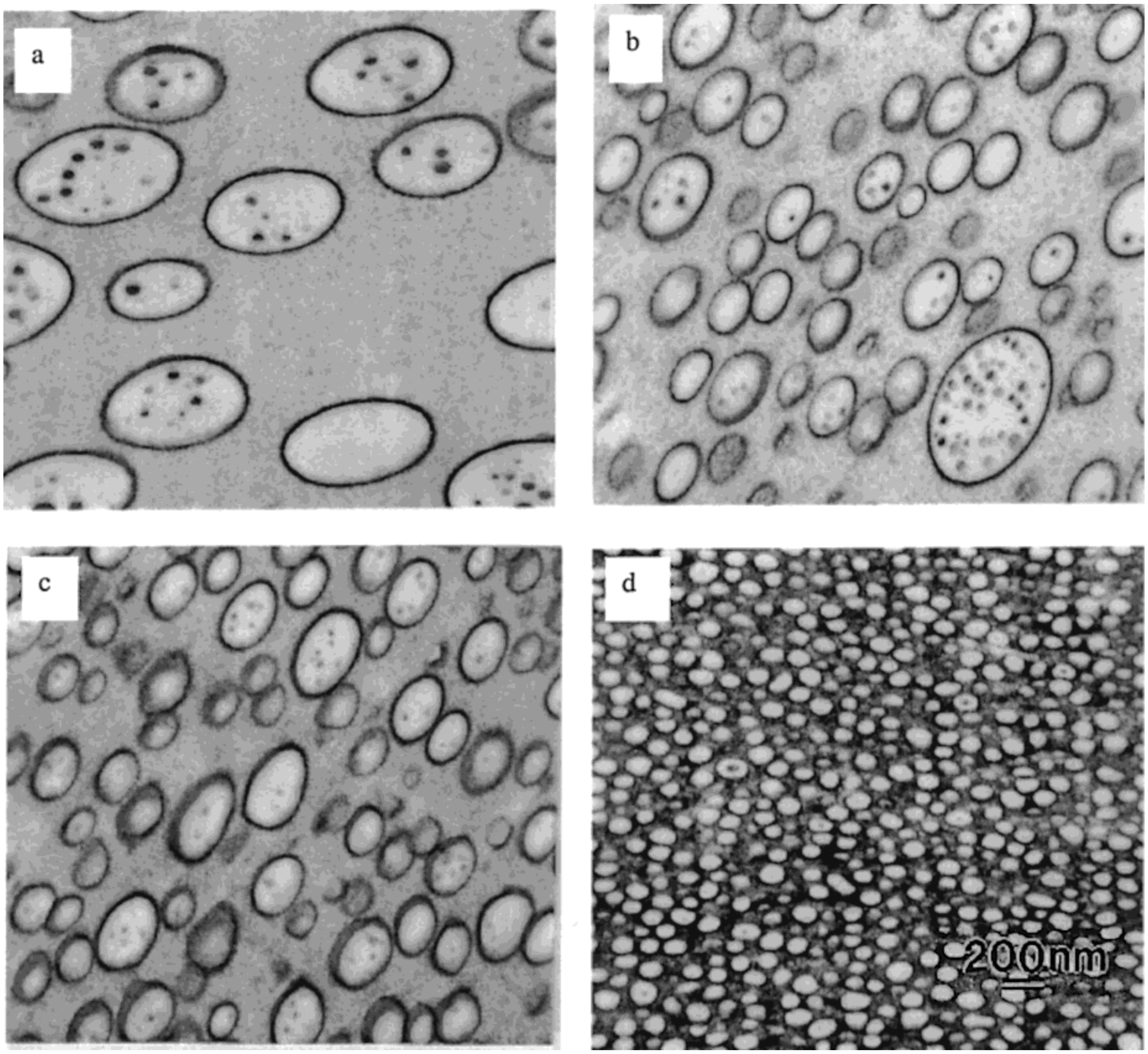

**Figure 4.** Blends containing PCHMA/PMMA11/SM160. Amount of PMMA11 is 20 wt %. Amount of PS-*b*-PMMA is 2 (a), 5 (b), 10 (c), and 30 wt % (d).

**Table 3. $\lambda_{PMMA}$, Ratios of $M_n$ of the PMMA Homopolymers to That of PMMA Block of PS−PMMA Block Copolymers**

| polymers | $M_n$[a] | SM55 | SM85 | SM160 |
|---|---|---|---|---|
| | | 23 | 38 | 80 |
| PMMA11 | 11 | 0.48 | 0.29 | 0.14 |
| PMMA35 | 35 | 1.52 | 0.92 | 0.44 |
| PMMA59 | 59 | 2.57 | 1.55 | 0.74 |

[a] $M_n$ in kg/mol; for the block copolymers $M_n$ is for the PMMA block only.

the PS blocks, since $\lambda_{PS} = 0.24$ for SM160 vs $\lambda_{PS} = 0.40$ for SM85. This is in agreement with the theoretical explanation and the observations of Adedeji et al.,[12] who extended the Leibler, Orland, and Wheeler[13] theory to more complicated exothermic systems. They showed that the miscibility of PCHMA and PS could lead to a large value of critical micelle concentration (cmc). Further, the PS-*b*-PMMA is drawn away from the PCHMA/PMMA interface into the favorable domain (PCHMA), and the PS-*b*-PMMA could be found as micelles. Thus, the increase in drop size and more micelles observed in Figure 3 and Table 2 going from PMMA11 to PMMA35 may also be attributed to reduced swelling of the PMMA brushes. The block copolymer should be less stable in the interface than as micelles in PMMA and thus allows more coalescence during mixing.

**Effect of Amount of Block Copolymer.** Keeping the amount of PMMA11 constant at 20 wt % and increasing the amount of SM160 (2−30 wt %), the domain size of PMMA was observed to decrease from 1 to 0.1 $\mu$m (Figure 4a−d). It is interesting to compare Figure 4c to Figure 2. Both have the same composition except for the molecular weight of the block copolymer. $M_n$ of SM obviously has a large effect on the morphology.

The calculated fractional coverage $\Sigma/\Sigma_0$ is approximately constant going from 5% to 30% SM160. This implies that the surface coverage is controlling the drop size. At 30% SM160 the blend morphology is very fine and uniform. The micelles essentially disappear, and there are no dark rings around the tiny PMMA drops. Their average size is 140 nm, about twice the diameter of the PMMA cores in the micelles of SM160 in Figure 1d. The matrix appears to be uniformly dark, indicating that SM160 has formed a microphase with PCHMA. However, it is hard to get a good image of the matrix because the microtomed samples are 50 nm thick, and the drops are so small that a cut through the matrix phase will include many sectioned tops and bottoms of spherical drops.

## Conclusions

The system poly(styrene-*b*-poly(methyl methacrylate)) block copolymers, poly(methyl methacrylate), and poly(cyclohexyl methacrylate) was shown to be very useful for identifying the location of block copolymers in blends. Block copolymers aggregated at the interface and in micelles were directly observed as dark regions using transmission electron microscopy combined with selectively staining of the polystyrene block using ruthenium tetroxide. It was observed that block copolymers started to form micelles before they saturated the interfaces. Micelles occurred in the poly(methyl methacrylate) phase when its molecular weight was lower than the PMMA block. Increasing molecular weight of poly(methyl methacrylate) above the block $M_n$ caused all the micelles to move to the poly(cyclohexyl methacrylate) matrix. Increasing block copolymer concentration decreased the PMMA drop size so as to keep the interfacial coverage of block copolymer roughly constant. These results agree qualitatively with Leibler's wet brush–dry brush theory, but more quantitative calculations are needed.

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