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Role of Block Copolymers on Suppression of Droplet Coalescence

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ABSTRACT: Block copolymer reduces particle size in immiscible polymer−polymer blends by suppressing droplet coalescence and by aiding droplet breakup through reduced interfacial tension. In this paper we separated coalescence from breakup and studied suppression of coalescence by block copolymers in a model blend composed of polystyrene (PS), high-density polyethylene (HDPE), and polystyrene−polyethylene (PS−PE) block copolymer. Coalescence was examined by monitoring particle size change vs shear strain while varying the shear rate, block copolymer concentration, molecular weight, and symmetry (coil size ratio of blocks). Even 0.5% PS−PE block copolymer significantly suppressed coalescence of HDPE droplets in a PS matrix. Assuming all of the PS−PE molecules were at the interface, the minimum concentration of block copolymers required to prevent coalescence under shear was found to be about 0.2 chain/nm^2 at a coalescence shear rate of 0.1 s^{-1} for PS−PE with a molecular weight of 20−20 kg/mol. We found that this minimum concentration decreased with shear rate and with increasing molecular weight of PS−PE. We also found that, with the total molecular weight being the same, a PS−PE with a larger PS block suppressed HDPE particle coalescence more efficiently than one with a smaller block. These results indicate that steric repulsive interactions due to the presence of block copolymer at the interfaces are more important than those due to interfacial tension gradients.

1. Introduction

The minor phase of immiscible polymer blends breaks up into smaller domains when such mixtures are subjected to mechanical mixing. For dilute blends in shear flow, the droplet diameter (D) is expected to follow the Taylor equation:[1]

$$\frac{D\eta_{\mathrm{m}}\cdot\dot{\gamma}}{2\Gamma} = Ca^* \qquad (1)$$

where η_{m}, $\dot{\gamma}$, and Γ are the matrix viscosity, shear rate, and interfacial tension, respectively. Ca^* is the critical capillary number, ~0.5, when the drop viscosity equals η_{m}. However, as illustrated in Figure 1 by a blend of high-density polyethylene (HDPE) in polystyrene (PS), droplet size is somewhat larger than predicted by eq 1 and increases strongly with concentration of the minor phase. By contrast, when a small amount of a polystyrene−polyethylene diblock copolymer (PS−PE) is added, the droplet size is closer to the Taylor limit and nearly independent of volume fraction. Early researchers attributed the decrease in droplet size to the block copolymer's ability to lower interfacial tension.[2−4] However, the reduction in interfacial tension is not sufficient to explain the size decrease (see Appendix). Such observations have caused researchers[5−10] to propose that block copolymer also reduces droplet size through suppression of coalescence.

Sundararaj and Macosko explained this suppression of coalescence in terms of a steric interaction between droplets that results from the compression between the block copolymer layers that are attached to the interfaces.[5] They predicted that the suppression of coalescence is more efficient with higher molecular weight block copolymers. Milner and Xi,[11] on the other hand, proposed that the suppression of coalescence by block copolymers was due to a force (referred to here as the Marangoni force) induced by a gradient of block copolymer concentration at interfaces. The gradient is caused by flow between the two approaching drops.[12−14] They predicted that the block copolymer concentration necessary for preventing coalescence is higher at higher shear rate. These two rival mechanisms of coalescence suppression are illustrated in Figure 2.

Determining which mechanism is more important for suppressing coalescence is often difficult because droplet

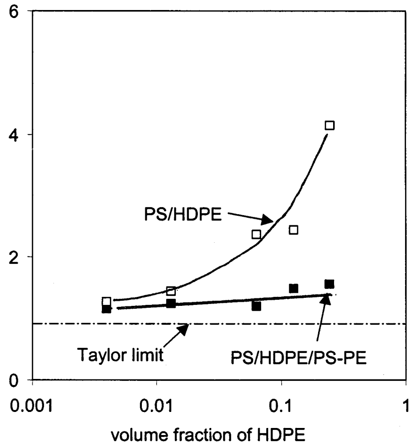

Figure 1. Particle size vs volume fraction after shearing for 20 min at 10 s^{-1}. The matrix is polystyrene (PS) of nearly equal viscosity to the minor phase, high-density polyethylene (HDPE). Adding PS−PE diblock copolymer (20−20 kg/mol, 4.3 vol % of the HDPE phase) greatly suppresses coalescence. The dashed line is the droplet diameter predicted by eq 1 using $\eta_{\mathrm{m}} = 400$ Pa·s at 10 s^{-1} (see Figure 3) and $\Gamma = 3.5$ mN/m (the interfacial tension found with 4.3% PS−PE, see Appendix).

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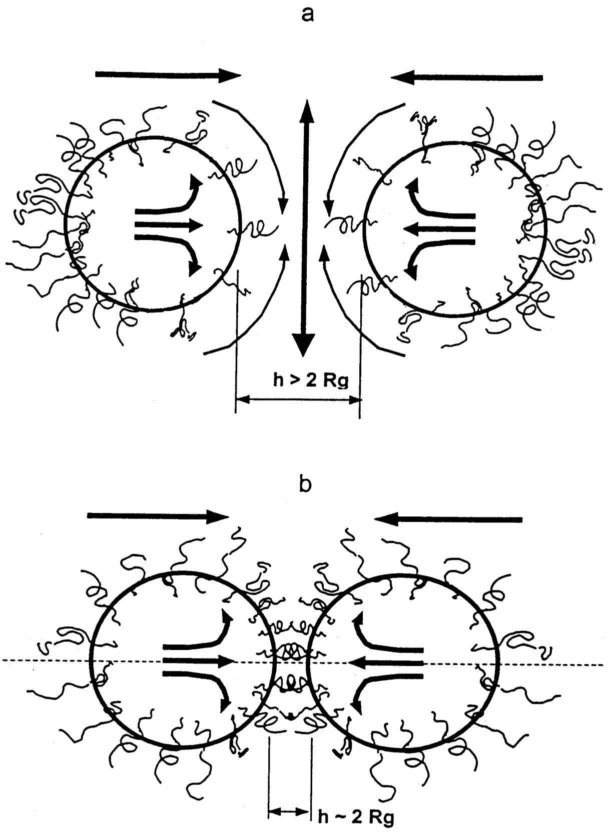

Figure 2. Two mechanisms proposed for block copolymer suppression of coalescence: (a) surface tension gradient (Marangoni) force and (b) steric repulsion.

coalescence and breakup occur simultaneously and the flows are typically complex. This report describes experiments based on well-defined flow fields that separate the effects of droplet coalescence from breakup. Suppression of coalescence was probed by varying shear rate, block copolymer concentration, molecular weight, and block symmetry. We begin this presentation with a quantitative description of the two competing mechanisms: steric interaction and the Marangoni force.

2. Theoretical Background

The origin of the Marangoni force is illustrated in Figure 2a. When two droplets approach each other, the matrix between them is squeezed out (film drainage). This squeezing flow carries the block copolymers at the interface out from the particle gaps, forming a concentration gradient. Milner and Xi estimated the total work required to remove all the block copolymer from the gap to the backside of particles,[11]

$$W \sim D^2 \Sigma kt \tag{2}$$

where D is the particle diameter. Taking $D \sim 1\ \mu\text{m}$ and $\Sigma \sim 0.1$ chain/nm^2, W is about $10^5 kT$, significantly larger than the thermal energy. They combined this Marangoni effect with a trajectory analysis due to Wang et al.[15] and estimated the minimum coverage of block copolymers to completely suppress coalescence. Taking their eq 16 and setting the dimensionless Marangoni force and the drop size ratio to unity gives

$$\Sigma_{\min} = \frac{5}{32}\frac{D\eta\dot{\gamma}}{kT} \tag{3}$$

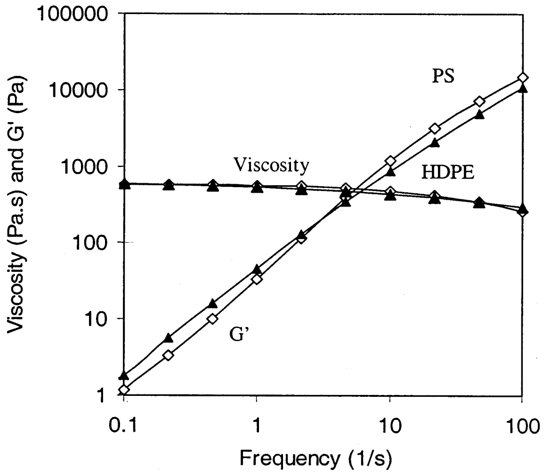

Figure 3. Complex viscosity and G' of HDPE (solid triangle) and PS (open diamond) at 220 °C.

Hence, the minimum coverage is proportional to the shear rate but is independent of molecular features such as the block copolymer molecular weight and composition.

Cristini et al. proposed another Marangoni type theory by incorporating the Marangoni force into the lubrication approximation[14] in a way similar to Chesters' film drainage theory.[13] Their estimate of the minimum interfacial coverage to completely prevent coalescence is proportional to eq 3, but the numerical coefficient is larger. Similar to Milner and Xi's theory, the predicted minimum coverage depends on shear rate but not on molecular details.

A second type of theory was proposed by Sundararaj and Macosko[5] and Macosko et al.[16] It assumes that the block copolymer cannot move on the interface. Resistance to coalescence arises from the steric repulsive force due to compression of block copolymer layers attached to the surfaces of two approaching droplets (Figure 2b). By equating the van der Waals force with the steric force, the minimum coverage of block copolymer was estimated to be

$$\Sigma_{\min} = \frac{20}{27\pi\langle r_0^{\,2}\rangle} \tag{4}$$

where $\langle r_0^2\rangle$ is the square mean end-to-end distance of the chains in the block copolymer layer. Assuming purely Gaussian chain statistics, the minimum coverage is predicted to vary inversely with the molecular weight of the block copolymer. This steric theory originally was developed to explain suppression of static coalescence and thus is independent of shear rate.

3. Experimental Section

3.1. Materials. Polystyrene (PS) and high-density polyethylene (HDPE) homopolymers were obtained from the Dow Chemical Co. Gel permeation chromatography (GPC) analysis yielded number-average molecular weights of 142 and 11 kg/mol and polydispersity indices of 2.2 and 7, respectively, based on calibration with monodisperse polystyrene standards. The densities of PS and HDPE at 220 °C, the temperature employed in the present study, were estimated to be 0.964 and 0.738 g/cm^3, respectively, based on values at 140 °C reported by Fetters et al.[19] and published thermal expansion coefficients.[20,21] Rheological properties of these materials were measured at 220 °C with a dynamic stress rheometer (DSR, Rheometric Scientific). As shown in Figure 3, the viscosity and

Table 1. Polymer Blend Components

	M_n (kg/mol)[a]	R_{gPS}/R_{gPE}[c]	M_w/M_n[a]	η_{PE}/η_{PS}[b]
PS	142		2.2	
HDPE	11		7	1.05
PS−PE	3−3	0.58	<1.1	
PS−PE	20−20	0.58	<1.1	
PS−PE	28.5−10.5	0.96	<1.1	
PS−PE	33−5	1.52	<1.1	
PS−PE	50−50	0.58	<1.1	
PS−PE	100−100	0.58	<1.1	

[a] Measured with gel permeation chromatography based on calibration with polystyrene standards. [b] Ratio of complex viscosities of HDPE to that of PS at 220 °C at 0.1 s^{-1}. [c] Statistical segment length of PS and PE are 0.67 and 0.59 nm, respectively.[19]

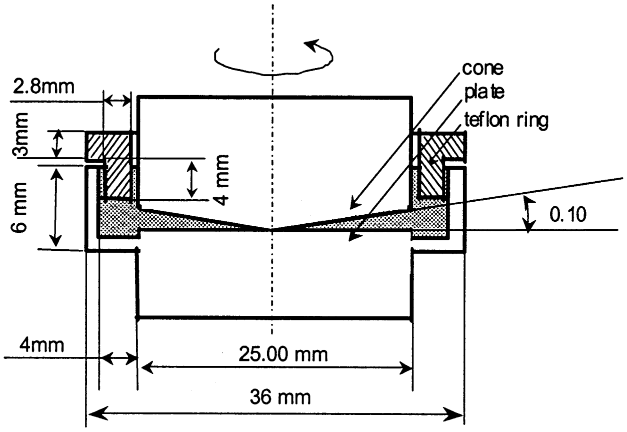

Figure 4. Cone−ring−plate shear cell used to reach shear rates up to 100 s^{-1} without edge failure.

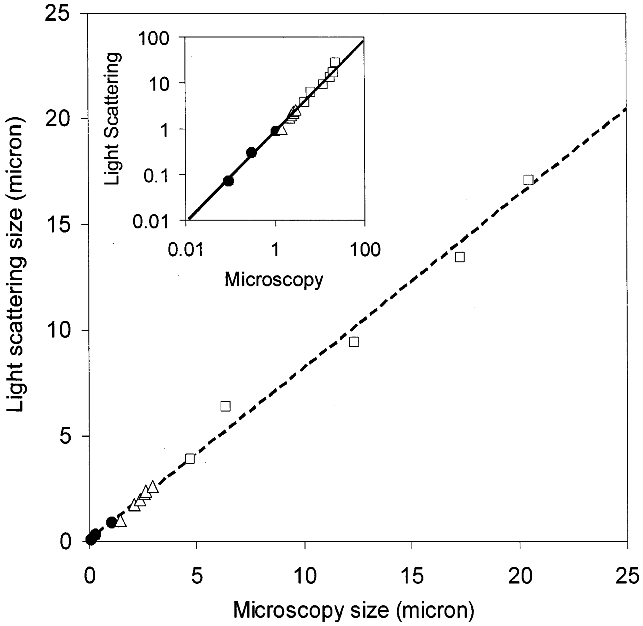

Figure 5. Comparison between particle diameter measured by light scattering (LS230 particle size analyzer) and scanning electron microscopy for standard PS latex particles (solid circles, number average), HDPE particles (square, volume average), and HDPE particles coated with PS−PE block copolymer layers (triangles, volume average). The inset shows the same data on a log−log scale to illustrate the agreement at small diameters.

elasticity of HDPE nearly match those of PS over the entire frequency range.

A series of poly(styrene−1,4-butadiene) (PS−PB) diblock copolymers were prepared by sequential anionic polymerization of styrene and butadiene in cyclohexane using a lithium counterion. Subsequent selective catalytic hydrogenation of the PB blocks resulted in PS−PE diblocks where the PE block contains approximately 18 ethyl branches per 1000 backbone carbon atoms. The block copolymer composition was determined by ^1H NMR while the molecular weight and polydispersity were estimated on the basis of GPC traces. These characterization results are listed in Table 1.

Blends were prepared by dry-mixing PS and HDPE pellets with PS−PE powder, followed by melt mixing in a batch mixer (Haake) equipped with roller blades at 180 °C and 50 rpm for 10 min and then at 5 rpm for 5 min. The rotation was stopped and the sample removed and cooled to room temperature on aluminum foil within 3 min. A piece from these samples was loaded directly in the rheometer. To prevent oxidation during processing, an antioxidant (Irganox 1010, Ciba-Geigy Corp.) was added to the mixture at a concentration of 0.05 wt %.

3.2. Coalescence. In previous papers,[22,23] we used a modified cone and plate shear device to obtain a maximum steady shear rate of 10 s^{-1}. In this work we further modified our shear device as illustrated in Figure 4. A Teflon ring was added to sit on top of the polymer melt. This ring sealed the cone−plate gap and applied a pressure to the polymer melt which prevented edge failure at shear rates up to 100 s^{-1}. This ring−cup−cone shear cell was mounted in a Rheometrics RMS800 rheometer and was used for steady shearing the blends at shear rates higher than 10 s^{-1}. For those experiments at shear rates of 10 s^{-1} or lower, the cup−cone (without the Teflon ring) was used. All experiments were conducted at 220 °C under N_2 purge. For the coalescence experiments, PS/HDPE blends were initially sheared at 10 s^{-1} for 20 min (without the ring) followed by a reduction of the shear rate to a lower value for a predetermined time. After cessation of shearing, the sample was quenched by blowing cold N_2 gas on the fixture. Typically 30 s was enough time to lower the temperature below 100 °C as measured by a thermocouple in the lower plate. This is the T_g of the PS matrix, thereby fixing the morphology. For all the experiments, samples were taken from the half radius position of the cone for subsequent particle size measurements.

3.3. Particle Size Measurement. We measured surface area average particle size using two methods. In the first method, we dissolved the PS matrix of the blends in chloroform at room temperature, leaving the semicrystalline HDPE particles unchanged and dispersed in the solution. We then filtered the solution through a mixed cellulose acetate and nitrate filter (Millipore Inc.) that is stable in the presence of chloroform. HDPE particles were collected on the filter and examined with a scanning electron microscope (JEOL 840). The surface area average size was calculated using the equation $D_{vs} = \sum D_i^3 n_i / \sum D_i^2 n_i$, where D_i and n_i are the diameter and number fraction of particle within the size category i. A detailed description of this procedure is described elsewhere.[22,24]

In the second method, we dispersed the blends in tetrahydrofuran which dissolves the PS matrix forming a suspension of the HDPE particles. These were measured with a LS230 particle analyzer (Coulter Beckmann Co.) that is based on Mie light scattering theory. (For details regarding the LS230 and Mie theory, see ref 25.) This particle analyzer uses two measurement systems. The first is normal laser light scattering (750 nm wavelength) with 126 detectors spanning a 35° angular range and suitable for use with particle diameters ranging from 0.4 to 2000 μm. For smaller particles a so-called polarized intensity differential scattering system was used.[25] It measures the scattering difference between vertically and horizontally polarized light (three wavelengths, specifically, 450, 600, and 900 nm, are provided in the LS230) and can size particles in the range of 40 nm−0.5 μm. Typically 1−10 mg of particles was dispersed in 200 mL of THF and measured for 2 min. For samples where particles tended to flocculate a sonicator was employed. Particle size histograms were collected, and from them averages were calculated.[24] D_{vs} values are reported here.

We compare results from these two methods in Figure 5 using three standard samples, polystyrene latex particles dispersed in water, with number-average sizes of 0.091, 0.304, and 1.07 μm (Ted Pella Inc.) and HDPE (2) particles from our blends. The number-average size of standard PS latex particles and the volume average sizes of the HDPE particles measured with the combined filtration and SEM method are plotted on the *X*-axis while sizes measured with the LS230 are represented on the *Y*-axis. As shown in Figure 5, the two methods were linearly correlated. The ratio of the sizes from the combined filtration and SEM method to that from light scattering was 1.2. This factor was used to correct all the results obtained with the LS230 analyzer.

In the filtration method particles smaller than 0.3 μm can be trapped inside the holes of the filter. The LS230, on the other hand, is able to measure particles down to 40 nm. To remain consistent, we imposed a size cutoff of 0.3 μm in calculating average particle sizes from the LS230 results. In the present study, most particles in the blends that did not contain PS−PE block copolymer were larger than 0.3 μm. Blends containing PS−PE block copolymers had particles ranging from 0.1 to 10 μm in diameter. However, since the volume fractions of the smaller particles were low for most samples, the effect of this imposed size cutoff on our experimental results gave negligible error in the surface area average sizes, D_{vs}. It should be pointed out that this cutoff did make a difference in the number-average size. However, in the present study, we have focused on surface area average size because it is directly related to the interfacial concentration of block copolymer.

We also have used transmission electron microscopy (TEM) (JEOL 1210, operated at 120 kV) to examine micelles in our samples. Films about 80 nm thick were prepared by cryomicrotoming (Ultracut Microtome, Reichert) at −130 °C with a diamond knife. The thin films were stained with ruthenium tetraoxide (RuO_4) vapor by hanging the microtomed films above the surface of a 0.5% aqueous solution of (RuO_4) in a sealed chamber for about 30 min. The PS portion was selectively stained and appears darker than HDPE in the micrographs.

4. Results and Analysis

4.1. Effect of Block Copolymer Concentration in Coalescence. Suppression of flow driven coalescence by block copolymer was first examined by adding various amounts (0−1.1 vol %) of PS−PE block copolymer (20−20 kg/mol) to a blend of PS/HDPE (87.3/12.7 vol). Coalescence was driven at a shear rate of 0.1 s^{-1} and monitored (by measuring particle size) as a function of accumulated strain (also referred to as coalescence strain). Figure 6 illustrates these results.

In the blend without block copolymer D_{vs} changed slightly at first and then shows a sharp increase in coalescence at a critical strain, $\gamma_s = 15$. The slope of the maximum coalescence rate, dD_{vs}/d log(γ), is about 17 μm per decade of strain (see Table 2). At a strain of 360, D_{vs} is about 18 μm, approximately 7 times larger than the initial diameter of 2.4 μm. SEM of the particles in this blend after 1 h of coalescence (Figure 7a) show only a few large particles with many small ones.

In the blend containing only 0.07 vol % of PS−PE, coalescence was significantly suppressed. The sharp increase was delayed to about 20 strain units, and the particle size after 1 h of coalescence was reduced by almost 3 times, to about 7 μm. Similar coalescence results were found in blends containing 0.14 vol % of PS−PE. Increasing the PS−PE content to 0.28 vol % eliminated γ_s (i.e., there is no abrupt increase in D_{vs}). D_{vs} increased from 1.43 μm to just 4.5 μm, after a strain of 360. The slope, dD_{vs}/d log(γ), is approximately equal to 1 μm per decade of strain over the entire strain history. In the blend containing 0.54 vol % PS−PE, dD_{vs}/d log(γ) was reduced to about 0.5 μm per decade of strain. Note that 0.54 vol % PS−PE is 4.3 vol % of the HDPE phase, the same concentration used to obtain the data in Figure 1. In the blends containing 1.1 vol % of PS−PE, D_{vs} remained nearly constant. A SEM picture of the particles in this blend taken after 1 h of coalescence is shown in Figure 7c. In sharp contrast to the blend without block copolymer, the particles in this blend are much smaller and more uniform in size. These results give unambiguous evidence that block copolymers significantly suppress coalescence.

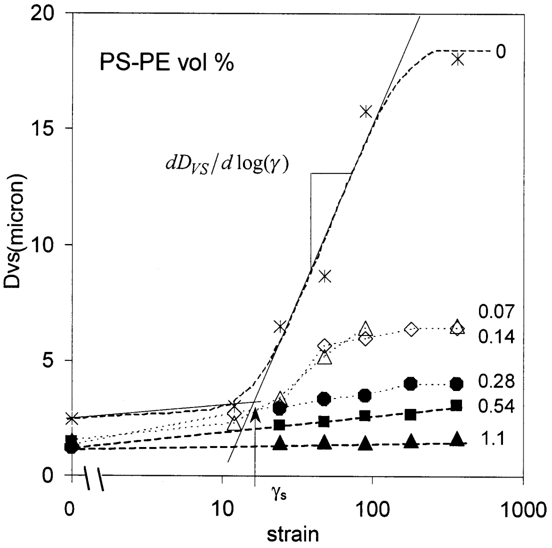

Figure 6. Surface area average particle size vs coalescence strain in PS/HDPE (0.873/0.127) blends that contain various amounts of PS−PE (20−20 kg/mol) diblock copolymer. Coalescence was conducted at 0.1 s^{-1}.

Table 2. Effects of PS−PE Block Copolymers on Coalescence in PS/HDPE (87.3/12.7) Blends

M_n (kg/mol)	vol %	$\dot{\gamma}$ (1/s)	$D_{vs,0}$ (μm)	γ_s	dD_{vs}/d log(γ) (μm)
	0	0.1	2.4	15	17
	0	1.0	2.1	39	7
3−3	0.54	0.1	2.3	15	8
20−20	1.1	0.1	1.4	*a*	0.06
20−20	0.54	0.1	1.5	*a*	0.5
20−20	0.28	0.1	1.2	*a*	1
20−20	0.14	0.1	1.3	20	7
20−20	0.07	0.1	1.5	20	7
20−20	0.54	1.0	1.5	*a*	0.3
20−20	0.28	1.0	1.2	*a*	0.4
20−20	0.14	1.0	1.3	170	2.6
20−20	0.54	2.5	1.5	*a*	0.2
50−50	0.54	0.1	1.4	*a*	0.5
100−100	0.54	0.1	1.0	*a*	0.5
100−100	0.28	0.1	1.4	20	4
100−100	0.14	0.1	1.6	20	7
100−100	0.28	1.0	1.4	*a*	0.9

[a] Coalescence judged to be suppressed.

Coalescence has been studied using four different symmetric diblock copolymers at various loadings and three shear rates. Table 2 lists three characteristic results extracted from these experiments: D_{vs}, γ_s, and dD_{vs}/d log(γ). Above a critical concentration of block copolymer coalescence is suppressed (e.g., ≥0.28 vol % in Figure 6) and γ_s is not defined; i.e., there is no break in dD_{vs}/d log(γ).

The block copolymer concentration at the interface, i.e., the interfacial coverage, Σ, is an important parameter for characterizing coalescence suppression effects. We calculated Σ using the following equation:

$$\Sigma = (\phi_{bcp}/\phi_{HDPE})(D_{vs}/(6\nu_{bcp})) \qquad (5)$$

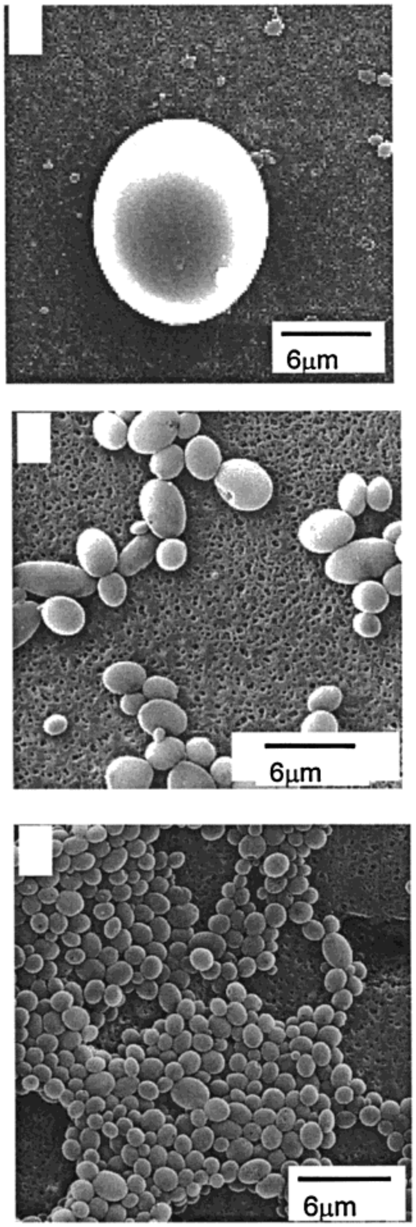

Figure 7. Micrographs of HDPE particles after 1 h coalescence at 0.1 s^{-1} in PS/HDPE blends with 0 (a), 0.54 (b), and 1.1 vol % (c) of PS−PE (20−20 kg/mol). Scale bars are 6 μm.

where ν_{bcp} is the volume per block copolymer chain and ϕ_{bcp} and ϕ_{HDPE} are the volume fractions of block copolymer and HDPE, respectively. Assuming the density, ρ, of block copolymer is equal to the average of PS and HDPE, or 0.855 g/cm^3, then $\nu_{bcp} = 77.5$ nm^3 per chain for the PS−PE of $M_n = 20 + 20 = 40$ kg/mol. In eq 5 we set ϕ_{bcp} equal to the volume fraction of copolymer added. Thus, we assume that the amount of block copolymer dissolved in the homopolymer phases is negligible. The volume fraction of the 20−20 kg/mol block copolymer dissolved in homopolymer phases was estimated to be less than 10^{-6} based on the Boltzman probability distribution:

$$\phi_{dis} \propto \exp(-N\chi) \tag{6}$$

where N is the number of statistical segments in the block copolymer and χ is the segment interaction parameter. This value of χ was estimated to be about 0.07 from the PS−PE interfacial tension,[26] 5 mN/m, and the Helfand and Tagami equation[27] $\Gamma = kTb\rho\sqrt{6\chi}$ where b is the statistical segment length, estimated to be 0.59 and 0.67 nm for HDPE and PS, respectively.[19]

In calculating Σ, we also neglected the amount of block copolymer that was trapped in micelles. However, from TEM micrographs we found that PS−PE formed some micelles in the blends, especially in those that contained 0.54 vol % (Figure 8a,b) or more PS−PE. It was difficult to quantify the number of micelles present because the thickness of the TEM film samples could not be precisely controlled or measured. For example, for the blend shown in Figure 8b containing 0.54 vol % PS−PE, $D_{vs} = 3$ μm from Figure 6 at $\gamma = 360$. Thus, eq 5 gives 0.28 chain/nm^2. On the basis of micrographs like Figure 8b, we can estimate the number of PS−PE chains in micelles, assuming a TEM film thickness of 80 nm, the minimum that could be obtained based on the microtome setting. Accounting for micelles reduces the interfacial coverage to 0.2 chain/nm^2.

We have chosen to define "complete suppression of coalescence" based on the disappearance of an inflection, γ_s, in the diameter vs strain results. Thus, in Figure 6 we designate 0.28 vol % as the concentration of PS−PE which completely suppresses coalescence. There is still a gradual increase in particle size at 0.28 vol %, but this increase is small. TEM images at this concentration show very few micelles while at 0.54 vol % micelles do appear, indicating that the interface must be at or near saturation. Using eq 5 and the diameter at large strain gives $\Sigma_{min} \approx 0.20$ chain/nm^2 as the minimum coverage to suppress coalescence.

To estimate the concentration of block copolymer necessary to saturate the interface, i.e., the maximum coverage Σ_{max}, we use the lamellar spacing, 39 nm, in a pure PS−PE (20−20 kg/mol) block copolymer sample measured by small-angle X-ray scattering[28] and obtain 0.25 chain/nm^2. Thus, the minimum coverage necessary to completely suppress coalescence is a significant fraction, or about 80%, of this saturation coverage.

We can compare these experimental values to the minimum block copolymer coverage predicted by the coalescence theories. Milner and Xi's theory (eq 3) predicts $\Sigma_{min} \approx 0.006$ chain/nm^2 while Cristini et al.'s gives $\Sigma_{min} \approx 0.03$ chain/nm^2 and Sundararaj and Macosko's steric interaction theory gives 0.003 chain/nm^2. None of the theories quantitatively predict the minimum block copolymer coverage. However, these theories can be tested qualitatively for dependence of the minimum coverage of block copolymer on shear rate and molecular weight, as presented in the following sections.

4.2. Shear Rate Effects. Coalescence suppression was tested at different shear rates with a blend of PS/HDPE/PS−PE (20−20 kg/mol) (87.3/12.7/0.54 vol). As shown in Figure 9, the coalescence rate decreased with increased shear rate over the range 0.1−2.5 s^{-1}; however, the effect is less pronounced than without block copolymer.[22] Theoretical treatments of the effect of shear rate on coalescence are discussed in ref 23.

Minimum block copolymer coverage also was estimated for coalescence at 1.0 s^{-1}. As shown in Figure 10, the increase in D_{vs} for different block copolymer concentrations at 1.0 s^{-1} was very similar to the behavior at 0.1 s^{-1} shown in Figure 6. Increasing the volume fraction of PS−PE prevented coalescence. When the concentration of block copolymer was 0.28 vol %, the sharp increase in D_{vs} almost disappeared, which again indicates the minimum coverage. Interestingly,

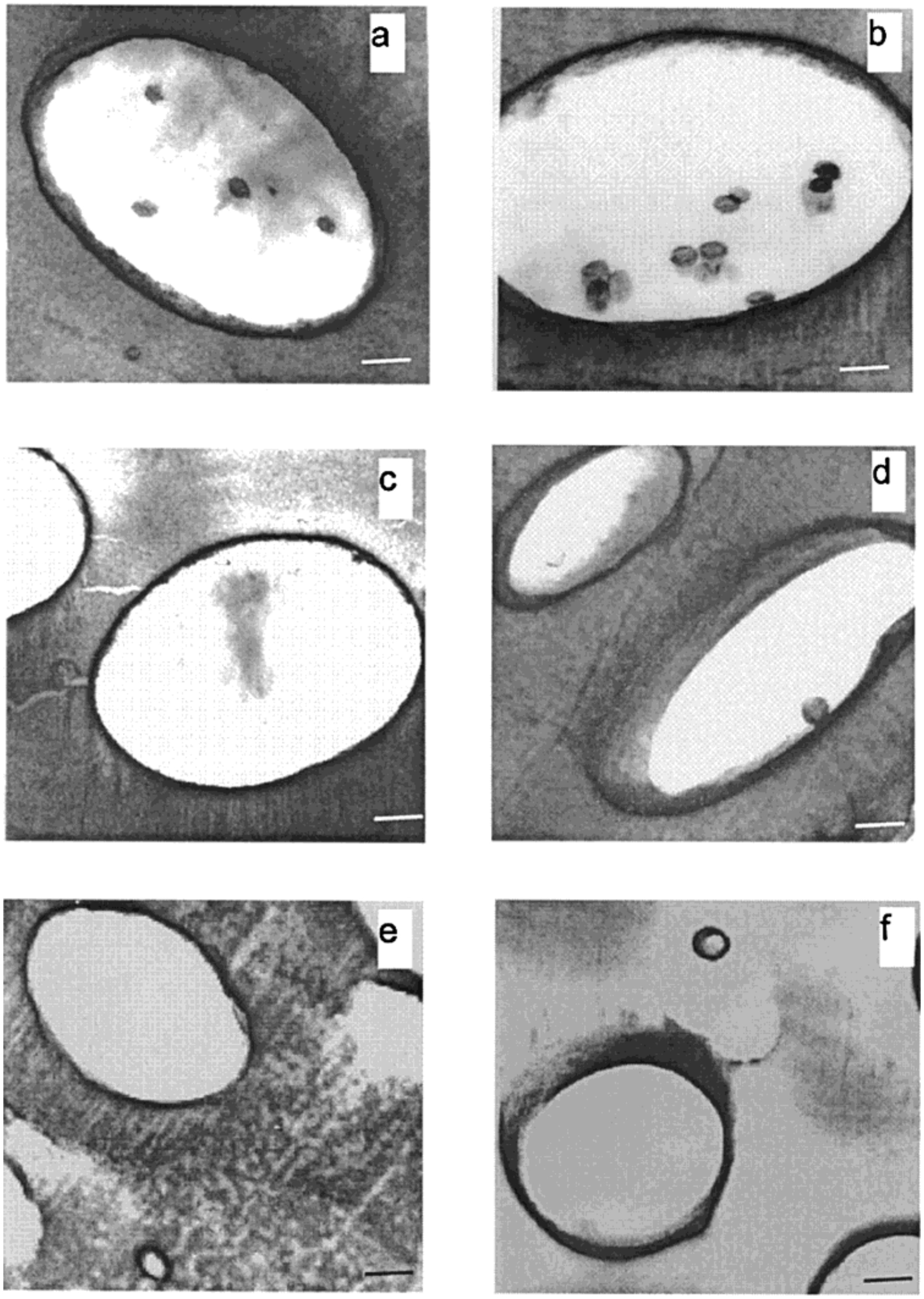

Figure 8. Transmission electron micrographs of PS/HDPE/PS−PE (87.3/12.7/0.54) blends after coalescence at 0.1 s^{-1} for 0 (a, c, and e) and 360 (b, d, and f) strain units. Molecular weight of the block copolymers is 20−20, 28.5−10.5, and 35−5 kg/mol for (a and b), (c and d), and (e and f), respectively. The length of the scale bars is 200 nm.

the minimum coverage at 1.0 s^{-1} was about 0.15 chain/nm^2, close to the value at 0.1 s^{-1}. Although the shear rates differed by an order of magnitude, the minimum block copolymer coverage did not change significantly, suggesting that the resistance to coalescence caused by block copolymers was not strongly dependent on shear rate.

We tried to obtain the minimum coverage for 10 s^{-1} using the same procedure. We presheared samples at 100 s^{-1} for 10 min and then decreased to 10 s^{-1}. Instead of droplets, we observed predominately long fibers formed at 100 s^{-1} which persisted even after 5 s of shearing at 10 s^{-1}.[24]

Although we have not obtained the minimum block copolymer coverage at 10 s^{-1}, the data in Figure 1, i.e., steady-state particle size at 10 s^{-1} vs HDPE volume fraction, can give an upper bound on the minimum coverage. As shown in Figure 1, coalescence was negligible. In these blends the volume ratio of PS−PE to HDPE was 0.043. From Figure 1 at 12.7% HDPE D_{vs} = 1.2 μm, and eq 5 gives $\Sigma_{min} \approx 0.10$ chain/nm^2. Thus, the minimum coverage at 10 s^{-1} should be no higher than 0.10 chain/nm^2. Interestingly, this number is similar to the values measured at 0.1 and 1.0 s^{-1}, indicating that the minimum block copolymer coverage does not depend strongly on the shear rate over this range (Table 3).

This observation that the minimum coverage was independent of shear rate (or even decreasing with $\dot{\gamma}$) gives strong evidence for the mechanism of coalescence. As discussed in the theoretical section, eq 3, which is

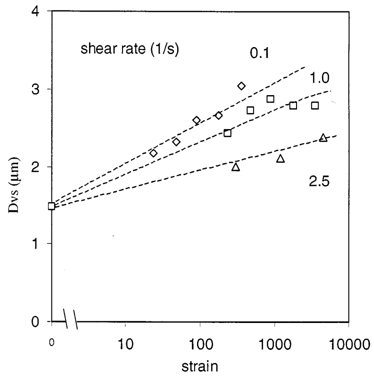

Figure 9. Effect of shear rate on coalescence in PS/HDPE/PS−PE (20−20 kg/mol) (87.3/12.7/0.54 vol) blends.

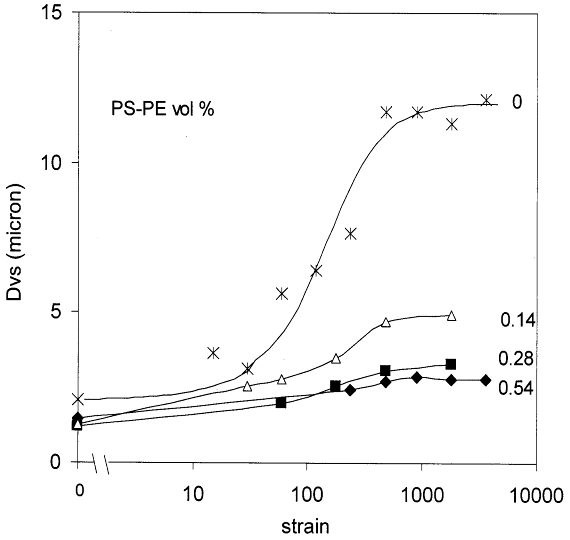

Figure 10. Coalescence at 1.0 s^{-1} in blends containing various amounts of PS−PE block copolymer (20−20 kg/mol). PS/HDPE = 0.873/0.127.

Table 3. Minimum Interfacial Coverage To Suppress Coalescence, Σ_{min}

shear rate (s^{-1})	0.1	0.1	1	10	0.1	0.1
mol wt (kg/mol)	3−3	20−20	20−20	20−20	50−50	100−100
min coverage (chain/nm^2)	*a*	0.20	0.15	≤0.10	0.1	0.05

[a] No coalescence suppression.

based on the Marangoni interaction, predicts that the minimum block copolymer coverage should increase linearly with shear rate. The steric interaction theory, on the other hand, assumes no dependence on shear rate.

4.3. Block Copolymer Molecular Weight. Coalescence as a function of molecular weight of the PS−PE block copolymer is shown in Figure 11. The relative volumes of PS, HDPE, and PS−PE were 0.873, 0.127, and 0.0054, respectively, for all these blends. Interestingly, three PS−PE block copolymers of 20−20, 50−50, and 100−100 kg/mol had very similar suppression effects on coalescence, with D_{vs} of the blends containing 50−50 and 100−100 kg/mol PS−PE's being slightly smaller than the blend containing 20−20 kg/mol PS−PE. This indicates that higher molecular weight PS−PE was somewhat more efficient in suppressing coalescence. Minimum coverages for the 50−50 and 100−100 kg/mol PS−PE were calculated to be 0.1 and 0.05chain/nm^2, respectively, less than the value for 20−20 kg/mol PS−PE. This result supports the steric interaction mechanism but not the Marangoni force mechanism.

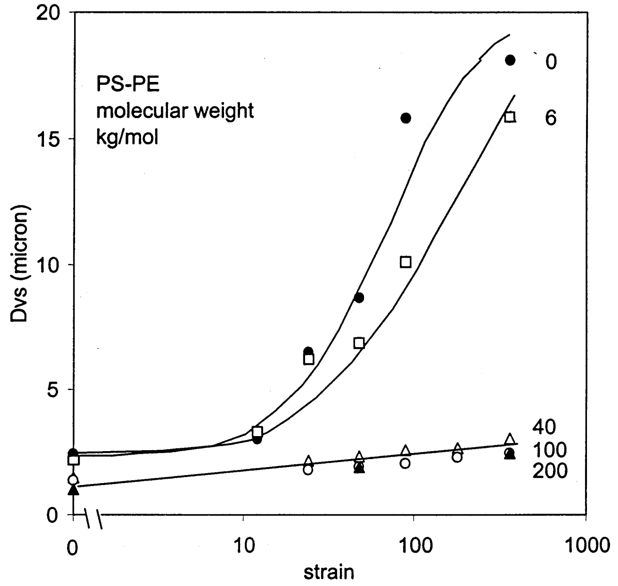

Figure 11. Effect of PS−PE molecular weight on coalescence of HDPE particles in PS matrix (0.873/0.127/0.0054). D_{vs} vs strain is very similar for the PS−PE block copolymers with molecular weights of 40 (20−20) (open triangle), 100 (50−50) (open circle), and 200 kg/mol (100−100) (solid triangle) while the 6 (3−3 kg)/mol PS−PE did not have a significant effect on coalescence. $\dot{\gamma}$ = 0.1 s^{-1}.

The particle size of the blend compatabilized with 3−3 kg/mol PS−PE was similar to that without any block copolymer. The molecular weight of this block copolymer is so low that most of it must be dissolved in the homopolymer phases. Using eq 6, we calculate that over 90% of the 0.0054 volume fraction of this 3−3 kg/mol PS−PE block copolymer is dissolved in HDPE. Thus, there is a critical molecular weight between 3−3 and 20−20 kg/mol, and only those block copolymers with molecular weights higher than this critical value are expected to be capable of preventing coalescence.

4.4. Symmetry of Block Copolymers. Block copolymer symmetry is another parameter that might affect coalescence efficiency. All the block copolymers discussed thus far are compositionally symmetric; i.e., the weight percentages of the PS and PE blocks are equal. However, because monomer molecular weights (104 and 28 g/mol) and statistical segment lengths (0.67 and 0.59 nm) of PS and PE are different, the coil sizes of PS and PE blocks are not equal. As indicated in Table 1, the ratio of radius of gyration of the PS block to that of the PE block for those block copolymers is about 0.58. To check the effects of block symmetry on prevention of coalescence, we compared the increases in particle size at 0.1 s^{-1} in blends that were compatibilized with three PS−PE diblock copolymers with M_n values of 20−20, 28.5−10.5, and 33−5 kg/mol. In this series the total molecular weights are approximately the same, but the ratios of radius of gyration (PS/PE) are 0.58, 0.96, and 1.52, respectively. As shown in Figure 12, all three block copolymers prevented HDPE drop coalescence; however, the block copolymer with radius gyration ratio of 1.52 had the most significant effect. This block polymer has the greatest PS block molecular weight, a result that agrees with the steric interaction mechanism.

As mentioned earlier, many micelles were dispersed in the HDPE phase in the blend with 20−20 kg/mol PS−

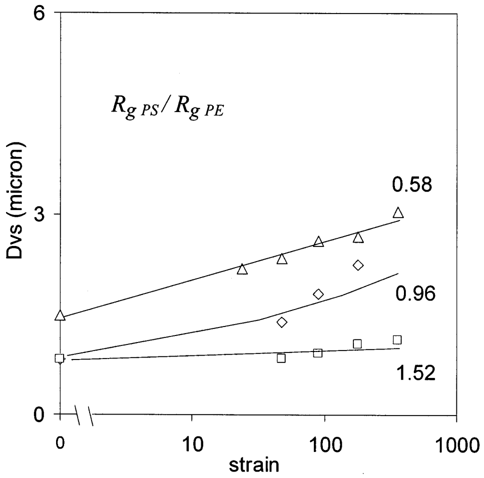

Figure 12. Effect of PS−PE symmetry on the coalescence of HDPE particles in PS matrix. Symmetry of PS−PE is characterized with the ratio of radius of gyration of the PS block to that of the PE block. Total molecular weights of all PS−PE diblock copolymers are approximately 40 kg/mol, shear rate 0.1 s^{-1}, PS/HDPE/PE−PS = 0.873/0.127/0.54.

PE (Figure 8a,b). However, the TEM micrographs revealed few micelles in the blends compatabilized with the two asymmetric PS−PE block copolymers (Figure 8c−f). Thus, block symmetry also may improve coalescence suppression by increasing Σ.

4.5. Block Copolymer Migration and Micelle Formation. Based on the above results, as little as 0.28 vol % PS−PE block copolymer can significantly suppress coalescence of HDPE particles. However, transmission electron micrographs taken from samples quenched during coalescence show that some block copolymer becomes localized in micelles rather than at interfaces as shown in Figure 8a,b for a blend containing 0.54 vol % PS−PE (20−20 kg/mol). Interestingly, most of these micelles are located in the HDPE particles; only a few are located in the PS phase.

All the PS/HDPE/PS−PE blends were prepared by dry-mixing PS and HDPE pellets with PS−PE powder (one-step mixing), followed by melt mixing in a Haake mixer. A natural concern is that the block copolymer might be trapped in micelles because migration of block copolymers in the blends is diffusion limited. To examine this kinetic effect, we conducted two other experiments (two-step mixing). First, we dry-mixed PS pellets (20.7 g) and PS−PE (20−20 kg/mol) powder (0.115 mg) followed by melt mixing in the Haake mixer at 50 rpm for 5 min. HDPE (2.3 g) was then added into the PS/PS−PE blend and further mixed at 50 rpm for another 10 min. The samples were placed in the cone and plate and sheared at 10 s^{-1} for 20 min and then at a reduced shear rate of 0.1 s^{-1} for another 1 h in order to make samples having the same treatment conditions as those shown in Figure 8a,b. In the second experiment we repeated the procedure, exchanging the PS for the HDPE. We then used TEM to examine these samples.

In the first blend (PS−PE premixed with PS) we found that micelles about 30 nm in diameter were formed after 5 min of mixing in Haake mixer. The staining in Figure 13a shows that, as expected, the PS block is on the outside of these micelles. We believe that the contrast with the PS matrix is caused by preferential diffusion of RuO_4 into the PS blocks which are stretched at the PS−PE junctions. After adding HDPE and mixing for another 10 min, HDPE droplets were dispersed inside the PS matrix, and most of the micelles had disappeared (Figure 13b). Interestingly, after steady shearing at 0.1 s^{-1}, the micelles re-formed but appeared in the HDPE particle phase (Figure 13c). This morphology is similar to that of the blend prepared by dry-mixing all three components (PS, HDPE, and PS−PE) at the same time, also denoted as one-step mixing (Figure 8a,b). We measured the average particle size in this blend and confirmed that it was similar to the size obtained with one-step mixing.

This experiment shows that the PS−PE chains were able to migrate from the PS through the interfaces and into the HDPE phase. Furthermore, PS−PE micelles preferred to stay in the HDPE phase. Thus, the distribution of PS−PE (20−20 kg/mol) block copolymers between interface and micelles in the present blends (HDPE particles dispersed in PS matrix) was controlled by thermodynamics rather than the mixing procedure or block copolymer kinetics.

Figure 13d−f shows the results for the second blend. In Figure 13d the micelles are now in HDPE and have PS cores, in contrast to Figure 13a. When PS homopolymer is added, a dispersion of PS particles was formed with a few micelles inside the HDPE matrix (Figure 13e). This morphology was preserved after shearing the blend for the same time as the first blend (Figure 13f), and the particle size stayed constant. This suggests that there is sufficient block copolymer in the interface to prevent coalescence and that the micelles also stayed in the HDPE phase even when the blend composition was reversed. Although we lack sufficient experimental information to explain why the micelles remained in the HDPE phase in this reverse blend, the fact that no significant amount of micelles were found in the PS particle phase suggests that the micelles of PS−PE (20−20 kg/mol) do not prefer the PS phase. Maric and Macosko[29] have done similar melt mixing experiments with PS/poly(dimethylsiloxane) blends and found that micelles of symmetric PS−PDMS block copolymers also have good mobility but prefer the PS phase.

5. Discussion

Our experiments on coalescence suggest the following points. (1) Premade block copolymer can suppress coalescence very efficiently. (2) There is a minimum block copolymer coverage required for completely suppressing coalescence. This minimum coverage did not depend on shear rate in the range of 0.1−10 s^{-1}, but it decreased slightly with increasing block copolymer molecular weight. For PS−PE of 20−20 kg/mol, this minimum coverage was about 0.20 chain/nm^2, or about 80%, of the saturation coverage. (3) With the total molecular weight the same, the PS−PE with a larger PS block is more efficient at suppressing coalescence. (4) None of the current theories quantitatively predict the minimum coverage for preventing coalescence. However, the steric repulsion mechanism qualitatively agrees with the experiments, while the Marangoni mechanism does not.

5.1. Mechanisms of Suppression of Coalescence. Why do theories based on the Marangoni force fail to capture the qualitative trends exhibited by the experiments? They assume a Marangoni force that is sufficiently weak that the drop surface remains mobile (as illustrated in Figure 2a). This assumption is equivalent to assuming that the concentration of block copolymer in the interface is dilute. Our results indicate that a

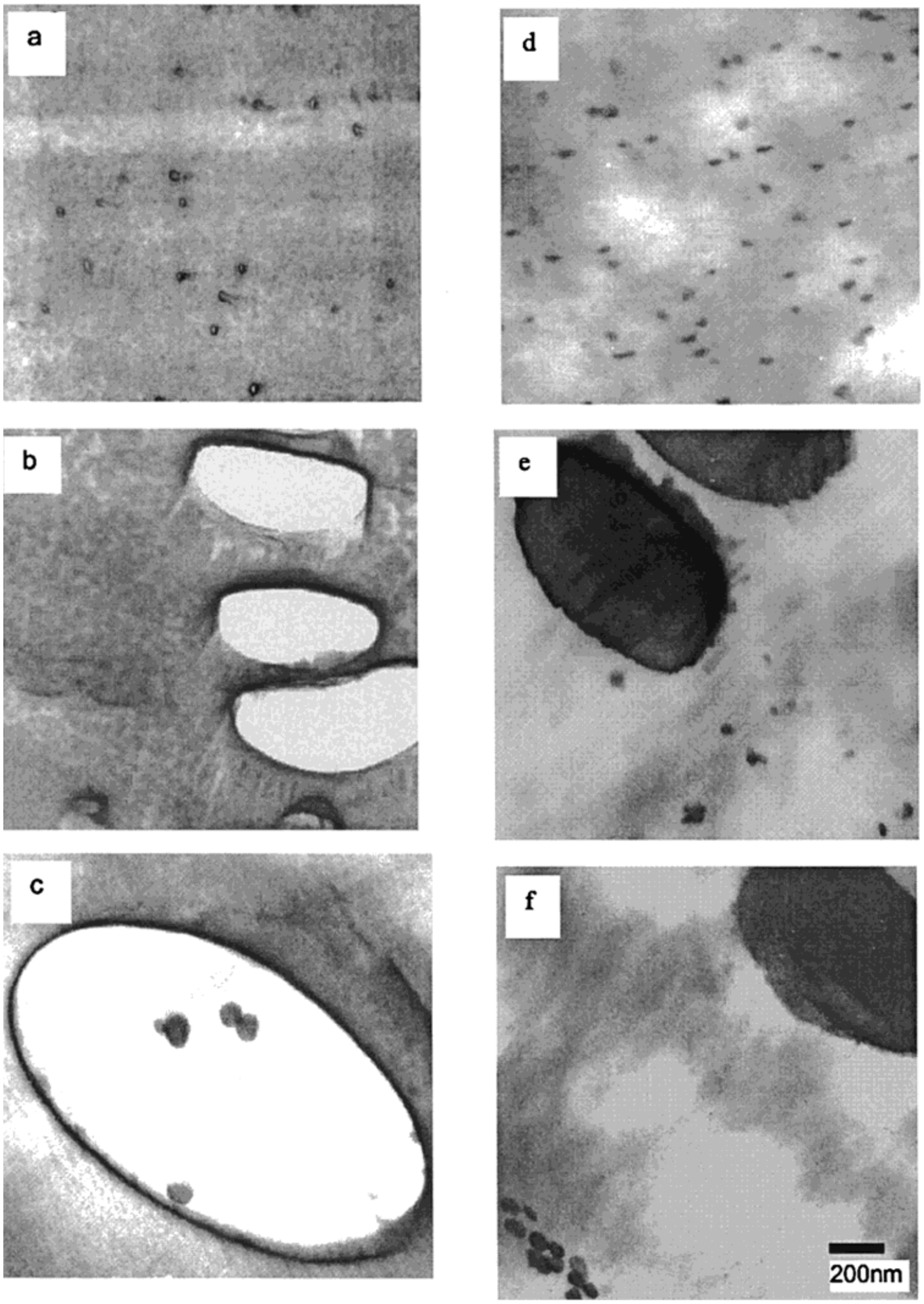

Figure 13. Micelles formed in PS/PS−PE (20−20 kg/mol) (87/0.54 vol) blend (a). These micelles disappeared after mixing 13 vol % HDPE with the blend (b) and showed up again in HDPE particle phase after the blend was steady sheared (c). In (d) micelles of PS−PE formed in HDPE. Some of these micelles persist after mixing 13 vol % PS with the blend (e) even after steady shearing for 1 h at 0.1 s (f).

relatively high interfacial concentration (80% of saturation) is required to prevent coalescence.

If there is no block copolymer present, droplet coalescence will occur when the gap is smaller than a critical value, $h_c \approx 5$ nm.[30,31] When block copolymers are attached to the interface, the corona outside each particle (PS block in the present experiments) begin to compress as the gap thickness approaches the block copolymer layer thickness, leading to a steric repulsive force that prevents the two drops from moving closer.[16] The higher the molecular weight of the outer block, the thicker the layer, so more compression is needed in order for the two particles to reach the critical gap (which may not equal the critical gap of 5 nm for the particles without block copolymers). This suggests that block copolymers with larger outer blocks will suppress coalescence more effectively. Indeed, our experiments show that the higher molecular weight PS−PE (i.e., 100−100 kg/mol) and the PS−PE with a larger portion of PS block (i.e., 33−5 kg/mol) were more efficient on a per chain basis in suppressing HDPE particle coalescence.

In addition, when the molecular weights of the block copolymers are too low, the corona layer is thinner than the critical gap. This suggests there exists a minimum degree of polymerization (molecular weight), $N_{\min}$, for this steric interaction. If we assume that the layer thickness of this minimum molecular weight is about half of the critical gap, then $h_{c/2} \approx R_g = (b^2N_{\min}/6)^{1/2}$. For our PS/HDPE system, $N_{\min} \approx 1.5(h_c/b)^2 \approx 1.5(5/0.67)^2 \approx 84$. That is, to completely suppress coalescence, the molecular weight of the PS block should be at least 9 kg/mol, or 18 kg/mol for symmetric PS−PE diblock copolymer. This calculation agrees with our results: The 20−20, 50−50, and 100−100 kg/mol block copolymers strongly suppressed the coalescence while the 3−3 kg/mol block copolymer did not. However, the 3−3 copolymer is probably soluble as discussed above.

Although the steric interaction is more likely to be the effective mechanism suppressing coalescence, the fact that the predicted minimum coverage was much lower than our experimental values remains to be explained. Macosko et al. assumed that each block copolymer chain in the interface of one droplet interacted with a block copolymer chain in the interface of the other droplet.[16] This will overpredict the interaction probability, especially when the coverage is dilute. The real probability for block copolymer chains on two different particle surfaces to interact with each other will be related to its volume fraction in the interfacial region. Another open question is how the shear force, which was ignored in this theory,[5,16] should be accounted for in balancing the steric interaction between the block copolymer layers.

5.2. Distribution and Transport of Block Copolymers in Blends. The distribution and migration of block copolymers is another interesting issue. As shown in Figure 13, micelles of 20−20 kg/mol PS−PE moved from the PS phase to the interface and into HDPE phase after coalescence for 1 h. This suggests that transport of block copolymer across PS/HDPE interfaces was fast when compared with the time scale of coalescence. Thus, the distribution of block copolymers between interfaces and micelles was controlled by thermodynamics. It is reasonable to assume that the maximum coverage is close to the saturation block copolymer coverage in the blends that were sheared for a long time, with correction for the block copolymer trapped in micelles. Using eq 5 and subtracting the micelles observed in Figures 13c and 8b, we estimate $\Sigma_{\max} \approx 0.2$ chains/nm^2, which is close to 0.25 chain/nm^2, the saturation coverage.

In the case of reactive blending, block copolymers form at interfaces. We may speculate that if their molecular weight is high and the diffusion process is slow, these block copolymers can be trapped at the interface, resulting in the interfacial coverage higher than its maximum value. This might be especially important for grafted copolymers that are less mobile. Thus, block copolymers and grafted copolymers made by reactive blending may compatabilize blends more efficiently than addition of premade block copolymers, where block copolymers may be more easily trapped in micelles rather than at interfaces within the processing time scale. Recently, Jones studied the reactive blending of an amine-terminated PS and an anhydride-terminated HDPE.[28] The particle size obtained from these reactive blends was around 0.3 mm, smaller than the sizes (>1 μm) obtained from all the blends of the present studies that were compatibilized with premade PS−PE blends, consistent with our speculation.

6. Conclusions

The role of polystyrene−polyethylene (PS−PE) diblock copolymer on suppression of droplet coalescence in PS/HDPE blends has been examined by first shearing PS/HDPE/PS−PE blends to a steady state, followed by continuing to shear at a reduced rate. Coalescence was significantly suppressed compared to blends that did not contain block copolymer. The minimum block copolymer required to completely suppress coalescence was measured to be about 0.20 chain/nm^2 for 20−20 kg/mol PS−PE. This value decreased with increasing block copolymer molecular weight and also with shear rate in the range of 0.1−10 s^{-1}. The effects of block copolymer symmetry on coalescence and micelle formation were measured. PS−PE with a larger PS block was more efficient in suppressing coalescence between HDPE particles. Steric repulsive interaction between the rigid block copolymer layers in particle surfaces was thought to contribute to this coalescence suppression. These results are inconsistent with theories based on the Marangoni interaction but support the notion of stabilization based on steric repulsion.

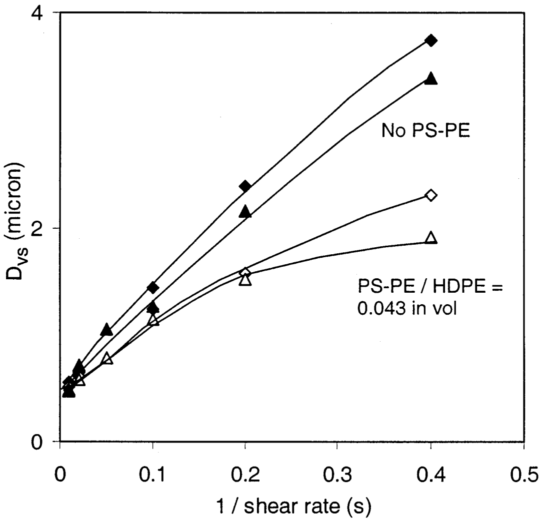

Figure 14. Surface area average diameter of PS/HDPE/PS−PE (open symbols) and PS/PE (solid symbols) blends vs 1/shear rate. The volume fractions of HDPE are 0.004 (triangle) and 0.013 (diamond) in these two blends. The ratio of the volume of PS−PE (20−20 kg/mol) to that of HDPE is 0.043.

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Appendix. Interfacial Tension Reduction by Block Copolymer

We studied the two lowest concentrations of PE drops shown in Figure 1, $\phi_{\mathrm{HDPE}} = 0.013$ and 0.004. At these low concentrations the number of collisions is very small so the main effect of block copolymer should be to assist particle breakup by lowering interfacial tension. We sheared these two samples in the modified cone and plate device shown in Figure 4 for 1 h at shear rates from 2.5 to 100 s^{-1}. Final particle sizes are plotted vs $1/\dot{\gamma}$ in Figure 14, which illustrates that block copolymer reduces the average particle size at low shear rate but hardly affects the size at high rate.

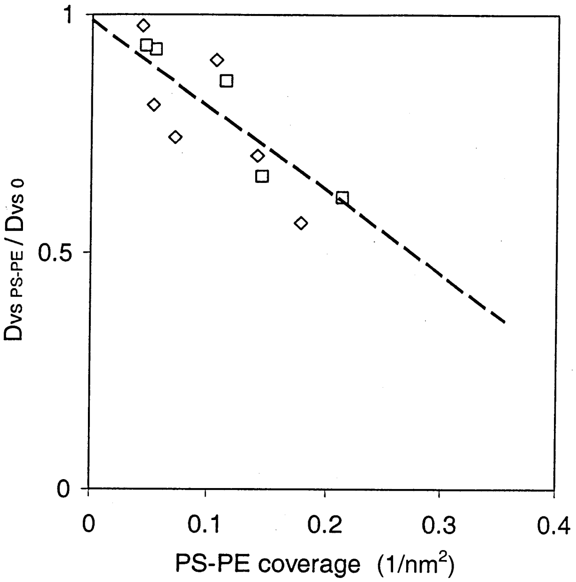

Figure 15. Ratio of surface area average diameter of PS/HDPE/PS−PE to that of PS/PE blends vs PS−PE-20−20 coverage at interface. Data from Figure 14, same symbols.

We can use the data in Figure 14 to estimate the reduction in interfacial tension due to the addition of block copolymers. According to Taylor's equation (eq 1), the ratio of the droplet diameter with block copolymer (open symbols) to that without (solid symbols) is equal to the ratio of interfacial tensions. The greatest reduction in interfacial tension is 0.6 at $\dot{\gamma} = 2.5\ \mathrm{s}^{-1}$; i.e., Γ_0 is reduced from 5 to 3 mN/m. The ratios of D/D_0 are plotted in Figure 15 vs Σ, the coverage of the droplet interfaces with block copolymer estimated using eq 5. We see that the reduction of interfacial tension is approximately linear in Σ; $\mathrm{d}\Gamma/\mathrm{d}\Sigma = 1.8\Gamma_0$.

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