Compatibilizers for Melt Blending: Premade Block Copolymers†

C. W. Macosko,* Philippe Guégan,‡ and Ashish K. Khandpur§

Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, Minnesota 55455

Akinari Nakayama,∥ Philippe Marechal,⊥ and Takashi Inoue

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152, Japan

Received February 15, 1996; Revised Manuscript Received May 30, 1996⊗

ABSTRACT: Poly(methyl methacrylate) (PMMA) was melt mixed 30:70 into polystyrene (PS) with and without symmetric P(S-*b*-MMA) diblock copolymers. The molecular weight of the components was varied. After 5 min of shear mixing, the PMMA was dispersed into roughly spherical, submicron particles. Particle size was measured by light scattering and transmission electron microscopy. As little as 1% copolymer led to a significant reduction in PMMA particle size, although larger amounts were needed to make the particles stable to annealing (180 °C for 15 min). The principle role of block copolymers in controlling morphology appears to be in preventing coalescence. Preventing dynamic coalescence leads to size reduction, while preventing static coalescence results in stability or compatibilization. We estimate that less than 5% of the interface needs to be covered to prevent dynamic coalescence while ∼20% is necessary to impart static stability. Mobility, critical micelle concentration, and molecular weight of the block copolymer also appear to be important. Lowering the molecular weight of the PMMA phase from 43 000 to 11 000 resulted in dramatically lower particle size (700 vs 60 nm). These variables are discussed in terms of a qualitative balance between rate of diffusion and rate of area generation during blending.

Introduction

About 30% of all plastics sold today contain more than one polymer, and this fraction continues to increase each year.[1−3] Nearly all of these polymer−polymer blends are immiscible, yet the resulting multiphase morphologies can produce desirable properties. For example, if spheres of poly(ethylenepropylene) rubber are dispersed in polyamide 6,6 at the correct size (∼0.8 μm) and concentration (∼15%), the fracture toughness of the polyamide 6,6 is greatly improved.[4]

Since these immiscible blends are thermodynamically unstable, they must be stabilized to prevent coalescence during melt processing.[5] This process of stabilizing polymer blends is commonly called *compatibilization*. A compatibilization strategy which is frequently proposed is the addition of a premade block copolymer composed of blocks that are each miscible with one of the homopolymers (e.g. see ref 6). Theory suggests that block copolymers will prefer to span the interface.[7,8] Most experimental studies have been carried out by casting from solution;[9−14] however, commercially, polyblends are prepared by melt mixing. Furthermore, it appears that all commercial blends made from highly immiscible polymers are compatibilized reactively.[2,3] That is, a block or graft copolymer is formed by coupling of reactive groups on each of the immiscible polymers. There are several problems in compatibilizing multiphase structures with block copolymer in the melt. The viscosity of block copolymers is high and thus may be difficult to disperse.[15] These copolymers are typically expensive so it is desirable to minimize their concentration. Finally, the block copolymer should prefer to lie at the interface rather than form micelles or a separate phase.[16]

The purpose of this study is to investigate the effect of adding small amounts of diblock copolymer in melt blends on the resulting morphology. We have chosen polystyrene (PS) and poly(methyl methacrylate) (PMMA), which are amorphous and have similar glass transition temperatures. Both homopolymers and the corresponding diblock copolymer can be readily synthesized anionically. For the molecular weights and the low concentration of diblock copolymer used in this study we expect that all our blends will be immiscible with no formation of ordered phases.[17] These two polymers have a sufficient difference in refractive index to allow light scattering measurements. Furthermore, since PS can be selectively stained by RuO_4, the morphology can be observed by transmission electron microscopy (TEM). Elsewhere we discuss reactively formed PS−PMMA block copolymers and compare their compatibilizing ability to these premade ones.[18,43]

Experimental Section

Materials. PS and PMMA were synthesized by living anionic polymerization as described by Guégan et al.[18] Three commercial, broad molecular weight distribution samples were also used. Molecular weights of the samples by SEC (size exclusion chromatography) are given in Table 1. M_w values are reported for the commercial samples since these values are more indicative of the melt viscosity. P(S-*b*-MMA) diblock copolymers were synthesized in THF at −78 °C. The styrene was added to *sec*-butyllithium, and the living chains were endcapped with diphenylethylene right before the addition of MMA. The living polymer was quenched with degassed methanol. The 780K diblock was obtained from Polymer Standards, Mainz, Germany. M_n values of the block copolymers are based on SEC with PS calibration. These values

* To whom correspondence should be addressed.

† Presented in part at the ACS Annual Meeting, September 1993, in Chicago and the PPS European Meeting, August 1994, in Strasbourg.

‡ Present address: Groupe de Laborataires de Thiais, 2 rue Henri Dunant, 94390 Thiais, France.

§ Present address: 3M Co., Bldg. 201-3E-03, St. Paul, MN 55144.

∥ Present address: Hitachi Cable, Ltd., 5-1-1 Hitaka-Cho Hitachi-Shi, Ibaraki-Ken, 319-14, Japan.

⊥ Present address: Fina Research (Dépt. Polymères, Division Développement Polyoléfines), Zone Industrielle C, 7181 Feluy, Belgium.

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1996.

S0024-9297(96)00248-3 CCC: $12.00

Table 1. Polymers Used for Blending

	comments	M_n	M_w/M_n	η^*, Pa·S at 180 °C, 100 s^{-1}	η^*, Pa·S at 180 °C, 0 s^{-1}
		Homopolymers			
PS43	anionic	42 600	1.03	350	400
PS53	Japan Ink	53 000[a]	2.3	350	660
	Chem Ind.				
PS95	anionic	95 000	1.07	3000[b]	6900[b]
PMMA11	anionic	11 000	1.09	1000[b]	6800[b]
PMMA14	Sumitomo	14 000[a]	2.1	330	660
PMMA22[c]	anionic	22 000	1.03	2000[b]	80000[b]
PMMA26	Sumitomo	26 000[a]	2.0	660	4600
PMMA36	anionic	36 000	1.09	2500[b]	300000[b]
PMMA43[c]	anionic	43 400	1.03	3700	600000
		Block Copolymers			
SM55	58 wt % styrene	55 000	1.05		
SM85	55 wt % styrene	85 000	1.05		
SM160	50 wt % styrene	160 000	1.08		
SM780	40 wt % styrene	780 000	1.24		

[a] M_w value. [b] Estimated by scaling from the other samples and the literature. [c] Terminated with glycidal methacrylate.[18]

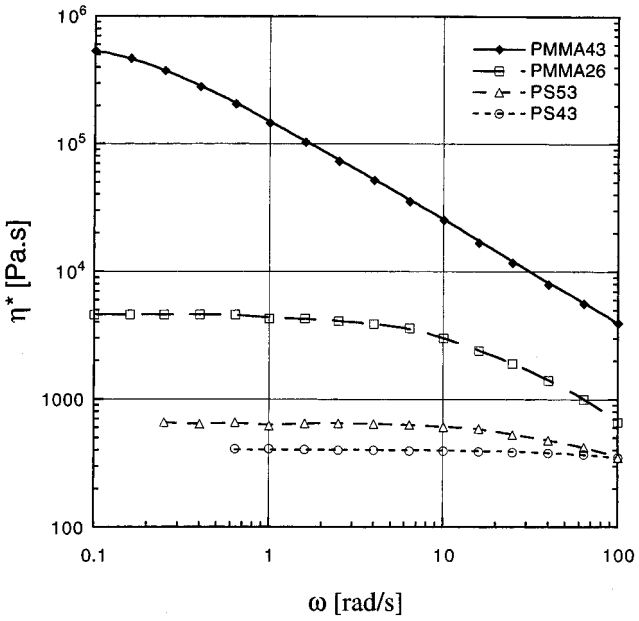

Figure 1. Complex dynamic viscosity (η^*) as a function of frequency for PMMA43, PMMA26, PS53, and PS43 at 180 °C.

agreed well with M_n values calculated from the polymerization recipe: monomer over initiator concentration. M_w/M_n values are by SEC.

The anionic polymers were freeze-dried from benzene. The PS particles have a roughly rectangular shape, about 20 × 80 μm. The shape of the PMMA particles is more spherical and about 300 μm in diameter. The commercial polymers were also powders about 250 μm diameter. Some powders were compressed into 10 mm diameter cylindrical tablets with a press at 600 kg_f/cm^2 for 3 min under vacuum at room temperature. Pellets were made from 0.4 g of these resulting tablets by shearing for 1.5 min and then extruding from a simple cup and rotor mixer (Mini-MAX Molder, CS-183MM, Custom Scientific Instruments, Cedar Knolls, NJ).[19,20] The temperatures used were 155 °C for the PS and 180 °C for the PMMA. The clear strand was chopped into pellets about 2 × 2 mm.

The complex dynamic viscosities (η^*) of several of the polymers were measured with a Rheometrics dynamic mechanical spectrometer using two 25 mm parallel plates and 5% strain amplitude. Figure 1 shows η^* versus frequency. Due to their higher T_g (~125 °C) the viscosities of the anionic PMMA samples are higher than that of similar molecular weight PS or free radical PMMA. Viscosities at 0 and 100 s^{-1} and 180 °C are given in Table 1. Several were not measured but estimated by interpolation between the other samples or from literature values on similar polymers.

Mixing Procedure. All blends contained 30 wt % PMMA and 70 wt % PS and were mixed at 180 °C. When block copolymer was added, this homopolymer ratio was maintained. The components of all the blends studied are given in Table 2. The sample code 43-22-55/5 means 67% PS43, 28% PMMA22, and 5% SM55. About 0.3 g of powder or pellets were dry blended on paper and put into the preheated mixer cup using a Teflon scoop. Then the rotor was inserted and rotated without lifting during the mixing except when sampling. The maximum shear rate reported in Table 2 was calculated from rotor speed, cup radius (6.5 mm), and sample thickness (~2 mm). At various mixing times the rotor was lifted and about 20 mg of mixed melt removed from near the cup edge and quenched in liquid nitrogen to freeze the two-phase structure. All samples were mixed for 20−25 min.

Sundararaj et al.[20] have shown that for uncompatibilized blends this kind of mixer typically generates a coarser melt dispersion than larger, Brabender-type laboratory batch mixers or twin-screw extruders. In their study with PS and polypropylene of equal viscosities, the size of the small particles in the cup mixer was the same as with the other mixers, ~1 μm, at the same maximum shear rate. However, in the cup mixer there were also many large, elongated particles, 5−10 μm. With compatibilized blends these large particles were not present. Periodically lifting the rotor reduced these large particles if the sample adhered to the rotor. We also found generally more consistent results when we fed the cup mixer powder (~300 μm) rather than pellets (2−4 mm).

In another effort to reduce inhomogeneities in the cup mixer, Marechal and Inoue[21] placed three 3 mm diameter stainless steel ball bearings into the cup. In the small clearances in this geometry the maximum shear rate is ~50 s^{-1} for their rotor speed. Furthermore, the rolling balls generate a periodic deformation which should be advantageous for drop breakup.[20] We did some blending with three balls in the cup.

We tried three methods for adding the block copolymer: premixing it into the PS, then adding the PMMA (sample 43-43-85/5(a)), freeze-drying it with the PMMA (all the 95-samples) and simply putting all three components into the mixer together (all the other samples in Table 2).

Light Scattering. A small piece (~1 mg) of the quenched specimen was placed between two cover glasses (40 mm, 0.3 mm thick) and melt-pressed to a thin film (10−15 μm thick) at 180 °C. For some of these melt-pressed films, square-shaped cover glasses were used, and each corner was taped by polyamide tape to keep the thickness constant during annealing. The sample was placed on a hot stage set on a light scattering apparatus. Immediately after melt-pressing, the remelted specimen was subjected to time-resolved light scattering measurements for 15 min at 180 °C. These were made at 2 s intervals with a light scattering photometer (HASC Co. Ltd., Kyoto), which is equipped with a 46 photodiode array (Hamamatsu Photonics Co. Ltd., Tokyo). The wavelength, λ, of the He−Ne laser (Melles Griot, 05-LHP-151, 5.0 mW) is 632.8 nm. The beam is vertically applied to the film specimen, and the scattering profile is observed under parallel polarization optical alignment. More details of the apparatus and data analysis have been given by Okamoto and Inoue.[22]

TEM Observation. Some of the quenched specimens were microtomed at ~1 mm/s with a diamond knife at room temperature giving ~50 nm thick sections. Sections were floated on distilled water and collected on 400 mesh uncoated copper grids. The sections were stained for 2 h with the vapor of 0.5% RuO_4 in water solution for TEM (transmission electron microscopy) observation. PS is preferentially stained and appears dark in bright field TEM. Micrographs were taken with a JEOL 100CX or JEOL 1210 transmission electron microscope operated at 100 kV.

Particle Size Determination. For all the remelted film specimens, the intensity of scattered light, I, monotonically decreased with increasing scattering angle, θ. Morphology parameters were obtained by a Debye−Bueche plot, i.e., by plotting $[I(q)]^{-1/2}$ vs q^2 where $q = (4\pi n/\lambda)\sin(\theta/2)$; n is the

Table 2. Effect of Homopolymer and Block Copolymer Molecular Weight on Morphology

blend PS−PMMA−SM/%	$\dot{\gamma}_{max}$, s^{-1}	η_r[g]	D_{scatt}, μm	Σ, chains/nm^2	Σ/Σ_0	stability after annealing[e]	comments
43-43-0	20	∼30	1.09	0	0	no	some PS trapped in PMMA
43-22-55/5[a]	20	∼10	1.03	0.28	>1[f]	no	
43-43-85/5[a]	20	∼30	1.01	0.14	>1[f]	yes	micelles in PS
43-43-780/5	20	∼30	>2		1[f]	no	undispersed SM780
53-26-0	50[b]	∼2	∼4	0	0	no	
53-26-55/3	50		0.22	0.036	0.25[f]	no	micelles in PMMA
53-26-85/3	50		0.20	0.02	0.16	yes	
53-14-0	50[b]	∼1	0.41	0	0	no	
53-14-55/3	50		0.22	0.036	0.25[f]	no	micelles in PMMA
53-14-85/1	50		0.21	0.007	0.06	no	
53-14-85/3	50		0.17	0.018	0.18	yes	
95-36-0	80[c]	∼1	∼0.7[d]	0	0	no	similar to 43-43-0
95-36-85/5	80		∼0.3	0.05	0.4[f]	yes	micelles in PMMA
95-11-0	80[c]	∼0.3	∼0.7	0	0	no	elongated particles
95-11-55/5	80		∼0.1	0.027	0.19		no micelles
95-11-85/5	80		0.06	0.011	0.09	no	no micelles
95-11-160/5	80		0.40	0.04	0.4[f]	no	micelles in PMMA

[a] PS43 and SM mixed first for 3 min, then PMMA was added. [b] Three steel balls in the mixer cup. $\dot{\gamma}_{max}$ estimated from ball clearances and rotor speed. [c] For the 95 series samples the block copolymer was freeze dried with the PMMA. This powder was premixed with PS95 and then added to the preheated mixer cup. [d] D_{vs} from TEM for all 95 series samples. [e] All samples were annealed for 10−15 min at 180 °C except the 95-11 series which was at 195 °C for 20 min. Stable means D_{vs} changed less than 50 nm. [f] Micelles observed by TEM. [g] Ratio of dispersed phase to matrix viscosity.

matrix refractive index.[22,23] The plots were observed to be linear. In such a case, one can obtain the correlation length ξ from the slope and the y axis intercept of a plot of $[I(q)]^{-1/2}$ vs q^2.

$$[I(q)]^{-1/2} = (8\pi\langle n^2\rangle\xi^3)^{-1/2}(1 + \xi^2q^2) \quad (1)$$

where $\langle n^2\rangle$ is the mean-square fluctuation of refractive index. Once the value of ξ is obtained, other morphology parameters, such as the specific interfacial area S_{sp} and the mean diameter of the dispersed particles D_{scatt} (assuming they are spherical), are obtained by

$$S_{sp} = 4\phi_p(1 - \phi_p)/\xi \quad (2)$$

$$D_{scatt} = 6\phi_p/S_{sp} \quad (3)$$

where ϕ_p is the volume fraction of the dispersed phase. D_{scatt} is a particle volume over surface area average diameter, D_{vs}. From the TEM micrographs, D_{vs} was determined by

$$D_{vs} = \sum^N D_i^3/\sum^N D_i^2 \quad (4)$$

where D_i are the diameters for equivalent spheres and N = 100−300. The micrographs are two-dimensional cuts through the blend and thus underestimate D_i, but also some small particles are missed.[23] These corrections were made to D_i but they are typically ≤10% since the two effects tend to cancel out.[24,25] We obtained good agreement between D_{scatt} and the uncorrected D_{vs} calculated from TEM micrographs, as shown in Figure 2.

To test the stability of each mixed melt, the change in D_{scatt} or D_{vs} was analyzed after static annealing for about 15 min at 180 or 195 °C. In some cases particles coalesce, leading to gross two-phase structures, as described later.

Results

The average diameters D_{scatt} of a blend with and without block copolymer are plotted as a function of mixing residence time in Figure 3. Less than 10 min of mixing even at such a low shear rate is sufficient to reach the final particle size. Macosko and co-workers[26,27] have shown that most of the size reduction occurs very rapidly during the softening of the pellets or powder. The particle size with the block copolymer present is slightly smaller than in the noncompatibilized case, 1.0 vs 1.1 μm (see also Table 2). This result is in good agreement with the TEM observations shown in Figure 4a,b.

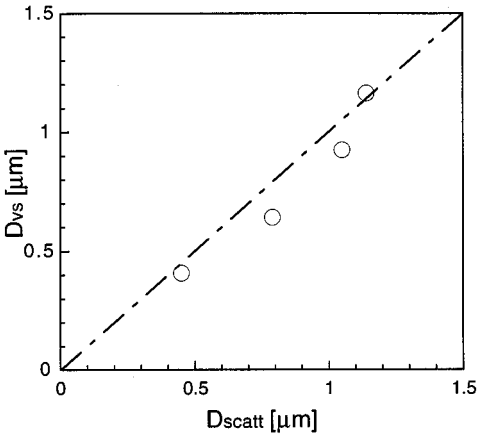

Figure 2. Comparison of particle diameters by light scattering and TEM (D_{vs}).

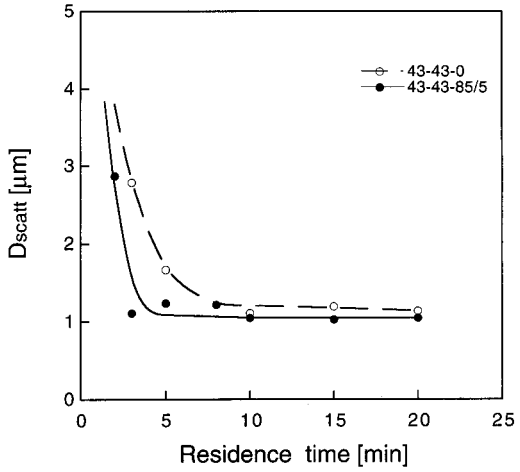

Figure 3. Particle size versus mixing time at 180 °C. Sample 43-43-0 is uncompatibilized, while in sample 43-43-85/5, 5% SM85 block copolymer was added to PS43 and then 27% PMMA43 was added.

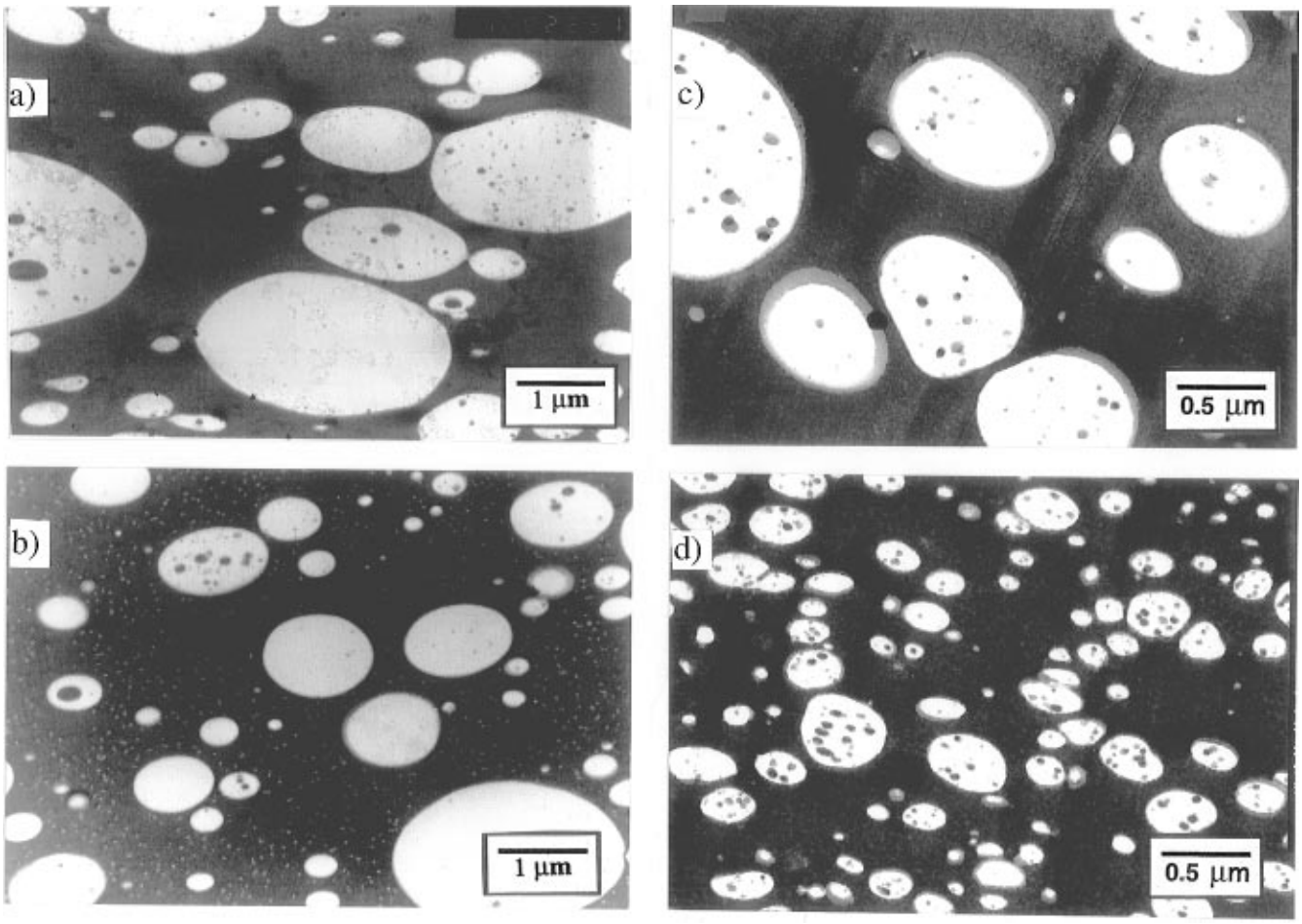

Figure 4. TEM of blends made without and with SM85: (a) 43-43-0; (b) 43-43-85/5; (c) 95-36-0; (d) 95-36-85/5. The PS major phase is stained with RuO_4. In (b) the white spots in the PS are micelles. Magnifications are same for pairs [(a) and (b)] and [(c) and (d)].

Figure 4b shows many white spots in the PS matrix. Higher magnification reveals these to be of ~10 nm diameter, a reasonable size for spherical micelles of P(S-*b*-MMA). In preparing this sample, SM85 was melt mixed into the PS first and then the PMMA was added. When all three components were added simultaneously, a somewhat smaller size resulted (0.77 vs 1.01 μm)[25] but much of the block copolymer was still wasted in micelles.

To increase the proportion of block copolymer in the interface, we increased the mixer shear rate and lowered η_r, the ratio of viscosity of PMMA to PS. Parts c and d of Figure 4 show this result. The uncompatibilized PMMA particles are somewhat smaller (~0.7 μm), but adding 5% SM85 dramatically reduces this size. Here the diblock was freeze-dried with the PMMA before mixing with the PS. In Figure 4d the PMMA particles contain many trapped PS droplets as well as copolymer micelles.

Reducing the PMMA molecular weight from 36K to 26K to 14K to 11K still using SM85 block copolymer produces a dramatic reduction in D_{vs} (see Table 2 and Figure 5). Figure 6c shows the 11K PMMA sample. Particle size has been reduced to a remarkably small 60 nm. Mobility of the block copolymer is expected to increase significantly as the homopolymer molecular weight decreases due to faster diffusion and higher critical micelle concentration.

The effect of block copolymer molecular weight is also illustrated in Figure 6. Both SM55 and SM85 give small particles without significant micelle formation. However, doubling the molecular weight of SM160

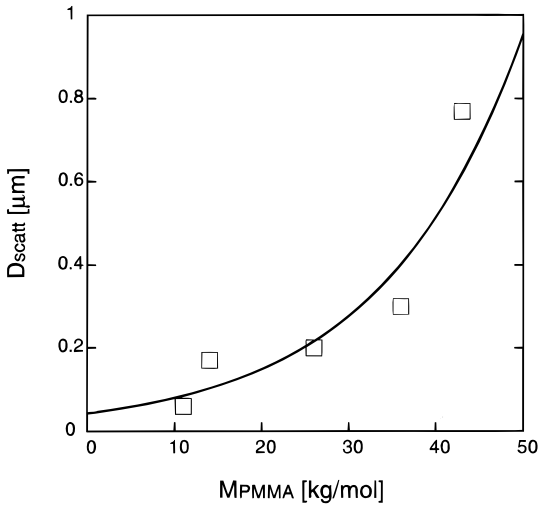

Figure 5. PMMA particle size vs PMMA molecular weight compatibilized with 3 or 5% SM85.

produces much larger particles and many micelles and trapped PS particles inside the PMMA. There must be a significant reduction in block copolymer mobility in going from 85 to 160K molecular weight. We also tried a very high M_n diblock (43-43-780/5 in Table 2). It could not even be dispersed to micelles but rather remained in micron size domains.[25]

We examined stability by annealing each of these blends. The results after 20 min at 195 °C are shown in Figure 7. We see that none of these blends are stable. The uncompatibilized blend shows the most coalescence;

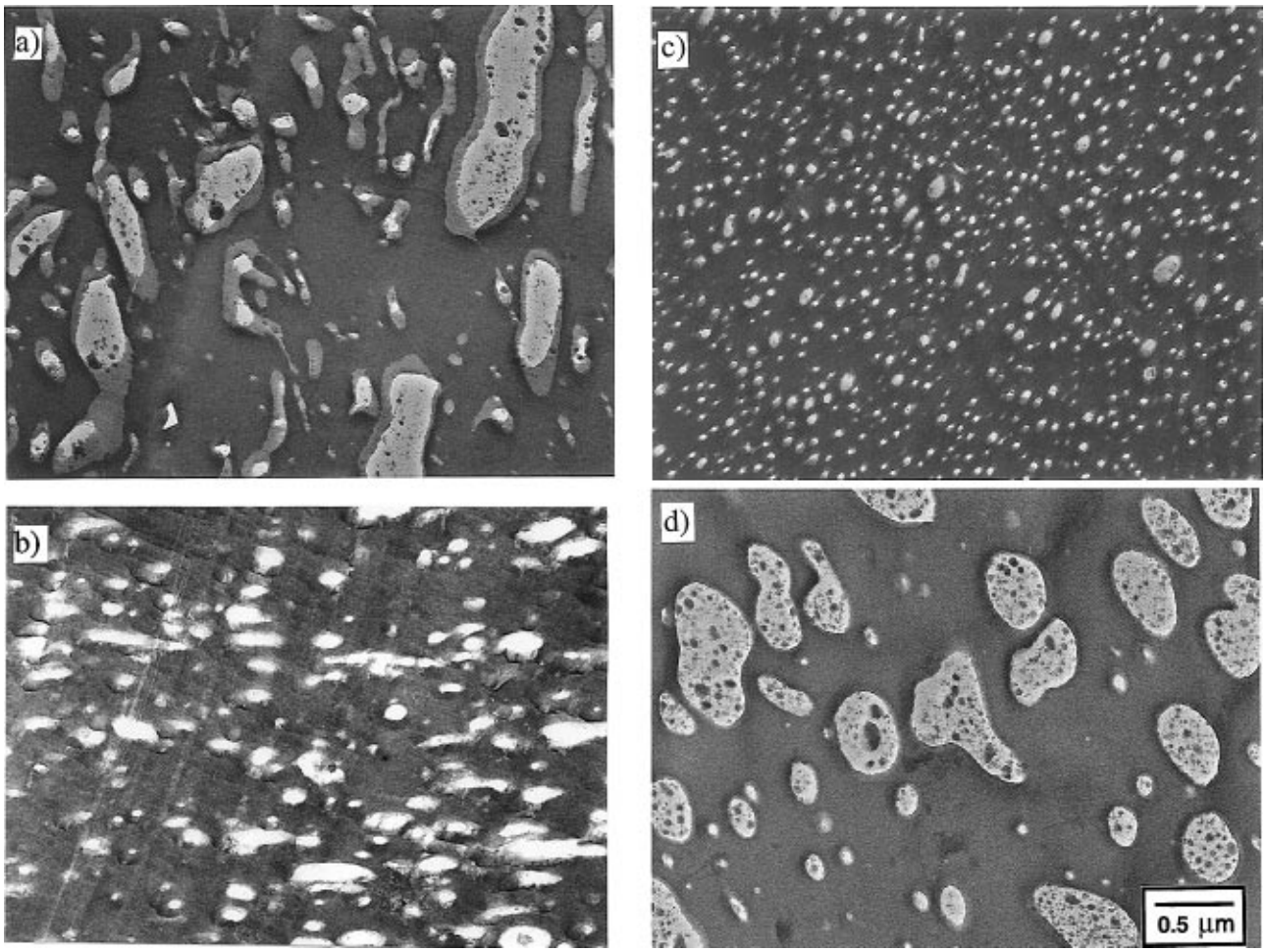

Figure 6. Effect of molecular weight of block copolymers on morphology for the 95-11 series: (a) no block copolymer; (b) 5% SM55; (c) 5% SM85; (d) 5% SM160.

the blend compatibilized with SM160 shows the least coalescence after 20 min of annealing. The annealed SM85 blend shows extended shapes indicating low interfacial tension. The higher molecular weight PMMA sample 95-36-85/5 was stable to static annealing; its diameter changed less than 50 nm, at 180 °C in 12 min.[28]

We also monitored stability continuously by annealing in the light scattering apparatus. Some results are shown in Figure 8. We see that the uncompatibilized sample 43-43-0 is quite unstable. With 5% of SM85 it becomes completely stable although the initial particle size is not significantly different. Although Figure 4b shows that much of the SM85 is in micelles, enough resides in the interface to prevent coalescence. Remarkably, reducing the block copolymer molecular weight to 55 000 results in an unstable blend. This is true for all the blends with SM55 (see Table 2). This low molecular weight copolymer goes to the interface and can be effective in reducing particle size but cannot prevent static coalescence. The molecular weight of the PS block in SM55 (32 000) may be insufficient to keep it in the interface. The entanglement molecular weight for PS is about 13 000.[29]

The lower half of Figure 8 shows diameter changes for the 53-14 series. The coalescence rate for these much smaller particles is slower even without compatibilizer. Adding 1% block copolymer decreases the initial particle size, but they are still unstable. With 3% SM85, particle size is further reduced and these small particles are quite stable.

Discussion

To better understand the role of block copolymers in compatibilizing these immiscible blends, it is helpful to calculate how much might be in the interface. If we assume that *all* the copolymer is in the interface, then the number of block copolymer chains/nm^2 is

$$\Sigma = \frac{\text{chains/vol}}{\text{interface area/vol}} = \frac{N_A \rho \phi}{M S_{sp}} \tag{5}$$

where ρ, ϕ, and M are the density, volume fraction, and molecular weight of the copolymer, respectively, and N_A is Avogadro's number. S_{sp} is the interfacial area per unit volume which can be calculated from D_{vs} by eq 3. Values of Σ are given in Table 2. These are all upper bounds since some of the copolymer is in micelles.

The *maximum* surface concentration of block copolymer, Σ_0, can be estimated by assuming a dense monolayer in the interface. If we consider symmetric diblock copolymers and ignore curvature of the particles ($D_{vs} \gg \langle r_0^2 \rangle$) then the thickness of the monolayer should be just half of the lamellar spacing, $\Lambda/2$, in the ordered bulk copolymer.

$$\Sigma_0 = \frac{\text{thickness of copolymer monolayer}}{\textit{volume} \text{ of one chain}} = \frac{\Lambda/2}{M/\rho N_A} \tag{6}$$

From small angle neutron scattering Russell et al.[30] found Λ = 39.8 nm for a deuterated PS−diblock

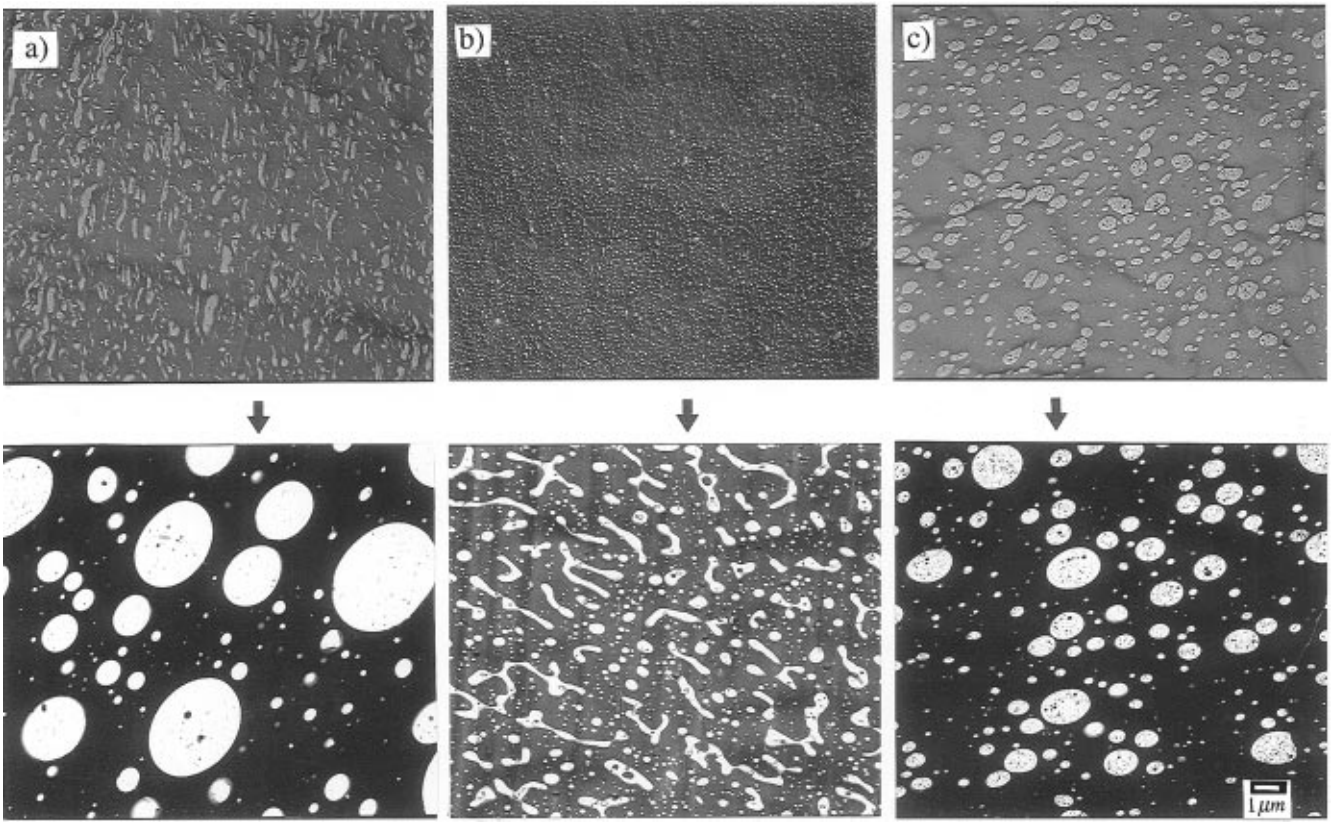

Figure 7. Effect of annealing on morphology for the 95-11 series: (a) no block copolymer; (b) 5% SM85; (c) 5% SM160. The top micrograph in each case shows the blend after 20 min of mixing at 180 °C, while the bottom micrograph shows the effect of annealing for 20 min at 195 °C. All these blends are unstable.

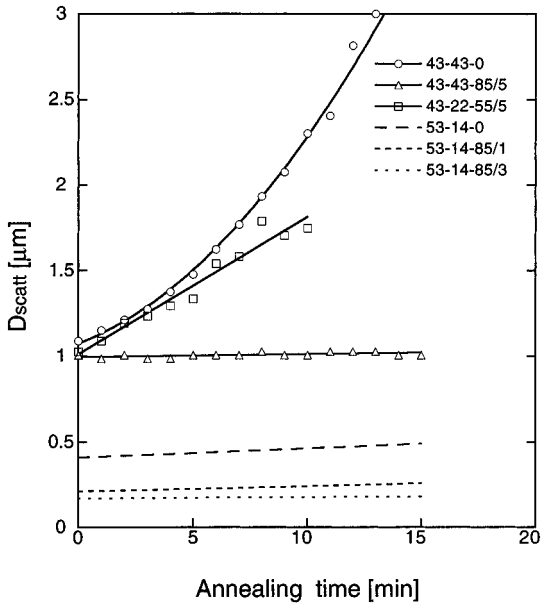

Figure 8. Light scattering diameter vs annealing time at 180 °C for the 43 series with no copolymer, 5% SM55 and 5% SM85 and for the 53-14 series with 0, 1, and 3% SM85.

copolymer dPS−PMMA, with $M_n = 100\,900$. Using $\rho = 1.0$ g/cm^3 gives $\Sigma_0 = 0.119$ chains/nm^2 for this diblock. For other molecular weight diblocks we can estimate Σ_0 by using the scaling of $\Lambda \sim M_n^{2/3}$ in the strong segregation limit.[31] For the diblocks in Table 2 then $\Sigma_0 = 0.145$ (SM55), 0.126 (SM85), and 0.102 (SM 160) chains/nm^2. These values are in reasonable agreement with 0.12 chains/nm^2, the equilibrium concentration of a PS−poly(vinylpyridine) diblock, $M_n = 47\,000$, measured by Dai et al.[32] at a PS/PVP interface.

The Σ_0 values calculated above were used to estimate the fractional coverage of the interface needed to stabilize the blends. The values of Σ/Σ_0 are tabulated in Table 2. Note blends 53-26-85/3 and 53-14-85/3. If it is assumed that *all* the block copolymer is in their interfaces, they are stable against static annealing with a fractional coverage of 0.16 and 0.18, respectively.

Coverage of only 15−20% to prevent static coalescence is not unreasonable. We envision that the block copolymer acts in the interface like steric stabilizers do for colloidal particles.[33,34] Neighboring spheres of radius R are attracted by van der Waals forces:

$$F_{vdW} = \frac{AR}{12H^2} \tag{7}$$

where A is Hamaker's constant ($\sim 5kT$ for PMMA in PS[34]) and H is their separation. At equilibrium the van der Waals attraction is just balanced by compression of the block copolymer chains on the surface of the particle, as illustrated in Figure 9. This confinement of the chains reduces the number of their possible conformations, generating an elastic repulsion between the spheres. From the theory for rubber elasticity[35]

$$F_{RE} = N\frac{3kTr_d}{\langle r_0^2 \rangle} \tag{8}$$

where $\langle r_0^2 \rangle$ is the average of the squares of the relaxed chain end-to-end distance, r_d is the end-to-end distance of the deformed chain, and N is the number of deformed chains. As Figure 9 indicates, not all the chains will be deformed equally. r_d ranges from $\langle r_0^2 \rangle^{1/2}$ at the edge of the contact area to approximately $H/2$ at the point of

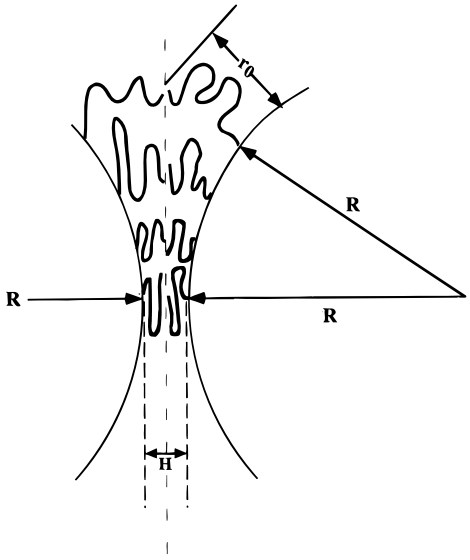

Figure 9. Schematic of two particles of radius R separated by a small distance, H. The entropic repulsion of polymer chains on the surface just balances van der Waals attractions.

closest approach. Let us assume an average value of $r_d = \langle r_0^2\rangle^{1/2}/2$ and $H/2 \sim \langle r_0^2\rangle^{1/2}/4$. The contact area πB^2 can then be estimated from

$$B^2 = (R + \langle r_0^2\rangle^{1/2})^2 - (R + \langle r_0^2\rangle^{1/2}/4)^2$$

$$B^2 \sim 3R\langle r_0^2\rangle^{1/2}/2 \quad \text{for} \quad R \gg \langle r_0^2\rangle^{1/2} \tag{9}$$

The number of deformed chains is the contact area times the concentration of chains in the interface

$$N = \pi B^2 \Sigma \tag{10}$$

Equating eqs 7 and 8 and substituting the above approximations allows us to estimate the critical interfacial concentration to prevent coalescence

$$\Sigma_c = \frac{20}{27\pi\langle r_0^2\rangle} \tag{11}$$

Using $\langle r_0^2\rangle = (4.34 \times 10^{-3}\ (nm^2\ mol)/g)\ M$ for molten PS[28] gives $\Sigma_c = 1.2 \times 10^{-3}$ chain/nm^2 or $\Sigma_c/\Sigma_0 \sim 1\%$ for SM85. We would expect the actual value of Σ_c to be higher since block copolymers can move along the interface out of the contact area. Presumably, at $\Sigma/\Sigma_0 \sim 20\%$ there is enough crowding of the coils to prevent SM85 from sliding along the interface. However, the lowest molecular weight block copolymer, SM55, was not able to stop static coalescence even at $\Sigma/\Sigma_0 > 20\%$. It may be that these short chains can be pulled out of the interface since they are not sufficiently entangled.

Note that for blends 95-11-85/5 (Figures 6b and 7b and Table 2) and 53-14-85/1 (Figure 8 and Table 2) that a coverage of <10% is able to reduce particle size significantly over the uncompatibilized case, but these blends are not *statically* stable. It is reasonable that a much lower coverage, probably close to the 1% calculated above, is sufficient to prevent *dynamic* coalescence and thus reduce particle size.

Under dynamic conditions particle contact times are short and there is little time for chains to slide along the interface. Figure 10 describes the mechanism of morphology development during polymer−polymer melt blending.[26,27,36−38] Pellets or powder of the minor component (PMMA in our case) is sheared by the major phase (PS). Stress from the surrounding melt pulls layers from the pellet surface, which rapidly stretch out in the flow. These sheets thin to ~1 μm and then break up by tearing or developing holes.[36] The regions between the holes stretch into fibers, which eventually break up into submicron droplets. Without compatibilizer in the interface (upper right of Figure 10) coalescence is rapid and the final size is determined by an equilibrium between coalescence and break up.[37]

The lower right of Figure 10 illustrates the effect of a compatibilizer. If enough block copolymer can diffuse to the freshly generated interface, it should reduce interfacial tension, permitting sheets to be drawn down thinner and prevent drop coalescence.

How much is *enough* block copolymer? If the time for block copolymer to diffuse to the interface is less than the time required for a new interface to form, then the surface should be rich in copolymer. This time ratio is a type of Peclet number[39]

$$Pe = \frac{t_D}{t_{def}} \sim \frac{l^2/D}{1/\dot\gamma} < 1 \tag{12}$$

We can crudely estimate the time to generate interfacial area from the reciprocal of maximum mixer shear rate, $\dot\gamma \sim 100\ s^{-1}$. D is the diffusion coefficient for the block copolymer through the homopolymer matrix, while l is the distance it must travel. We can estimate l by assuming that it is the depth into the bulk needed to get enough copolymer to fill 1 nm^2 of newly generated interface. If we assume that the bulk concentration of copolymer is $\phi N_A \rho/M$ and the amount needed in the interface is Σ_c, then $l = \Sigma_c M/(\phi N_A \rho)$ and

$$D > \dot\gamma\left[\frac{\Sigma_c M}{\phi N_A \rho}\right]^2 \tag{13}$$

For $\phi = 0.05$, $M = 55\,000$, and $\Sigma_c = 0.001$ chain/nm^2, $D > 4 \times 10^{-12}$ cm^2/s. From Antonietti et al.[40] for PS of this molecular weight diffusing through PS at 180 °C, $D = 6 \times 10^{-12}$ cm^2/s. For 55K PMMA diffusing through 11K PMMA at 180 °C D will be even higher. However, from Green's measurements[41] we might expect this value to decrease by 100 or more when P(S-*b*-MMA) diffusing through PS is considered. Furthermore, as M increases, ϕ may be limited by the critical micelle concentration. Pepin has extended Whitmore and Noolandi[42] to calculate $\phi_{CMC} \sim 0.003$ for SM55 in 11 000 PMMA using $\chi = 0.05$. Factors which may aid block copolymer mobility are circulation in the drops and the rheology of block copolymer.

Conclusion

PMMA has been melt blended into 70% PS without and with symmetric P(S-*b*-MMA). The molecular weight of the homopolymers and molecular weight and concentration of the diblocks were varied. The PMMA particles were always nearly spherical. These spheres are stable to melt annealing if 15−20% of their interfaces are filled with block copolymer. However, much less copolymer is needed to reduce particle size, probably ~1% of a saturated monolayer.

Particle size appears to be controlled by diffusion of block copolymer to the interface as it is created during mixing. A very simple analysis suggests that to maintain $\Sigma/\Sigma_0 = 0.01$ in the freshly formed interface, $D > 4 \times 10^{-12}$ cm^2/s for the block copolymer. Diffusion coefficients for the block copolymers used in this study are probably significantly less than this value. Since the block copolymers are effective in reducing particle size,

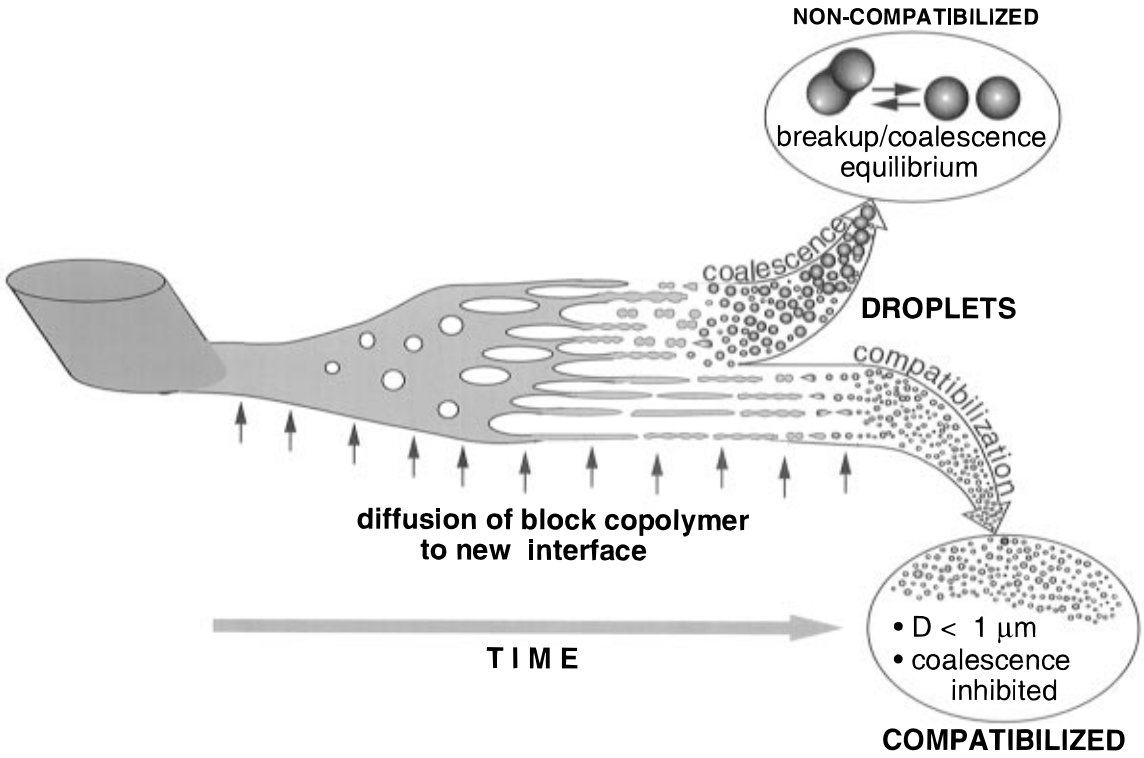

Figure 10. Schematic of morphology development during melt blending. As pellets or powder of the minor phase soften, layers peel off. These stretch out into sheets which break up into fibers and then droplets. Unless block copolymer can rapidly cover the new interface these droplets will coalesce to larger particles. (Adapted from ref 26.)

their mobility must be aided by the flow field. However, more measurements of D values for block copolymers in homopolymers are needed as well as more sophisticated analysis.

A strong effect of block copolymer molecular weight was observed. There appears to be an optimum value. Low molecular weight diblocks are able to get quickly to the interface, reduce interfacial tension, and prevent dynamic coalescence. However, they cannot provide static stability. They are not entangled enough in the homopolymer to prevent them from being pushed out of the interface by an approaching particle at long times. High molecular weight diblocks are not effective because their critical micelle concentration is very low. So even if diffusion is aided by the mixing flow field, these long diblocks get stuck in micelles. Further theoretical work is needed in this area, particularly direct comparison of the free energy of diblock copolymer in micelles vs in the interface between the two homopolymers.

Several of these conclusions are supported by our work on reactive coupling of PS and PMMA.[18,43]

Acknowledgment. This work was supported by research grants from the National Science Foundation's US−Japan Programs (C.W.M.), the Ministère de la Researche et de la Technologie, France (P.G.), and the Japanese Society for the Advancement of Science (P.M.). Additional support was received from NSF's Chemical Reaction Processes and Polymer Materials Programs and the General Electric Corp. The authors wish to thank Mark Schulz, University of Minnesota, who synthesized the SM85, Tsuneo Chiba of T.I.T. and Adeyinka Adedeji, University of Minnesota, who did some of the electron microscopy, Angela Lueking at the University of Minnesota who performed some of the mixing and particle size analysis, and H. Ted Davis of the University of Minnesota for helpful discussions on the surface coverage.

References and Notes

(1) Paul, D. R.; Barlow, J. W.; Keskkula, H. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley: New York, 1988; Vol. 12, p 399.
(2) Utracki, L. A. *Polymer Alloys and Blends*; Hanser: New York, 1989.
(3) Utracki, L. A. *Polyblends '93 Preprints*, Montreal, October 1993; pp 1−2 to 1−29. *Encyclopedic Dictionary of Commercial Polymer Blends*, Utracki, L. A., Ed.; ChemTec: Toronto, 1994.
(4) Wu, S. *Polym. Eng. Sci.* **1987**, *27*, 335.
(5) Sundararaj, U.; Macosko, C. W. *Macromolecules* **1995**, *28*, 2647.
(6) Teyssié, P.; Fayt, R.; Jerome, R. *Makromol. Chem.* **1986**, *187*, 837.
(7) Noolandi, J.; Hong, M. K. *Macromolecules* **1982**, *15*, 482.
(8) Leibler, L. *Macromolecules* **1982**, *15*, 1283.
(9) Riess, G.; Kohler, J.; Tournut, C.; Bandert, A. *Makromol. Chem.* **1970**, *101*, 58.
(10) Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. *Macromolecules* **1970**, *3*, 87.
(11) Patterson, H. T.; Hu, K. H.; Grindstaff, T. H. *J. Polym. Sci.* **1971**, *C34*, 31.
(12) Xie, H.; Liu, Y.; Jiang, M.; Yu, T. *Polymer* **1986**, *27*, 1928.
(13) Brown, H. R. *Macromolecules* **1989**, *22*, 2859.
(14) Gleinser, W.; Braun, H.; Friedrich, C.; Cantow, H. J. *Polymer* **1994**, *35*, 128.
(15) Ghijsels, A.; Raadsen, J. *Pure Appl. Chem.* **1980**, *52*, 1359.
(16) Hobbs, S. Y.; Dekkers, M. E. J.; Watkins, V. H. *Polymer* **1988**, *29*, 1598.
(17) Brosetta, D.; Frederickson, G. H. *J. Chem. Phys.* **1990**, *93*, 2927.
(18) Guégan, P.; Macosko, C. W.; Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1994**, *27*, 4993. Nakayama, A.; Inoue, T.; Guégan, P.; Macosko, C. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (2), 840.
(19) Maxwell, B. *SPE J.* **1972**, *28* (2), 24.
(20) Sundararaj, U.; Macosko, C. W.; Nakayama, A.; Inoue, T. *Polym. Eng. Sci.* **1995**, *35*, 100.
(21) Marechal, P.; Inoue, T. Polymer Processing Society European Meeting, Strasbourg, Aug 1994. *Polym. Eng. Sci.*, in press.
(22) Okamoto, M.; Inoue, T. *Polym. Eng. Sci.* **1993**, *33*, 175.
(23) DeHoff, R. T.; Rhines, F. N. *Quantitative Microscopy*; McGraw-Hill: New York, 1968; Chapter 6.
(24) Scott, C. E. Ph.D. Thesis, Department of Chemical Engineering and Materials Science, University of Minnesota, 1990.

(25) Nakayama, A. M.S. Thesis, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 1994 (in English).
(26) Scott, C. E.; Macosko, C. W. *Polym. Bull.* **1991**, *26*, 341; *Polymer* **1995**, *36*, 461.
(27) Sundararaj, U.; Macosko, C. W.; Rolando, R.; Chan, H. T. *Polym. Eng. Sci.* **1992**, *32*, 1814.
(28) Khandpur, A. K. Ph.D. Thesis, Department of Chemical Engineering and Materials Science, University of Minnesota, 1995.
(29) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.
(30) Russell, T. P.; Menelle, A.; Hamilton, W. A.; Smith, G. S.; Satija, S. K.; Majkrzak, C. F. *Macromolecules* **1991**, *24*, 5721.
(31) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(32) Dai, K. H.; Kramer, E. J.; Shull, K. R. *Macromolecules* **1992**, *25*, 220.
(33) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: London, 1983.
(34) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: Cambridge, 1989.
(35) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(36) Sundararaj, U.; Dori, Y.; Macosko, C. W. *Polymer* **1995**, *36*, 1957.
(37) Sundararaj, U.; Macosko, C. W. *Macromolecules* **1995**, *28*, 2647.
(38) Levitt, L.; Macosko, C. W.; Pearson, S. D. *Soc. Plastics Eng., ANTEC* **1996**, 3565; *Polym. Eng. Sci.* **1996**, *36*, 1471.
(39) Treybal, R. E. *Mass Transfer Operations*; McGraw Hill: New York, 1980.
(40) Antonietti, M.; Coutandin, J.; Sillescu, H. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 525.
(41) Green, P. F. *Macromolecules* **1995**, *28*, 2155.
(42) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 657. M. P. Pepin, University of Newfoundland, personal communication.
(43) Guégan, P.; Khandpur, A. K.; Macosko, C. W.; Nakayama, A.; Inoue, T.; Hirao, A. *Macromolecules*, submitted for publication.

MA9602482