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Effect of Added Block Copolymer on the Phase-Separation Kinetics of a Polymer Blend. 2. Optical Microscopic Observations

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ABSTRACT: The Ostwald ripening occurring in the very late stage of the phase-separation process has been investigated by observation under an optical microscope. Samples studied are blends of low molecular weight polystyrene and polybutadiene to which small amounts of styrene–butadiene block copolymer have been added. The presence of the block copolymer depresses the rate of growth of the average particle size of the dispersed phase. The extent of the retardation increases with an increase in the amount of added copolymer and with an increase in the molecular weight of the copolymer. A copolymer of much smaller molecular weight, having its microphase-separation temperature below the temperature of the experiments, exhibits no such retardation effect. The effect arises as a result of the reduction in the interfacial tension due to an accumulation of the block copolymer at the interface. Application of the Lifshitz–Slyozov theory to the particle growth rate data then enables evaluation of the interfacial tension as a function of the concentration of the added copolymer. Comparison of this result against the theory by Leibler suggests that the copolymer molecules adsorbed at the interface are highly swollen with homopolymer molecules and packed rather loosely with each other. The possibility of the formation of thermodynamically stable droplets stabilized by a layer of adsorbed block copolymer, recently proposed from theoretical considerations, does not appear to arise in the systems studied here.

Introduction

The interfacial activity of a block copolymer added to homopolymer blends is displayed most clearly by the reduction in the interfacial tension between two coexisting phases. Such a reduction in the interfacial tension arises as a result of the tendency for block copolymer molecules to accumulate at the boundary between the two immiscible homopolymer phases. This has been demonstrated by experimental determinations of interfacial tensions[1,2] and has also been predicted from theoretical considerations.[3-5] From a practical point of view the most important utility of block copolymers lies in their use as compatibilizing agents for polymer blends.[6] Here the presence of a block copolymer is beneficial in two ways. First, the block copolymer molecules that accumulated at the interface act as bridges binding the two homopolymer phases and thus mechanically enhance the adhesion[7] between the two. Second, they help make the average size of the dispersed phases small. The efficacy of block copolymers toward this objective has amply been demonstrated by the numerous electron micrographs[8-10] published in the literature. The precise mechanism by which this particle size reduction is achieved is, however, not completely understood yet. One or more of the following three factors may contribute to this. (1) During shear mixing of incompatible polymer melts the reduced interfacial tension may help break up the dispersed phases into smaller particles. In the extrusion blending of nylon (or polyester) with rubber, Wu[11] found that the particle diameter of the dispersed phases obtained was directly proportional to the interfacial tension. (2) Subsequent to phase separation or to forced mechanical dispersion, the dispersed particles coalesce and grow in size with time, but this tendency is reduced when the interfacial tension is lower. According to the condensation–evaporation mechanism[12] of the Ostwald ripening process, the growth rate of the dispersed particle volume is directly proportional to the interfacial tension. (3) Some recent theoretical considerations[5,13,14] led to the suggestion that stable droplet phases, protected by the block copolymers accumulated at the interface, might exist as a thermodynamic equilibrium phenomenon. The radius of such stable droplets is determined by the balance between the elastic rigidity and the spontaneous radius of curvature of the interfacial film.

Recently, by means of light scattering, we examined[15] the phase-separation kinetics of low molecular weight polystyrene–polybutadiene blends and found that the rate, in the late stage of the phase separation, was reduced when small amounts of styrene–butadiene diblock copolymer were added. We interpreted the results as evidencing the accumulation of the block copolymer at the phase boundaries, giving rise to a lowering of the interfacial tension and in turn to a reduced rate of particle growth in the Ostwald ripening process. In order to confirm these findings, we reexamine the problem in this work. Instead of using the light scattering technique, however, this time we make direct microscopic observations of growing dispersed particles in closely similar (but not identical) blend systems, with a view, in particular, to learn how the effect depends on the size of the added block copolymer. The results are then compared with predictions from a recent theory by Leibler.[5]

Experimental Section

Materials. The characterization data of the polymer samples used are tabulated in Table I. All polymers were prepared by anionic polymerization. The polybutadiene and copolymer SB2 are the same materials as used in our previous studies.[15-17] According to our small-angle X-ray investigation, copolymers SB2 and SB3 are in ordered (microphase-separated) states at 83.5 °C, at which the present study was performed. Their microphase transition temperatures (MST) are higher than 160 °C and could not be determined. The low molecular weight copolymer SB1 has its MST around 40 °C and is therefore in a disordered state at the temperature of phase-separation experiments performed in this work.

Microscopic Observation. The blend, consisting of polystyrene and polybutadiene in the weight ratio of 20 to 80 and containing in addition a varying amount of one of the copolymers, was dissolved in toluene, and an amount of this solution was

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Table I
Characterization of Polymers Used

polymer	compsn, wt % styrene	M_n	M_w/M_n
polystyrene[a]	100	1900	1.06
polybutadiene[b]	0	2350	1.13
copolymer SB1[c]	50	8000	
copolymer SB2[d]	52.2	25000	1.04
copolymer SB3[e]	51.1	47900	1.04

[a] Purchased from the Pressure Chemical Co. [b] Purchased from the Goodyear Chemical Co. [c] Synthesized in our laboratory. [d] Synthesized by Dr. H. L. Hsieh of the Phillips Petroleum Co. [e] Synthesized by Dr. L. H. Tung of the Dow Chemical Co.

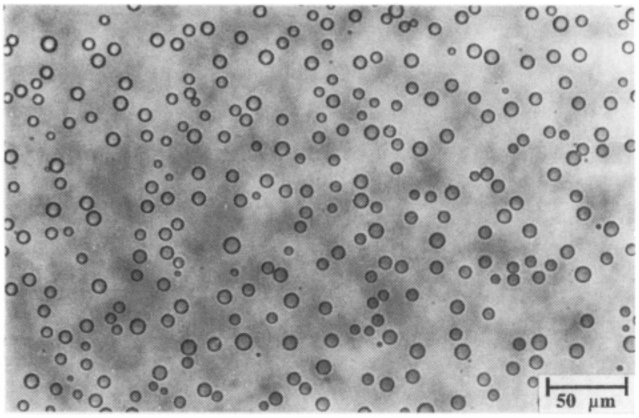

Figure 1. Photomicrograph showing the dispersed particles of a polystyrene-rich phase suspended in the matrix of a polybutadiene-rich phase.

placed on a microscope cover glass to form a film 100–130 μm thick, which was further dried under vacuum for 2 days. The film, sandwiched between two cover glasses, was at first heated to well above its cloud point and kept there for ca. 80 min under a nitrogen gas purge to ensure homogeneity of the mixture. It was then quickly transferred to the hot stage of an optical microscope, maintained at 83.5 ± 0.2 °C under a continuous stream of nitrogen gas. The progress of the phase separation and particle growth was then monitored visually at a 100 × magnification. Periodically a photographic record was taken, from which an average diameter of at least 70 particles was evaluated. Figure 1 gives an example of such photomicrographs.

Results

The cloud points of the binary mixtures of polystyrene and polybutadiene at various compositions were measured by the light scattering method described earlier,[18] and the result is shown in Figure 2. This cloud-point curve defines the thermodynamic properties of this binary blend in the absence of block copolymers. The addition of the small amounts of block copolymers used in this work affects the cloud point barely beyond the experimental error. The blend studied in this work contains 20 wt % polystyrene, which is well off the critical composition, and its cloud point is 92 °C. The phase-separation experiments were performed at 83.5 °C, at which the degree of supercooling is therefore 8.5 °C. From the data in Figure 2 the compositions of the two coexisting phases at the temperature 83.5 °C are estimated to be 17 and 94 wt % polystyrene, respectively, and therefore the minority phase rich in polystyrene occupies about 4% of the total volume on completion of the phase separation. The interaction energy density, Λ, between the two components in the mixture can be defined[19] by means of the expression for the free energy of mixing

$$\Delta G_m/RT = (\phi_1/V_1)\ln\phi_1 + (\phi_2/V_2)\ln\phi_2 + (\Lambda/RT)\phi_1\phi_2 \qquad (1)$$

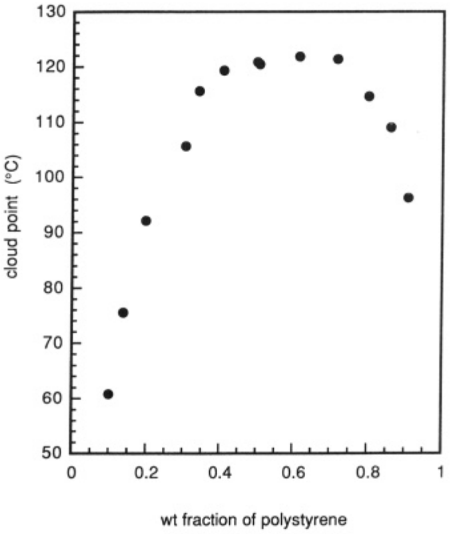

Figure 2. Cloud-point curve of the mixtures of low molecular weight polystyrene and polybutadiene, determined by the light scattering method.[18]

where ΔG_m is per unit volume of the mixture, V_1 and V_2 are the molar volumes of components 1 and 2, and ϕ_1 and ϕ_2 are their volume fractions. The interaction energy density, Λ, is related to the more commonly used Flory–Huggins interaction parameter, χ, by

$$\chi = \Lambda V_{ref}/RT \qquad (2)$$

where V_{ref} is the reference volume, equal to the volume of a lattice site on the basis of which χ is defined. The advantages of using Λ over χ have previously[19,20] been pointed out. From the compositions of the coexisting phases we evaluate by means of eq 1 that the value of Λ at 83.5 °C is equal to 0.87 cal/cm^3, which is in good agreement with the following expression that summarizes[20] the values of Λ previously determined from cloud-point curves of a number of mixtures containing polystyrene, polybutadiene, and styrene–butadiene copolymer:

$$\Lambda = 0.718 \pm 0.051 - (0.0021 \pm 0.00045)[t\ (°\mathrm{C}) - 150] \qquad (3)$$

If we take the reference volume V_{ref} to be equal to the segmental volume of polystyrene, i.e., 100 cm^3/mol, then the value of χ at the temperature of our study is equal to about 0.12.

The average radii of the dispersed particles, measured as a function of time, in the mixtures containing various amounts of copolymers SB1, SB2, and SB3 are presented in Figures 3–5, respectively. In almost all cases the logarithm of the radius is linear with the logarithm of time, giving the power law relationship

$$R \propto t^m \qquad (4)$$

where m is equal to about 0.4 Figures 4 and 5 show that in the presence of various amounts of added copolymers SB2 and SB3 the plots remain parallel and simply shift to longer times. Thus the effect of the added copolymers is seen to be not to alter the mechanisms of dispersed particle growth but simply to retard the rate of such growth. This is in agreement with our previous finding[15] obtained by means of light scattering measurement. The results shown in Figure 3, obtained with the low molecular weight copolymer SB1, are exceptional to this and display no apparent effect on the rate of particle growth. As stated in the Experimental Section this copolymer remains in the disordered state at the temperature of this experiment. Lacking a sufficient driving force for segregating styrene from butadiene blocks in its own bulk state, the copolymer evidently experiences a driving force that is not quite sufficient to achieve an appreciable accumulation at the

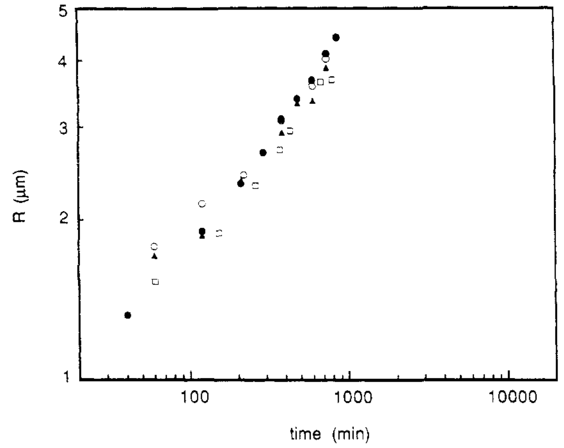

Figure 3. Average radius *R* of the dispersed polystyrene-rich particles determined as a function of time. Filled circle: no block copolymer present. Open circle: 0.2 wt % copolymer SB1 added. Open square: 0.5 wt % SB1 added. Filled triangle: 1.0 wt % SB1 added.

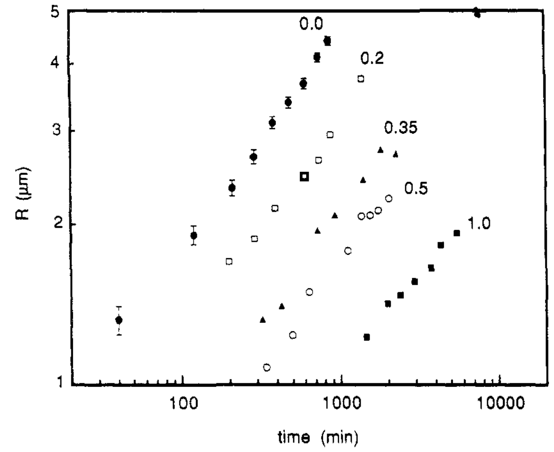

Figure 4. Average radius *R* of the dispersed polystyrene-rich particles determined as a function of time, in the mixtures containing the indicated amounts (wt %) of copolymer SB2.

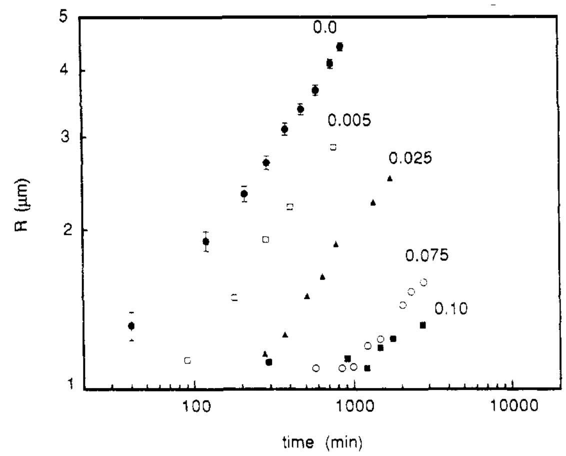

Figure 5. Similar to Figure 4 but with added copolymer SB3.

interface between two homopolymers. In this regard the disordered block copolymer probably behaves essentially as a random copolymer.

In comparing Figure 4 with Figure 5, one can immediately notice the striking difference in the amount of block copolymer needed to produce comparable retardation effects. Such a strong dependence of the effect essentially reflects the strong (exponential) dependence of the chemical potential of the copolymer on its molecular weight. A similar dependence on molecular weight is also manifested in the critical micelle concentration (cmc) of the copolymers. The cmc of SB2 in the polybutadiene used here was previously[17] measured to be about 1.0 wt % at 83.5 °C. The cmc of SB3 was determined in this work by the method described previously.[17] Figure 6 gives the plot of the scattered X-ray intensities measured at a fixed scattering angle ($2\theta = 0.26°$) with samples containing various amounts of the copolymer. The extrapolation to zero intenity gives the cmc to be equal to 0.07 wt %. A doubling of the molecular length is thus seen to produce a reduction in cmc by more than 1 order of magnitude. Similarly, we see that to produce a comparable degree of retardation in the particle growth rate the amount of SB3 required is smaller by at least 1 order of magnitude than that required of SB2.

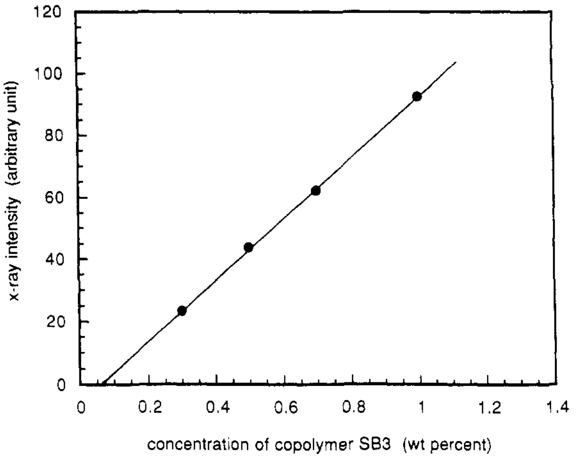

Figure 6. Intensity (in arbitrary units) of X-rays scattered (at a fixed angle 2θ of 0.26°) from samples of polybutadiene containing various amounts of copolymer SB3. The scattered intensity arises mostly from the presence of block copolymer micelles. Extrapolation to zero intensity gives the critical micelle concentration, 0.07 wt %.

Discussion

Among the mechanisms[21] that might account for the Ostwald ripening process occurring in the late stage of phase separation, the coarsening through collision and coalescence of droplets is ruled out here in view of the relatively high viscosity of the matrix and of the fact that clusters of particles that are in the process of coalescence have never been observed under the microscope. In the evaporation-condensation mechanism, examined in detail by Lifshitz and Slyozov,[12] particles with a radius larger than a critical radius R_c grow at the expense of particles with a radius smaller than R_c, the critical radius depending on the degree of supercooling prevailing at the time. The larger particles are fed of the minority component molecules from the smaller particles by a diffusion current of these molecules through the matrix. These workers concluded that the average radius *R* of the dispersed particles grows according to

$$R^3 = (4/9)D\alpha t \qquad (5)$$

where *D* is the diffusion coefficient, and α is a factor characterizing the thermodynamic properties of the system, given by[22]

$$\alpha = \frac{2\gamma}{(\Delta C)^2(\partial\mu/\partial C)_A} \qquad (6)$$

Here γ is the interfacial tension, ΔC is the concentration difference between the two phases, and $(\partial\mu/\partial C)_A$ is the chemical potential gradient with respect to *C*, evaluated at the binodal point A. Equation 5 shows that the exponent

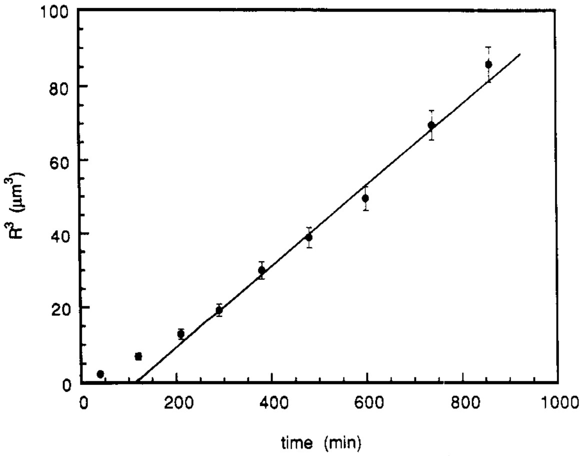

Figure 7. Data of the average radius against time, obtained with the mixture containing no added copolymer and shown in Figures 3–5, replotted here to show that an approximate linear relationship between R^3 and t holds.

m in eq 4 should be equal to $^1/_3$. The results in Figures 3–5 give an exponent a little higher than $^1/_3$. The data for the sample containing no block copolymer are replotted in terms of R^3 against t in Figure 7, which shows that it is possible to pass a straight line through most of the data points, thus forcing a $^1/_3$ exponent. The data obtained with other mixtures that contain block copolymers can also be approximated by a linear relation between R^3 and t to at least a comparable degree of fit. In all these plots the straight line cuts the time axis not at zero but at a finite time. This may reflect, at least in part, the initial delay required for the phase separation, either by nucleation–growth or by spinodal decomposition, to come substantially to completion before the Ostwald ripening becomes important.

The thermodynamic factor α can be estimated to a fair degree of accuracy as follows. The interfacial tension between polystyrene (M_n = 2200) and polybutadiene (M_n = 7800) has been determined[2] to be 0.60 dyn/cm at 145 °C. Assuming a temperature coefficient[23,24] $d\gamma/dT \approx -0.01$ and a $M_n^{-0.5}$ dependence on molecular weight,[24] we obtain γ equal to 0.6 dyn/cm at 83.5 °C. The chemical potential gradient $(\partial\mu/\partial C)_A$ is evaluated from eq 1 with Λ = 0.87 cal/cm³, and this gives $(\Delta C)^2(\partial\mu/\partial C)_A = 1.35 \times 10^7$ erg/cm³ and $\alpha = 0.9 \times 10^{-7}$ cm. From Figure 7 the slope of R^3 vs t is evaluated to be 1.80×10^{-15} cm³/s. Equation 5 therefore gives the diffusion coefficient D of polystyrene in the polybutadiene matrix phase to be about 4.4×10^{-8} cm²/s. Unfortunately there are no experimental data against which this D value can be compared. An order of magnitude estimate of D may be attempted by means of

$$D = kT/6\pi\eta R_G \tag{7}$$

where η is the viscosity of the medium and R_G is the radius of gyration of the diffusing polymer. We take the R_G of our polystyrene[20] to be equal to 1.3 nm. According to the estimation scheme due to Van Krevelen,[25] the viscosity of polybutadiene of critical entanglement length (M_{cr} = 6000) at 83.5 °C is equal to 8.9 P. A linear dependence of the viscosity on molecular weight would then give η = 3.9 P for M_w = 2650. Equation 7 then gives the value of D to be 5.2×10^{-9} cm²/s, which gives an agreement within 1 order of magnitude with the value 4.4×10^{-8} cm²/s obtained from eq 5. The agreement should be considered very satisfactory in view of the many uncertainties involved in estimating D by means of eq 7. It therefore lends strong support to the validity of our interpretation of the experimental result in terms of the Lifshitz–Slyozov theory.

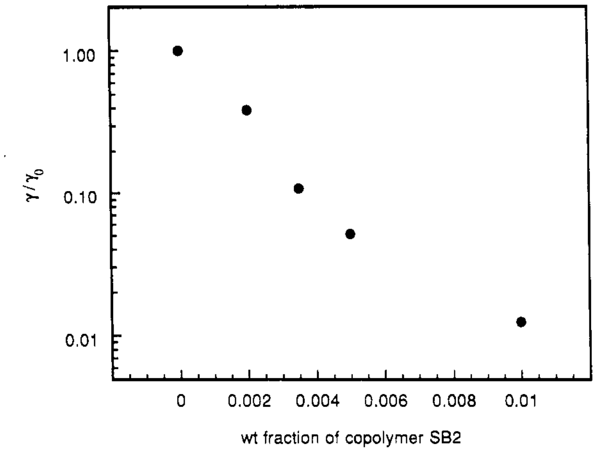

Figure 8. The ratio of γ/γ_0, where γ is the interfacial tension in the mixture containing an amount of copolymer SB2 and γ_0 is the interfacial tension in the mixture with no added copolymer, was evaluated on the basis of the Lifshitz–Slyozov theory, by comparison of the slopes in the plots of R^3 against t.

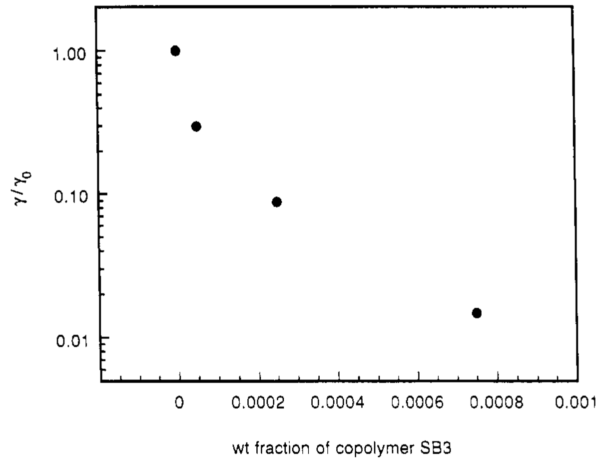

Figure 9. Similar to Figure 8 but with added copolymer SB3.

Encouraged by the above result, we apply eq 5 further to the data obtained in the presence of block copolymer and thereby evaluate the changes in the interfacial tension as a function of the added copolymer amount. By comparing the slopes in the plots of R^3 vs t for mixtures with and without added copolymer, the ratio γ/γ_0 of the interfacial tensions can be determined, and the results are given in Figures 8 and 9. It is seen that the interfacial tension decreases to nearly vanishingly small values as the copolymer concentration approaches the cmc for both copolymers. The plots in these figures might be represented very approximately by

$$\gamma/\gamma_0 \sim \exp(-c\phi) \tag{8}$$

where ϕ is the volume fraction of the copolymer and c is a constant. The only experimental results available in the literature that might be compared against Figures 8 and 9 are those obtained by Anastasiadis et al.[2] These workers utilized the pendent drop method to determine the interfacial tension between a polystyrene of M_n 2200 and a polybutadiene of M_n 7800 in the presence of a styrene–butadiene diblock copolymer of M_n 18 600 (49% styrene) at 145 °C. Their results show a rapid drop in γ initially with addition of increasing amounts of block copolymer but appear to level off to a value of γ/γ_0 equal to about 0.5 when several percent of the block copolymer was added. The cmc of SB2 and SB3 in our system at 83.5 °C are 1.0 and 0.07 wt %, respectively, and Figures 8 and 9 indicate that γ values are reduced to vanishingly small values when the block copolymer concentration has reached the cmc. The cmc of the copolymer utilized by Anastasiadis et al. is not known but may well exceed 10–20 wt % at 145 °C. If this estimate is correct, then the concentration of block copolymer used by them was far short of cmc and thus was not sufficient to reduce γ to the extent suggested in our results in Figures 8 and 9.

At this point we make a comparison of our result with predictions from the theory by Leibler.[5] All the molecular and thermodynamic parameters required to obtain numerical predictions exactly from the theory are available with our experimental system. We make only approximate calculations here, however, partly for the sake of simplicity but also because of the fact that precise quantitative agreements may not be expected. Earlier we found that the cmc and the size of spherical micelles of block copolymers obtained from our small-angle X-ray studies could not be predicted quantitatively but their general trends could still be correctly interpreted by the theory due to Leibler et al.[26] Anticipating a similar difficulty, we here seek to obtain only a qualitative or semiquantitative guideline for the general trends by comparing the theory against our results. Toward this object we find it sufficient to write down equations applicable only to symmetrical systems, which our system approximates reasonably well.

The theory treats two limiting cases, one in which the copolymer chain length N is much longer than the lengths P of the homopolymers (wet brushes limit) and the other in which the copolymer is shorter than the homopolymers (dry brushes limit). The former case applies to our system, in which the block copolymer accumulating at the interface is expected to be swollen by homopolymer molecules that have penetrated into it. According to the theory, the reduction $\Delta\gamma$ in the interfacial tension then depends on the amount of copolymer accumulated at the interface by

$$a^2\Delta\gamma/kT = (3/4)^{1/3}(\Sigma/a^2)^{-5/3}NP^{-2/3} \qquad (9)$$

where a is the segment length, and Σ is the average interfacial area per adsorbed copolymer chain. The interfacial tension γ_0 in the absence of copolymer is related[27] to χ by

$$\gamma_0 = (kT/a^2)(\chi/6)^{1/2} \qquad (10)$$

The surface coverage Σ/a^2 of copolymer is related to the chemical potential μ of the copolymer in the coexisting phases by

$$\Sigma/a^2 = (375/32)^{1/2}\mu^{-3/2}N^{3/2}/P \qquad (11)$$

The chemical potential μ is related to the volume fraction ϕ of copolymer by

$$\mu = \ln\phi + 0.5\chi N \qquad (12)$$

Combining eqs 9–12, we therefore obtain

$$\Delta\gamma/\gamma_0 = 0.29(\ln\phi + 0.5\chi N)^{5/2}\chi^{-1/2}PN^{-3/2} \qquad (13)$$

In the calculations utilizing these equations, we take the segment size equal to 100 g/mol, so that the average chain length P of the polystyrene and polybutadiene is equal to 21 and the chain lengths N for copolymers SB2 and SB3 are 250 and 479, respectively. As anticipated above, we do not get quantitative agreement with experimental results if we calculate $\Delta\gamma/\gamma_0$ by means of eq 13 using the χ value obtained from the cloud-point curve shown in Figure 2. Instead, we have decided to regard χ as an adjustable parameter and evaluate the best values of χ that lead to agreement between experimental and calculated $\Delta\gamma/\gamma_0$ in each case. The results are summarized in Table II. In each set of results involving a single copolymer the values of χ thus evaluated are seen to be fairly constant, although the values are somewhat smaller than 0.12 deduced from the cloud-point curves. The results given in Table II thus suggest that the theory at least reproduces qualitative trends correctly. The values of Σ/a^2 given in the last column of Table II were calculated with the use of these best values of χ and could be considered credible to about the same extent that the theory succeeds in explaining the reduction in the interfacial tension. The Σ/a^2 values at least display the correct trend that one would expect, namely, being larger for the larger copolymer molecule and getting smaller with increasing concentration of the copolymer.

Table II
Parameters Evaluated from Equations 11-13

ϕ	$\Delta\gamma/\gamma_0$[a]	χ[b]	Σ/a^2[c]
	Copolymer SB2 (N = 250)		
0.002	0.611	0.1056	34.9
0.0035	0.904	0.1113	27.1
0.005	0.943	0.1093	26.6
0.010	0.988	0.1044	26.3
	Copolymer SB3 (N = 479)		
0.00005	0.702	0.0850	50.5
0.00025	0.912	0.0828	43.6
0.00075	0.985	0.0793	42.1

[a] From Figures 8 and 9. [b] From eq 13. [c] From eq 11.

Using these Σ/a^2 values one can calculate the amount of copolymer molecules accumulated in the interfaces. With a^3 taken equal to a segment volume (i.e., 100 cm^3/mol of segments), the total amount of SB2 adsorbed is calculated to be ca. 0.0005 and 0.0001 g/cm^3 when the average particle radius is equal to 1 and 5 μm, respectively. These figures suggest that a sufficient amount of block copolymer was always available in the bulk phase as a reserve to maintain a dynamic equilibrium with those molecules adsorbed at the interface. In the case of SB3 the corresponding figures are 0.0006 and 0.0001 g/cm^3 for average particle radii of 1 and 5 μm, respectively. Thus, in this case, especially when the total concentration of added copolymer was very small, a starvation of available copolymer in the bulk phase and hence a competition for it among the growing particles could have taken place. The rate of diffusion of the copolymer molecules could then have influenced the growth kinetics of the particles, and the diffusion coefficient D in eq 5 may have to reflect the diffusion of copolymer as well as the diffusion of polystyrene. Our data in this work are not detailed enough to reveal any such subtleties, and further work will be needed to elucidate these aspects fully.

The extent of swelling of the copolymer chains adsorbed at the interface can be estimated by comparing the Σ/a^2 values in Table II with the boundary area Σ^*/a^2 per molecule in a neat block copolymer. From small-angle X-ray measurements with styrene–isoprene block copolymers having approximately 50/50 compositions, Hashimoto et al.[28] obtained the following dependence of Σ^* on the molecular weight of the copolymer

$$\Sigma^*/\mathrm{nm}^2 = 0.14M_n^{\,1/3} \qquad (14)$$

Assuming its validity for styrene–butadiene block copolymer studied in this work and again taking a^3 equal to 100 cm^3/mol, we calculate Σ^*/a^2 to be 13.55 and 16.83 for SB2 and SB3, respectively. Comparing these with the Σ/a^2 values in Table II leads to the conclusion that the block copolymers at the interface are indeed swollen by the penetrating homopolymer so that the area occupied per molecule is now larger by a factor of 2–3. As the amount of added copolymer is increased toward its cmc, the interfacial tension is reduced rapidly to extremely small values (1 or 2% of the original interfacial tension γ_0), yet this occurs evidently without any abrupt increase in the adsorbed amount and without any appreciable further lateral compression of the copolymer.

In recent theoretical treatments[5,13,14] the possibility has been raised that stable emulsion of the dispersed phase protected by an adsorbed layer of block copolymer could be sustained in polymer blends as an equilibrium phenomenon. According to these considerations, a block copolymer forms a layer at the interface with a finite *spontaneous* curvature that depends on the degree of asymmetry in its two blocks. Droplets of the dispersed phase are stabilized when they reach a radius that is determined by a balance between the spontaneous curvature and the elastic constant of the copolymer layer. These considerations apply only to the situations where the copolymer molecules at the interface are tightly packed with little inclusion of homopolymer molecules in the layer (the dry brushes limit). The values of Σ/a^2 given in Table II show that this is not the case in the present work. Here, the copolymer molecules adsorbed at the interface are swollen with homopolymer chains and are rather loosely packed with each other. In such a case the copolymer layer would display a very small elastic constant and would present no appreciable resistance to changes in the curvature. In the present work, of course, the block copolymers employed were fairly symmetrical in their composition, which makes them, even when tightly packed, incapable of stabilizing the dispersed phase through the spontaneous curvature effect. Indeed, the data presented in Figures 4 and 5 do not give any indication that the growth of the average radii might be slowing down, at least during the period of our observation, which lasted up to about 6000 min (ca. 4 days).

Conclusions

In the very late stage of phase separation, observed in this work under an optical microscope, the rate of coarsening of the dispersed particles is appreciably reduced by the addition of block copolymer. This confirms our earlier result[15] obtained on similar blend systems by means of light scattering measurements. The retardation in the rate of Ostwald ripening arises apparently from the reduction in the interfacial tension between the two phases, which in turn is due to the accumulation of block copolymer at the interface. The effect becomes more pronounced as the concentration of the added copolymer is increased and also as the molecular weight of the block copolymer is increased. Thus, the amount of copolymer SB3 that is required to produce the same extent of retardation is less than a tenth of the amount required of SB2, the latter being about half as large in molecular weight as the former. Copolymer SB1, which is even smaller in molecular weight and has its microphase-separation temperature below the temperature of our experiment, produces no such retardation effect at all. The theory of Ostwald ripening by Lifshift and Slyozov, based on the evaporation–condensation mechanism of particle growth, has been applied to interpret the result. From the particle growth data without added copolymer, the diffusion coefficient of polystyrene molecules through the polybutadiene matrix can be calculated on the basis of the theory and the known value of interfacial tension between polystyrene and polybutadiene, and the value obtained agrees satisfactorily with an independently estimated diffusion coefficient. Encouraged by this agreement in support of our interpretation, we further apply the Lifshitz–Slyozov theory to those data obtained in the presence of added copolymer and thereby evaluate the interfacial tension as a function of the concentration of the added copolymer. The values of $\Delta\gamma/\gamma_0$ thus obtained are compared against the theory developed by Leibler[5] to predict the adsorption of block copolymer and the consequent reduction in interfacial tension, and the result of the comparison suggests that the theory can be utilized as a useful tool to provide a qualitative guideline for the general trends to be expected. The surface density of the adsorbed copolymer calculated from the theory shows that the copolymer molecules are swollen with homopolymer chains and are packed rather loosely with each other. It thus appears that the possibility of formation of thermodynamically stable droplets stabilized by adsorbed copolymer, as envisioned in recent theoretical considerations,[5,13,14] is not borne out at least in the systems studied here.

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References and Notes

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Registry No. Polystyrene, 9003-53-6; polybutadiene, 9003-17-2; butadiene block copolymer, 106107-54-4.