Segregation Dynamics of Block Copolymers to Immiscible Polymer Blend Interfaces

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ABSTRACT: We report the first application of dynamic interfacial tension measurements to characterize segregation rates of diblock copolymers to a polymer−polymer interface. The system investigated is a poly(styrene-*b*-dimethylsiloxane) [P(S-*b*-DMS); $M_n = 13\,000$] symmetric diblock copolymer added to a molten blend of the corresponding immiscible homopolymers. Interfacial tensions are measured by the pendant drop technique with poly(styrene) [PS; $M_n = 4000$] as the pendant drop phase and a mixture of poly(dimethylsiloxane) [PDMS; $M_n = 1600$] with silane-terminated P(S-*b*-DMS) as the surrounding phase. The pendant drop technique is found to suffer from two intrinsic limitations in this application: short time data are inaccessible due to the finite time required for the drop shape to equilibrate, and long time data may not be readily analyzed as a result of the finite drop size. Intermediate time data are compared to the predictions of diffusion-limited segregation models proposed by Budkowski, Losch, and Klein (BLK) and by Semenov that have been modified to treat interfacial tension data. The apparent block copolymer diffusion coefficients obtained from the two analyses fall in the range of 10^{-5}−10^{-6} cm^2/s, in agreement with the estimated self-diffusion coefficient of the PDMS homopolymer matrix.

Introduction

Interface-active block copolymers are of great interest because of their usefulness as additives to promote release at the air−polymer surface as well as their effectiveness as compatibilizers to modify the interphase in immiscible polymer blends. In the former case, diblock copolymers containing a surface-active block, such as poly(dimethylsiloxane), segregate and self-assemble at the surface of the polymer matrix to produce a minimally adhesive surface of low surface energy.[1] The second block is either identical to or compatible with the matrix polymer and serves to anchor the copolymer surface monolayer to the bulk matrix by means of entanglement. When the surface-active block is functionalized at its terminus, the copolymer surfactant functions as a surface delivery vehicle that carries the end-functional group to the surface and can impart selective adhesion properties to the surface that depend on the nature of the end group.[2,3]

In the case of polymer blends, the diblock copolymer preferentially locates at the interface between two immiscible homopolymers in order to minimize repulsive interactions between the two unlike copolymer sequences and the homopolymers.[4] Adsorption of the copolymer at the interface leads to a decrease in interfacial tension[5, 6] and helps to inhibit coalescence of dispersed phases.[7] The bridging action of the copolymer across the interphase can increase significantly the interfacial energy release rate or interfacial fracture toughness of a polymer−polymer interphase.[8,9] Block copolymer addition is therefore an effective means to control the morphology and properties of polymer blends.

Block copolymer segregation equilibrium is known to be affected by several factors, including the molecular weight of matrix homopolymers and block copolymers,[10−15] the formation of brushes by segregated block copolymers,[13,16,17] and the formation of micelles in the bulk.[18,19] An effective design for a polymeric surface or interface therefore requires careful consideration of the matrix polymer and block copolymer characteristics. A wide variety of experimental techniques, including forward recoil spectrometry,[11,14,15,18−24] nuclear reaction analysis,[10,12,13,25,26] neutron reflectometry,[17,24,27−29] and secondary ion mass spectroscopy,[30−32] have been used to study block copolymer modified surfaces and interphases. These investigations have led to an extensive body of literature describing the equilibrium properties of block copolymer modified interphases.

In practice, however, equilibrium properties are seldom attained because of the short time scales involved with polymer processing operations. It is therefore of increasing interest to understand the dynamic aspects of interfacial modification with block copolymers. The dynamics of interfacial segregation have been discussed by relatively few authors,[16,17,23,24,26,29] and only a limited amount of experimental data has been presented on this subject. In a theoretical treatment, Semenov[16] proposed a two-stage process for interfacial segregation of block copolymers. The initial stage, governed by Fick's diffusion equation with a sink boundary condition, occurs when the concentration of block copolymers at the interphase is very low. Here, the surface excess is predicted to scale with the square root of time where the proportionality constant is related to the magnitude of the diffusion coefficient, *D*. During the second stage

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Table 1. Characteristics of the Polymers Used in This Study

polymer	M_n	M_w/M_n
PS-4K	4000	1.06
PDMS-1.6K	1600	1.12
P(S-*b*-DMS)-13K	13000	1.15

of the process, the block copolymers form a dense brush at the interface leading to an entropic energy barrier that hinders further diffusion to the interface.

Budkowski, Losch, and Klein (BLK)[26] found that segregation kinetics based on Fickian diffusion did not describe their experimental data well, even for the early stages of segregation. They also noted that the sink condition was not met for typical surface segregation cases. An alternative model was proposed that calculates the concentration distribution of block copolymers near the surface by assuming a local equilibrium of adsorbed and nonadsorbed chains. This approach predicts the time dependence of segregation continuously from onset to the equilibrium state and considers both kinetic and thermodynamic effects throughout the entire process.

In the present paper, we report experimental segregation rates of a diblock copolymer to a blend interface measured by interfacial tensiometry. We also modify the Semenov and BLK theories to treat interfacial tension reduction and apply them to estimate diblock copolymer diffusion coefficients.

Experimental Section

Materials. The homopolymers employed were poly(styrene) ($M_n = 4000$) from Pressure Chemical Co., designated PS-4K, and poly(dimethylsiloxane) ($M_n = 1600$) from Petrarch System Inc., designated PDMS-1.6K. The poly(styrene-*b*-dimethylsiloxane) diblock copolymer, P(S-*b*-DMS)-13K, has a number-average molecular weight of 13 000 and contains 50 wt % of poly(styrene). It was synthesized at the Institute Charles Sadron by standard anionic methods using *sec*-butyllithium as an initiator and benzene as a solvent. The copolymers were terminated by dimethylchlorosilane to produce a reactive silane end group on the PDMS copolymer sequence.[2] Characteristics of the polymers used in this study and their designations are listed in Table 1.

Sample Preparation. The P(S-*b*-DMS)-13K was mixed with PDMS-1.6K by melt blending. A simple home-built microextruder device, held under vacuum at a controlled temperature, was used to extrude the drop phase material, PS-4K, into glass capillaries for pendant drop tensiometry. The PS-4K was heated at 180 °C under vacuum for 1 h and then was loaded into the capillary. The surrounding polymer melt phase, PDMS-1.6K, was placed inside a quartz cuvette and degassed in a vacuum for 1 h prior to the measurements. Once the temperature had stabilized at 140 °C, the capillary was placed in the tensiometry cell, and the drop was formed.

Interfacial Tension Measurements. Interfacial tensions were measured by a modified pendant drop method that employs digital imaging techniques to determine the drop profile and a robust shape comparison algorithm to regress the profile to theoretical ones.[33] Digital images of pendant drops were collected and stored automatically at programmed time intervals. Drop profiles were subsequently determined, and then interfacial tensions were calculated from the shape parameters obtained from drop profile analysis and the measured density of the homopolymer melt. All interfacial tension measurements were performed under argon atmosphere at 140 ± 1 °C where PS and PDMS are highly immiscible. The interfacial tension between PS-4K and PDMS-1.6K without added copolymer was 4.02 ± 0.09 dyn/cm.[6] The error reported for this value indicates the typical precision obtained in the measurements. Procedures employed for determining the equilibrium interfacial tensions for these ternary systems have been reported previously.[6]

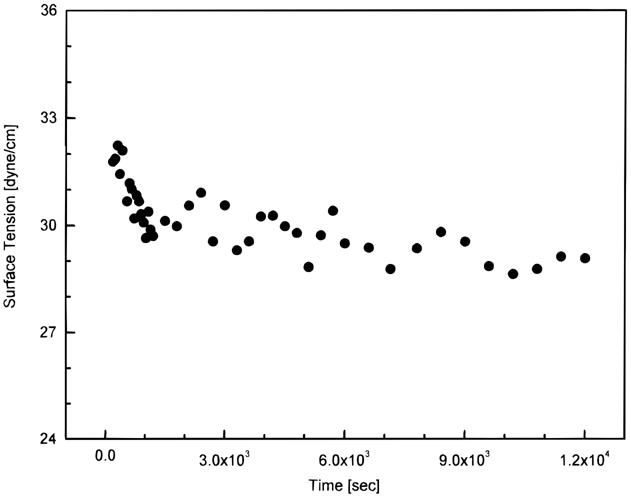

Figure 1. Time dependence of surface tension for PS-4 at 140 °C.

There exist several limitations to performing time-dependent interfacial tension measurements on polymers due to their viscoelastic nature. First, a finite time is required to extrude the drop of molten polymer, and second, considerable time may be required for the drop shape to equilibrate. Both of these factors depend on the rate and manner of drop formation. In the present case, the drop is formed manually at the tip of a positive displacement syringe. The operator forms the drop by rotating the threaded plunger by hand until an appropriate drop volume is obtained. Considerable dexterity is necessary to complete this task, and the time scale required to form the drop is therefore dependent on the skill and experience of the operator. Figure 1 illustrates the time dependence of surface tension for the polymer melt phase employed in subsequent interfacial tension measurements. The time to reach an equilibrium surface tension for PS-4 is about 1000 s. The shortest time at which kinetic measurements may be interpreted is therefore on the order of 1000 s.

Modeling Segregation Dynamics

The time dependence of block copolymer segregation to an immiscible polymer blend interface was treated in theories by Budkowski, Losch, and Klein (BLK)[26] and by Semenov,[16] and we extend these theories herein to consider the present case of interfacial tension reduction.

Semenov first treated block copolymer segregation by assuming Fickian diffusion with a sink boundary condition at the interface. Within this model, which is applicable at the early stages of segregation in the dilute limit of interfacial copolymer concentration, the interfacial excess, Γ (in units of length), is given by

$$\Gamma = 2\phi_0\left(\frac{Dt}{\pi}\right)^{1/2} \tag{1}$$

where D is the block copolymer diffusion coefficient, t is time, and ϕ_0 is the initial bulk copolymer concentration. A quantitative relationship between the molar interfacial excess, Γ^*, and interfacial tension reduction, $-\Delta\gamma$, was shown by Gaines and Bender[34] to follow from the approximate form of the Gibbs adsorption equation.

$$\Gamma^* = -\left[\left(\frac{1}{RT}\right)\left(\frac{\partial\gamma}{\partial \ln C}\right)\right] \cong -\frac{\Delta\gamma}{RT} \tag{2}$$

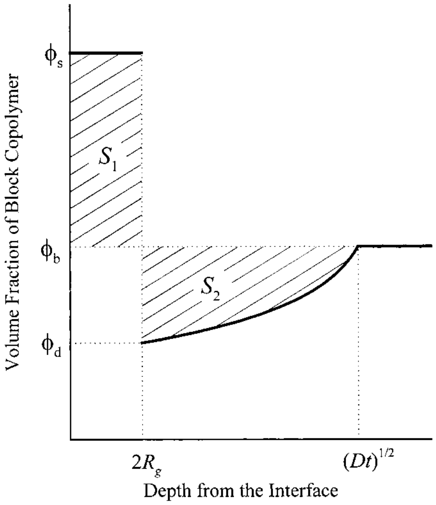

Figure 2. Schematic diagram of the concentration distribution of block copolymers near the polymer–polymer blend interphase.[23,26]

where R is the gas constant, T is temperature, and C is the bulk concentration of block copolymer. Γ^* is related to Γ by

$$\Gamma^* = \frac{\rho}{M}\Gamma \tag{3}$$

where ρ and M are the density and molecular weight of the block copolymer, respectively. It should be noted that the approximate Gibbs adsorption equation is valid only when the copolymer concentration is very low. Combination of eqs 1–3 yields the following expression for the time dependence of interfacial tension reduction.

$$\frac{-\Delta\gamma(t)M}{RT\rho} = 2\phi_0\left(\frac{Dt}{\pi}\right)^{1/2} \tag{4}$$

The diffusion coefficient can be obtained by linear regression of experimental $-\Delta\gamma(t)$ data to this relation for short times.

Budkowski, Losch, and Klein (BLK)[26] proposed an alternative model for diffusion-limited segregation of block copolymers to interfaces. In this model, the first stage of segregation is the adsorption, by reorientation, of copolymers within a distance of $2R_g$ from the interface, where R_g is the radius of gyration of block copolymer. The first process creates a depletion zone just below the interface that drives the diffusion of block copolymers from the bulk phase. Consequently, the depth of the depletion layer increases with increasing diffusion time, and the degree of depletion decreases with time and increasing distance from the interphase. A simplified schematic representation of the associated interphase gradient appears in Figure 2. The depth of the depletion layer scales approximately as $(Dt)^{1/2}$, and the thickness of the interfacial excess layer is about $2R_g$. Considering a mass balance, the integrated excess concentration (S_1) in the excess layer must equal the integrated depleted concentration (S_2) in the depletion zone. The interfacial excess of the adsorbed block copolymers is therefore equal to

$$\Gamma_a(t) \cong (\phi_b(t) - \phi_d(t))[(Dt)^{1/2} - 2R_g] \tag{5}$$

where ϕ_b and ϕ_d are the volume fractions of block copolymers in a bulk state and of nonadsorbed or free copolymers at the end of the depletion zone, respectively.

To obtain the interfacial excess as a function of time and $\phi_b(t)$ only, local equilibrium is assumed.[23,26,35] That is, the adsorbed copolymer chains at the interface are assumed at all times to be in equilibrium with nonadsorbed copolymer chains at the end of the depletion zone. The interfacial excess is subsequently related to $\phi_d(t)$ by

$$\Gamma_d(t) \equiv \Gamma[\phi_d(t)] \tag{6}$$

The explicit form of $\Gamma[\phi_d(t)]$ can be obtained experimentally from the equilibrium adsorption isotherm, i.e., Γ_{eq} vs $\phi_b(t\rightarrow\infty)$. At sufficiently low block copolymer concentrations, the segregation isotherm is usually of the linear form[5,10,11]

$$\Gamma_{eq} = \alpha\phi_b(t\rightarrow\infty) \tag{7}$$

where the constant α is dependent on the molecular weights of polymers and is nearly independent of temperature. Since $\Gamma_d(t)$ and $\phi_d(t)$ are analogous to Γ_{eq} and $\phi_b(t\rightarrow\infty)$, respectively, one obtains

$$\Gamma_d(t) = \alpha\phi_d(t) \tag{8}$$

Thus, $\phi_d(t)$ increases gradually during the segregation process until it reaches $\phi_b(t\rightarrow\infty)$. Setting $\Gamma_a(t) = \Gamma_d(t) = \Gamma(t)$ at any time leads to

$$\Gamma(t) = \alpha\phi_b(t)\left(1 - \frac{\alpha}{\alpha + (Dt)^{1/2} - 2R_g}\right) \tag{9}$$

If the reservoir is assumed to be infinite, that is $\phi_b(t) \cong \phi_b(t\rightarrow\infty)$, it follows that

$$\Gamma(t) = \Gamma_{eq}\left(1 - \frac{\alpha}{\alpha + (Dt)^{1/2} - 2R_g}\right) \tag{10}$$

This relation produces the known initial and asymptotic conditions of $\Gamma[t=(2R_g)^2/D] = 0$ and $\Gamma(t\rightarrow\infty) = \Gamma_{eq}$, respectively. Implicit in this derivation is that the diffusion distance of block copolymers, $(Dt)^{1/2}$, always exceeds the thickness of the interface excess layer, $2R_g$, i.e., $t \geq (2R_g)^2/D$.

Insertion of eqs 2 and 3 into eq 10 yields the final relationship that describes the time dependence of interfacial tension reduction

$$-\Delta\gamma(t) = -\Delta\gamma_{eq}\left(1 - \frac{\alpha}{\alpha + (Dt)^{1/2} - 2R_g}\right) \tag{11}$$

where the constant α retains dimensions of length. Regression of the experimental data to eq 11 furnishes estimates of the diffusion coefficient, D, as well as the equilibrium interfacial tension reduction, $-\Delta\gamma_{eq}$.

Results and Discussion

The time-dependent reduction of interfacial tension afforded by the addition of P(S-*b*-DMS)-13K to immiscible blends of PS-4K and PDMS-1.6K homopolymers is shown in Figure 3. In general three regions of behavior can be distinguished. At short times (region I), the interfacial tension changes rapidly with time. The data in this region of time, however, are an artifact of

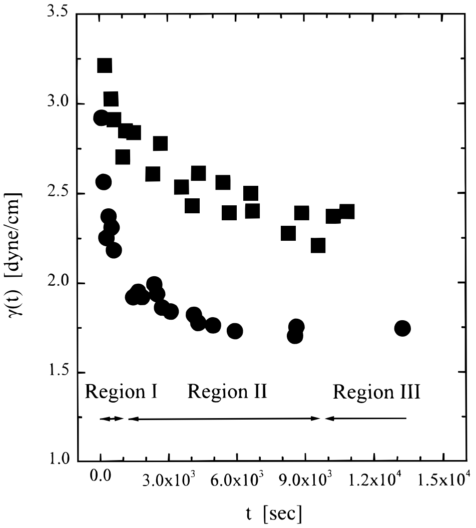

Figure 3. Time-dependent reduction in interfacial tension for PS-4K/PDMS-1.6K+P(S-*b*-DMS)-13K. Data are shown for two initial copolymer concentrations: $\phi_0 = 1.4 \times 10^{-5}$ (squares) and $\phi_0 = 2.0 \times 10^{-5}$ (circles).

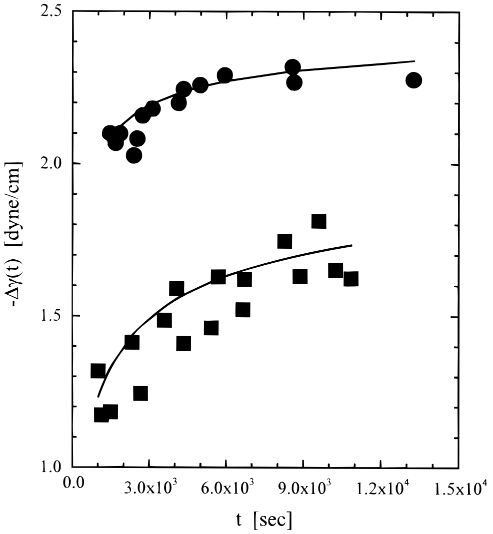

Figure 4. Interfacial tension reduction as a function of time. The solid symbols show data for two initial copolymer concentrations: $\phi_0 = 1.4 \times 10^{-5}$ (squares) and $\phi_0 = 2.0 \times 10^{-5}$ (circles). The lines are the results of regression of the modified BLK model equation, eq 11, to these data.

the pendant drop technique associated with the finite rheological time scale required to form a drop and for the drop shape to come to equilibrium. That is, there is a characteristic time for the matrix polymer, in the absence of copolymer, to attain an equilibrium drop shape. For the PS-4K homopolymer at 140 °C, the more viscous of the two homopolymers, the equilibration time (see Figure 1) is approximately 1000 s, corresponding well to the end of the first region of behavior. It may therefore be concluded that the apparent changes in interfacial tension visible in region I cannot be interpreted because the drop shape has not yet reached rheological equilibrium. At intermediate times (region II), the interfacial tension decreases with time as a result of block copolymer diffusion to the interphase. If the block copolymer concentration is high enough (data not shown), the intermediate time behavior is not observed because the majority of diffusion takes place while the drop shape is equilibrating in region I. If sufficient time was allotted for the experiment, the interfacial tension reaches a constant value at long times, indicating the attainment of equilibrium (region III).

The value of the constant, α, is determined from the adsorption isotherm (i.e., measured by pendant drop tensiometry) according to

$$(-\Delta\gamma_{\mathrm{eq}}/RT)(M/\rho) = \alpha\phi_0 \tag{12}$$

where the values of $-\Delta\gamma_{\mathrm{eq}}$ are obtained by regression of eq 11 to experimental data. Here, we make the assumption that the initial copolymer volume fraction ϕ_0 is approximately equal to the bulk volume fraction at infinite time $\phi_b(t\rightarrow\infty)$. This assumption is reasonable when the distance from the surface or interface is sufficiently large compared to the diffusion length $(Dt)^{1/2}$. We note that eq 12 is valid only at volume fractions below the critical micelle concentration, ϕ_{cmc}, of the block copolymers where linearity of interfacial tension with concentration is observed. Hu et al.[6] demonstrated that P(S-*b*-DMS)-13K forms a nearly dry brush at surface saturation and reported a value of $\phi_{\mathrm{cmc}} = 3.0 \times 10^{-4}$. The value of α determined from the equilibrium interfacial tension[6] data for $\phi_0 = 1.4 \times 10^{-5}$ and $\phi_0 = 2.0 \times 10^{-5}$ is 0.0543 cm.

Table 2 summarizes the values of D and $-\Delta\gamma_{\mathrm{eq}}$ in the BLK model obtained by regression of eq 11 to experimental data using the Origin software (Microcal Software, Inc.). The value of R_g required for the regression is estimated from literature data[36] to be 3.76 nm. The BLK theory provides a reasonable description of the dynamic interfacial tension reduction as shown in Figure 4. The apparent diffusion coefficients for P(S-*b*-DMS)-13K in PDMS-1.6K obtained from the BLK regression to experimental data are 4.3×10^{-6} and 4.0×10^{-5} cm²/s at $\phi_0 = 1.4 \times 10^{-5}$ and $\phi_0 = 2.0 \times 10^{-5}$, respectively. The self-diffusion coefficient of PDMS-1.6K, for comparison, is estimated to fall within the range of 7×10^{-6}–5×10^{-5} cm²/s,[37] in reasonable agreement with the experimental diffusion coefficients. The errors involved, however, are appreciable, both for estimation of the self-diffusion coefficient and for the regression required to estimate the experimental values. The analysis at present can furnish only order of magnitude estimates of the block copolymer diffusion coefficient. These values may still be of considerable practical utility however for estimating block copolymer interfacial segregation rates that are important to the design of surface modification or compatibilization processes.

The values of equilibrium interfacial energy reduction obtained from the analysis are subsequently used to

Table 2. Regression Results from the BLK and Semenov Models

	BLK model				Semenov model
initial vol fraction ϕ_0	equilib interfacial tension reduction $-\Delta\gamma_{\mathrm{eq}}$ [dyn/cm]	equilib interfacial excess Γ_{eq}* [mol/cm²]	equilib interfacial excess Γ_{eq} [nm]	apparent diffusion coeff D [cm²/s]	apparent diffusion coeff D [cm²/s]
1.4×10^{-5}	2.11 ± 0.13	6.03×10^{-11}	8.36	$(4.3 \pm 1.9) \times 10^{-6}$	$(1.4 \pm 0.4) \times 10^{-5}$
2.0×10^{-5}	2.49 ± 0.05	7.46×10^{-11}	10.3	$(4.0 \pm 1.0) \times 10^{-5}$	$(7.9 \pm 1.5) \times 10^{-6}$

calculate the interfacial excesses Γ_{eq} and Γ^*_{eq} reported in Table 2. The Γ_{eq} correspond to $2.2R_g$ and $2.7R_g$ for $\phi_0 = 1.4 \times 10^{-5}$ and $\phi_0 = 2.0 \times 10^{-5}$, respectively. These values are comparable in magnitude to previous excesses reported to be about $2.5R_g$[26] and are consistent with Hu's finding[6] that P(S-*b*-DMS)-13K forms a nearly dry brush at surface saturation. Γ^* is defined as the number of block copolymers in the "surface" volume given by the unit surface area multiplied by the gradient depth, $2R_g$; it provides information on the degree of localization of block copolymers at the interface. Considering that the initial concentration of block copolymers per unit volume can be obtained from the initial volume fraction by the relation $C_0 = (\rho/M)\phi_0$, the average number of block copolymers in that volume at the initial stage is of the order of 10^{-15} mol. There is therefore a factor 10^4 increase in the block copolymer concentration at the equilibrated interface compared to the bulk value.

The diffusion distances in our experimental time scale are quite large. For example, for $\phi_0 = 2.0 \times 10^{-5}$, $(Dt)^{1/2}$ is about 0.1−0.3 cm at $t = 10^4$ s. Since the diameter of a pendant drop is of similar size, typically a few millimeters, a gradient of this depth cannot be achieved experimentally when the copolymer is placed within the drop phase. The pendant drop technique is therefore limited in its applicability to the study of interfacial segregation at intermediate times where the concentration gradient has not reached the center of the drop. Because of this limitation, we have added the copolymer to the surrounding PDMS phase in the present experiments. As was discussed previously, the technique is also limited at short drop times by the time required for drop shape equilibration. The applicability of the pendant drop technique for dynamic interfacial tension measurements therefore requires careful selection of the matrix and block copolymer molecular weights so that the majority of diffusion takes place after equilibration of the drop shape, but before the gradient reaches the center of the drop. While we have performed an extensive set of dynamic interfacial tension experiments that examine the segregation of block copolymers to surfaces and interfaces,[3,38] only the two data sets reported herein satisfy the required experimental conditions and allow for some limited interpretation of the results.

In addition to limitations associated with the long drop equilibration times, there is an additional factor that limits the ultimate accuracy of dynamic interfacial measurements on polymer melts. That is, the drop surface area is not constant during the measurement, as is demonstrated in Figure 5 for a surface tension measurement. The drop area increases rapidly during extrusion of the drop because the drop volume increases. After the drop is formed (zero time in Figure 5), however, the drop shape continues to change. In the case of an interfacial tension measurement in the presence of block copolymer, the drop area changes in response to the reduction in interfacial tension associated with block copolymer diffusion to the interphase. The degree of drop elongation (i.e., drop shape) is governed by the ratio of gravitational forces to interfacial forces. The drop therefore elongates as the interfacial tension is reduced due to interfacial segregation of the block copolymer.

The drop surface area increases during the experiment by about 10%, but the effect of this change on the dynamic surface tension is extremely complex. The increase in surface area changes the areal density of adsorbed block copolymer in a calculable fashion but also alters the geometry of the diffusion experiment in a manner that is too complicated to calculate. As the drop elongates, the location of the interphase moves, and the local concentration gradients responsible for block copolymer diffusion may be altered. While the magnitude of the area change is not large, usually less than 10% throughout a typical experiment, it is impossible to estimate how this effect may influence the apparent diffusion coefficients obtained from the modeling.

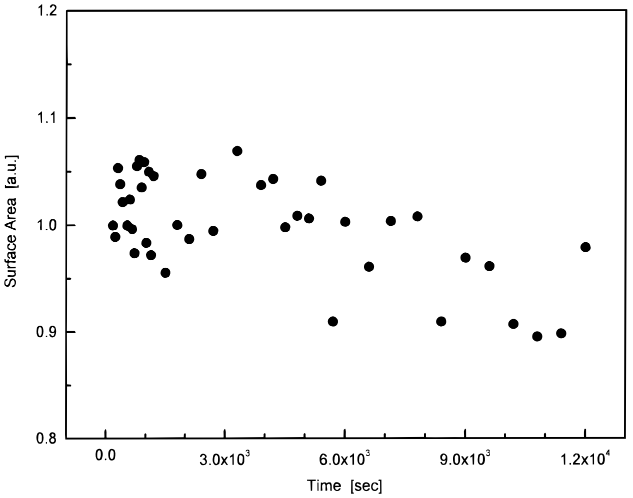

Figure 5. Time dependence of pendant drop surface area during a surface tension measurement of PS-4 at 140 °C.

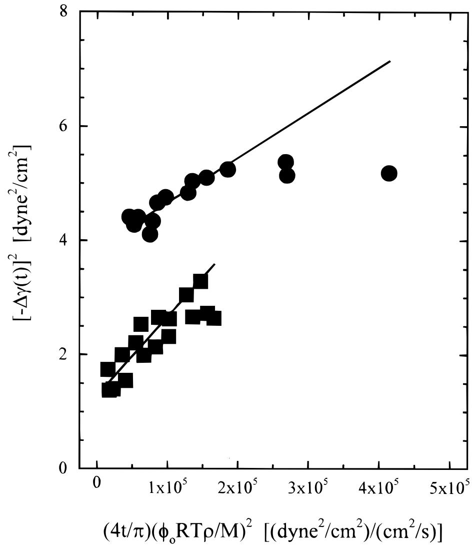

Figure 6. Time dependence of interfacial tension reduction plotted according to the modified model equation of Semenov. The solid symbols show data for two initial copolymer concentrations: $\phi_0 = 1.4 \times 10^{-5}$ (squares) and $\phi_0 = 2.0 \times 10^{-5}$ (circles). The lines are the results of regression of the modified Semenov model equation, eq 4, to these data.

The dynamic interfacial tension data may also be compared to the model proposed by Semenov[16] for the early stages of segregation. The interfacial tension reduction given by this approach is predicted to follow eq 4, and the regression results are presented in Figure 6. The apparent diffusion coefficients determined by the Semenov analysis (Table 2) are of the same order of magnitude as those obtained from the BLK model. In performing the regression, however, the fit was not constrained to pass through the origin as suggested by the form of eq 4. The regression results are therefore not truly consistent with the Semenov model, since they extrapolate to finite $\Delta\gamma(t\rightarrow 0)$. Although there is considerable uncertainty in the determination of zero time in the experiment due to the finite time required to form a drop, the extrapolation results deviate too much from the origin to be accounted for by this uncertainty. In addition, we have minimized this effect by regressing a plot of $\Delta\gamma(t)^2$ against t.

The observation of finite $\Delta\gamma(t\rightarrow 0)$ is, however, consistent with the BLK model wherein there is a rapid initial decrease in interfacial tension due to reorientation of copolymer chains within a distance of $2R_g$ from the interface. The BLK model therefore appears to produce a more physically realistic description of the data, even though both approaches yield similar values for the diffusion coefficients. This statement cannot be made unequivocally, however, since the pendant drop technique is incapable of providing data at short time scales where the Semenov treatment is most applicable. In addition, the accuracy of the pendant drop technique, given its limitations for viscous polymer melts, does not appear to be sufficient to provide better than order of magnitude estimates of the diffusion coefficients.

Summary

The pendant drop technique has been employed to measure the apparent time-dependent reduction in interfacial tension when a block copolymer diffuses to the interphase between two immiscible homopolymers. The technique is not readily applicable for either short or long segregation times due to the finite time required for equilibrium drop formation and the experimental limitations associated with the finite drop diameter, respectively. Intermediate time data correspond well to the predictions of models for diffusion-limited segregation of block copolymers to surfaces and interfaces proposed by Semenov and by Budkowski, Losch, and Klein. These comparisons provide order of magnitude estimates of the diffusion coefficients that are consistent with the estimated self-diffusion coefficient of the homopolymer matrix. Although both models yield similar values for the diffusion coefficient, the Budkowski, Losch, and Klein model provides a better qualitative description of the experimental data and is a more physically realistic model of the segregation process. The changes in drop shape and drop area during the experiment, however, compromise rigorous quantitative interpretation of the data. Because of several intrinsic limitations of the pendant drop technique, dynamic interfacial tension measurements on polymer melts can provide, at best, order of magnitude estimates of the diffusion coefficients associated with block copolymer segregation to interphases. The theories of interfacial segregation of block copolymers and the diffusion coefficient estimates they provide may nonetheless be important as a practical means to design processes that employ block copolymers to modify surfaces or to compatibilize immiscible polymer blends.

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