Direct Energy Transfer Studies of the Domain−Boundary Interface in Polyisoprene−Poly(methyl methacrylate) Block Copolymer Films

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Received June 15, 1995; Revised Manuscript Received October 16, 1995[⊗]

ABSTRACT: Direct nonradiative energy transfer (DET) experiments were carried out on five polyisoprene−poly(methyl methacrylate) diblock copolymers with polyisoprene volume fractions ranging from 0.07 to 0.5 (polyisoprene microdomains dispersed in a poly(methyl methacrylate) matrix). These experiments yield the ratio R/δ of the microdomain size R to the thickness of the domain−boundary interface δ as a function of the block copolymer overall chain length N. A plot of $\ln(R/\delta)$ vs $\ln N$ indicates that the microdomain size varies as $N^{0.65}$, close to the $N^{2/3}$ predicted by theory, while the interfacial thickness δ (26 Å) is independent of the degree of polymerization covered in this work. In addition, the Flory−Huggins interaction parameter χ for PI−PMMA was determined from the DET data (0.077). We conclude from these experiments that PI−PMMA belongs to the class of strongly segregated systems.

Introduction

We recently reported fluorescence decay measurements on polystyrene−poly(methyl methacrylate) [PS−PMMA] diblock copolymers in which each polymer was substituted at the PS−PMMA junction with a fluorescent dye.[1] Matched pairs of polymers were prepared, of similar chain lengths and compositions, one substituted with a donor dye D, and the other, with an acceptor dye A. In these experiments the donor dye was phenanthrene [Phe] attached at the 9-position, and the acceptor dye was anthracene [An] attached at the 2-position. These dyes undergo direct nonradiative energy transfer [DET] by the dipole-coupling mechanism with a characteristic (Förster) distance R_o of 24 Å. In the bulk, these polymers self-assemble into periodic structures, generating lamellae, cylinders, or spherical phases, depending upon the relative lengths of the PS and PMMA chains. Because of the way in which the dyes are attached to the polymers, they become localized in the interface between the two polymers. In this way, they sample a portion of the system of great theoretical interest.

Individual fluorescence decay traces were fitted to the Klafter−Blumen expression (see eq 1, below) developed for analysis of energy transfer in restricted dimensions.[2−4] By analyzing a series of samples composed of different mixtures of D- and A-labeled polymers, we were able to obtain the local acceptor dye concentration C_A. The ratio of the bulk concentration, $C_{A,0}$, to C_A may be thought of as the "confinement fraction" of the system. The ratio $C_{A,0}/C_A$ is related in a straightforward way to δ/R, where δ is the interfacial thickness and $2R$ is the length of the minor phase in the periodic structure. There are two approaches to obtaining the interfacial thickness. One can determine R independently by small angle X-ray or neutron scattering [SAXS or SANS], or one can take advantage of a theoretical treatment of Ohta and Kawasaki[5] to obtain δ directly from the fluorescence data. Using both approaches, we obtained a value of δ = 51 Å for the PS−PMMA interfacial thickness. This value is identical to that obtained by Russell and co-workers using specular neutron reflectivity [SNR] on samples containing one deuterated block.[6,7]

Here we extend our experiments to the case of polyisoprene−poly(methyl methacrylate) [PI−PMMA] diblock copolymer pairs similarly labeled at the junction with Phe and An. Because the polymers were prepared in tetrahydrofuran (THF) as solvent, the isoprene polymerization is predominantly (1,2 and 3,4), generating a polymer rich in pendant vinyl groups. From analysis of our fluorescence decay measurements, we calculate that the interface thickness in this system is on the order of 26 Å. We use this value, in conjunction with recent theoretical results of Semenov[8] to calculate an effective χ-parameter of 0.077 ± 0.004 at 22 °C for this polymer pair.

Experimental Section

Polymer Synthesis and Characterization. The diblock copolymers were synthesized by anionic polymerization at −78 °C in THF as a solvent, using *sec*-butyllithium as the initiator of isoprene polymerization. Following completion of the isoprene polymerization, a 2-fold excess of either 1-phenyl-1-(9-phenanthryl)ethylene or 1-phenyl-1-(2-anthryl)ethylene was added, followed by slow vapor phase addition of MMA (by distillation from triethylaluminum). The reaction was quenched with methanol. The block copolymer, purified by repeated precipitation from methylene chloride solution into excess methanol, still contained measurable amounts of PI homopolymer. This was removed by Soxhlet extraction of the block copolymer with cyclohexane. An aliquot of the PI block (after addition of the fluorescent group) was analyzed by gel permeation chromatography (gpc). M_n and M_w/M_n values of the PI block were calculated from the retention times by comparison with polystyrene standards using the universal calibration curve approach.

Compositions of the block copolymers and PI tacticity were determined by ^{1}H NMR at 400 MHz. These data were used to calculate M_n(gpc) for the block copolymers. Very similar values were obtained by gpc analysis of the block copolymers themselves in THF using polystyrene standards, and these traces were used to estimate M_w/M_n values. The microstructure of the PI block was 40% 1,2-addition, 55% 3,4-addition, and 5% 1,4-addition, typical of PI prepared by anionic polymerization in THF. M_n(uv) values of the PI block and of the final polymer were also determined by uv absorption spectroscopy, assuming 100% chromophore incorporation. From the similarities of M_n(uv) and M_n(gpc) values, the efficiency of dye incorporation f_{dye} was calculated to be 92−100%. The

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

Table 1. Sample Characteristics for PI–Phe(An)–PMMA Diblock Copolymers Labeled at the Junction

	sample pair	dye	M_n(gpc) PI/PMMA	M_w/M_n	Φ_{PI}[a]	f_{PI}[b]	f_{dye}[c]	χN[d]
1	I-1	Phe	1K/16.6K	1.09	0.07	0.08	100	14
	I-2	An	1K/19K	1.07	0.06	0.07	100	
2	I-17	Phe	10K/17K	1.18	0.43	0.46	96	24
	I-12	An	8K/17.5K	1.07	0.37	0.40	98	
3	I-14	Phe	10K/22K	1.06	0.37	0.40	100	28
	I-13	An	10K/22K	1.15	0.37	0.40	100	
4	I-36	Phe	19K/25K	1.17	0.50	0.53	90	42
	I-37	An	19K/28K	1.17	0.47	0.50	100	
5	I-21	Phe	10K/47K	1.11	0.20	0.23	100	51
	I-22	An	10K/55K	1.09	0.19	0.21	98	

[a] Φ_{PI} = volume fraction of PI-block. [b] f_{PI} = mole fraction of PI-block. [c] f_{dye} = efficiency of dye attachment (percent of labeled chains). [d] $\chi = 0.077 \pm 0.004$ was determined from DET data.

volume fraction of each block was calculated by assumption that the density of PI and PMMA blocks is the same as that for pure homopolymers ($\rho_{PI} = 0.913$ g/cm^3 and $\rho_{PMMA} = 1.188$ g/cm^3). The characteristics of the samples prepared are collected in Table 1.

Sample Preparation. The casting protocol for the block copolymers was designed to prepare samples reproducibly near thermodynamic equilibrium. Toluene, a nonpreferential solvent, was used as the solvent to avoid preferential swelling of either phase during the casting process, which can lead to trapping of nonequilibrium morphologies. Films were prepared from block copolymer solutions (3 wt %) in toluene containing various mixtures of donor- and acceptor-labeled block copolymers with similar chain lengths and compositions. The composition ranged from [A]/[D] ratios of 0 to 3. Film thickness ranged from 3 to 6 μm. The films were air-dried at room temperature and then further dried under vacuum at 50 °C for 8 h.

Fluorescence Measurements. Fluorescence decay profiles were obtained by the time-correlated single photon counting technique with a pulsed lamp as an excitation source. Films were excited at the phenanthrene absorption maximum (300 nm), and the fluorescence was detected at the maximum in the fluorescence spectrum of phenanthrene (366 nm). Data were collected at 90° to the excitation, at room temperature, 22 °C, to 20 000 counts in the maximum channel. The reference profile, used for the convolution analysis, was obtained by exciting a solution of *p*-terphenyl in aerated cyclohexane ($\tau = 0.96$ ns). Data analysis employed a Levenberg–Marquardt nonlinear least squares algorithm[9–11] with minimization of the reduced χ^2 function. The reduced χ^2, the weighted residuals, the shape and amplitude of the autocorrelation function of the weighted residuals, and the 95% confidence interval for fitting individual parameters were calculated to estimate the reliability of the fitting. For error analyses of the individual fit parameters we used the common method of approximating the residuals by an affine model.[10] Examination of the covariance matrix showed no significant correlation of the two key fitting parameters, P and β (see below). According to our estimates the uncertainty of the fitting parameters for each individual donor decay was less then 2%. The uncertainty in determination of R/δ, obtained from the linear dependence of the fitting parameter P upon the global acceptor concentration $C_{A,0}$, obtained for a series of samples, was, in most of cases, less than 5%. The total uncertainty in determination of the interface thickness, by reference to the molar mass dependence of R/δ, was estimated to be on the order of 10%.

Data and Data Analysis

For block copolymers dye-labeled at the junction, the donor and acceptor chromophores will be confined to the domain–boundary interface when the polymers form periodic structures in the bulk phase. Since the thickness of this interfacial domain δ is on the order of R_o, the kinetics of energy transfer from D to A will be governed by the dynamics (rate) of DET in a restricted geometry. A common strategy for analyzing donor fluorescence decay profiles for energy transfer in a spatially restricted medium is to fit the donor decay $I_D(t)$ to the Klafter–Blumen equation:[3,4]

$$I_D(t) = A \exp\{-(t/\tau_D) - P(t/\tau_D)^{\beta}\} \qquad (1a)$$

where τ_D is the lifetime of the donor in the absence of the acceptor. The term P is proportional to the acceptor concentration in the system, incorporated into the theory in terms of the probability of finding an acceptor within a distance R_o of an excited donor. The term β is a concentration-independent parameter sensitive to the details of the local geometry, but difficult to interpret in terms of a physical picture of the system. Simulations involving uniform donor and acceptor distributions in, for example, spheres of small radii, indicate that β is primarily sensitive to edge effects of the local geometry.[12]

Equation 1 predicts that individual decay profiles will fit to a stretched exponential form and, more importantly, that a series of experiments carried out at different acceptor concentrations will yield P values proportional to the global acceptor concentration $C_{A,0}$ and β values independent of $C_{A,0}$. To vary acceptor concentration, we make different mixtures of Phe- and An-labeled block copolymers. Since the compositions and total chain lengths are similar for each pair, we assume that within the mixture, morphology is conserved along with the period spacing. A useful parameter for comparing experiments with different block copolymers is the composition ratio [An]/[Phe].

The individual decay profiles obtained here are to the eye indistinguishable from those reported by us for PS–PMMA block copolymers. Computer analysis of the data indicate a similar contribution to the data for PI–PMMA of a second population of donors which do not undergo energy transfer. Thus when fitting experimental data, it was necessary to add an additional term to eq 1a to accommodate these small amounts of donor, presumably outside the interface, unquenched by acceptor

$$I_D(t) = A_1 \exp\{-(t/\tau_D) - P(t/\tau_D)^{\beta}\} + A_2 \exp(t/\tau_D) \quad (1b)$$

When the composition ratio of [An]/[Phe] > 1, the A_2 term represents no more than 5% of the signal decay. We defer a detailed discussion of the strategy for curve fitting and the meaning of the A_2 term in eq 1b to a later publication.

According to the theory of DET in restricted geometries, the preexponential term P in eq 1 is a factor proportional to the local acceptor concentration C_A, here localized in the interfacial volume. It is related to the global acceptor concentration by the expression

$$P = (4R_o^{\,3}N_A/3\lambda\Phi_B)g_I^{\,\beta}\Gamma(1-\beta)C_{A,0} \qquad (2)$$

where N_A is Avogadro's number, Φ_B is the volume fraction of the minor component, g_I is the orientation factor for DET, $\Gamma(1 - \beta)$ is the gamma function, and β is defined in eq 1. One can think of the ratio $C_{A,0}/C_A$ as the confinement fraction for groups attached to the junction point. The term λ is a geometry-dependent proportionality constant that relates $C_{A,0}/C_A$ to δ/R

$$\frac{C_A}{C_{A,0}} = \frac{1}{\lambda \Phi_B} \tag{3}$$

with the following definition for λ:

$$\lambda = [1 + (\delta/R)]^{\alpha} - 1 \tag{4}$$

where $\alpha = 1, 2, 3$ for lamellae, cylinders, and spheres, respectively.

From eq 2 we see that for a series of experiments, the plot of P vs $C_{A,0}$ is predicted to be linear, and from the slope of the plot, one can calculate λ, and thus determine δ/R. Data for five samples of PI−PMMA are plotted in Figure 1. Each of the plots is linear, and all the lines pass through the origin, as expected. Thus the general features of data analysis in terms of the Klafter−Blumen equation for DET in restricted geometries are satisfied.

To proceed further, we need to obtain independent values for R and δ. In the theoretical analysis of block copolymer morphology by Ohta and Kawasaki [OK],[5] the authors consider a diblock copolymer made up of components of similar statistical segment lengths b and relate the ratio R/δ to the overall chain length N of the polymer

$$\frac{R}{\delta} = C\left(\frac{b}{\delta\sqrt{2}}\right)^{4/3} N^{2/3} \tag{5}$$

(Here R is the spatial period of a lamellar structure, but the radius of a spherical or a cylindrical minor phase in those periodic structures.)

Equation 5 incorporates a geometry-related constant C dependent upon the mole fraction f and the volume fraction Φ_B of the minor component. For the samples we examine here, we infer from their composition that three of them form lamellar structures and two form spheres:

lamellae $\quad C = [2^{5/2} f(1-f)/3\Phi^2(1-\Phi)^2]^{1/3}$ (6a)

spheres $\quad C = [2^{1/2} f(1-f)/12(0.2 + 0.1\Phi - 0.3\Phi^{1/3})]^{1/3}$ (6b)

Expressions similar to eq 5, with R/δ proportional to $N^{2/3}$, are common to all recent theories of block copolymers in the strong segregation limit. This dependence arises from the variation of R with N, since in the theory of strongly segregated systems, δ is found to be, or taken to be, constant. The advantage of the OK contribution for us is that it permits simultaneous analysis of experimental data from block copolymer samples with different morphologies. Our samples permit us to examine in terms of eq 5 whether R/δ is in fact proportional to $N^{2/3}$. Once this behavior is established, the prefactor in eq 5 allows a value for δ to be calculated. When this analysis was applied to junction-labeled samples of PS−PMMA, we obtained a value of $\delta = 51$ Å, essentially identical to that determined by Russell[6,7] using SNR for partially deuterated PS−PMMA samples giving lamellar microphases.

In Figure 2, we plot $\ln(R/\delta C)$ vs $\ln N$ for our five samples of PI−PMMA. The straight line which represents the best fit to the four highest molecular weight polymers has a slope of 0.65, which is very close to the value 0.666 predicted by recent theories for strong segregated block copolymer systems. For calculation of the interface thickness we have assumed that the statistical segment length of the block copolymer corresponds to a simple average of the two values, $b = 5.9$ Å for PI with the same microstructure,[13] and $b = 6.7$ Å for PMMA. From the intercept, and with $b = 6.3$ Å, we calculate $\delta = 26$ Å, slightly larger than the value (18 Å) obtained by Hashimoto[14,15] by SAXS for PS−PI.

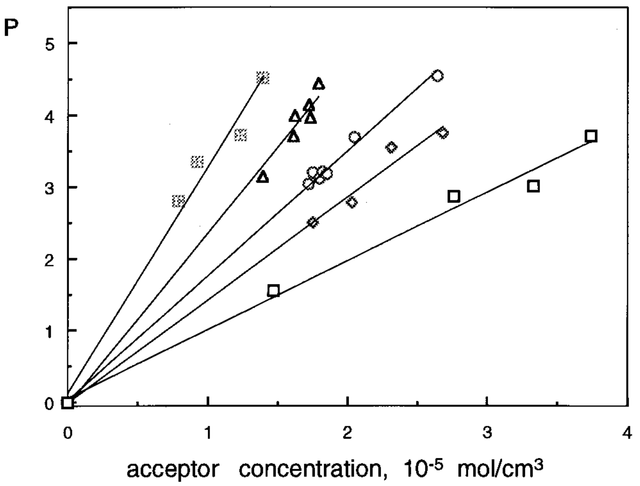

Figure 1. Variation of the fitting parameter P versus the global acceptor concentration $C_{A,0}$ in PI−Phe(An)−PMMA films. For the samples shown, the block copolymer number-averaged chain length N has the values (top-to-bottom) of 656, 544, 367, 305, and 193 (with corresponding mole fractions of PI of 0.22, 0.51, 0.4, 0.43, and 0.07).

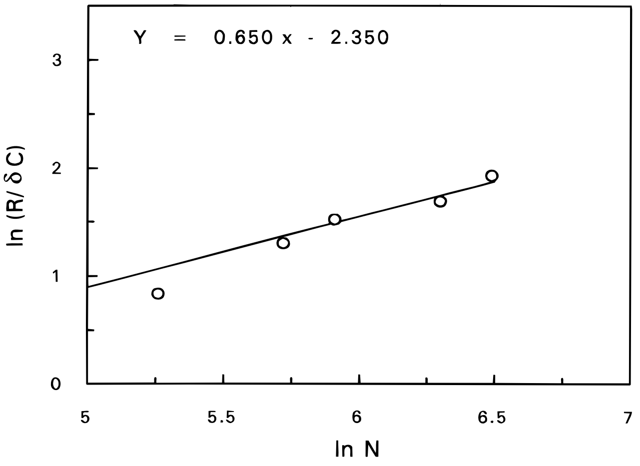

Figure 2. Plot of $R/\delta C$ as a function of chain length N for the PI−PMMA samples shown in Figure 1.

We now return to the question of whether the best fit to the data in Figure 2 should include all five points or only the four points of highest molecular weight. The sample of lowest molecular weight contains about 7 mol % of PI with a degree of polymerization of only 15. Using the value of the Flory−Huggins χ-parameter determined in this work (see below), we calculate $\chi N \approx 14$. This low χN value suggests to us that the sample may lie outside the strong segregation limit. If we arbitrarily fit a line to all five points in Figure 2, we obtain a slope of 0.85, which is much too large. On the other hand, if we limit the fit to the samples of larger χN, we obtain a slope of 0.65, close to the theoretical value of $^2/_3$.

From the DET experiment we can obtain not only the ratio R/δ but also the value of the interface thickness δ for the system. From these data we can calculate the microdomain size R and total period (lattice constant, D) of the periodic structure. We also have calculated

Table 2. Microdomain Size R_{PI} and Interdomain Distance D for PI−PMMA Films (Interface Thickness δ = 2.6 nm)

			R_{PI}, nm		D, nm	
structure	N_{PI}/N_{PMMA}	Φ_{PI}	exptl	theor	exptl	theor
lamella	132/172	0.40	7	8	19	20
lamella	147/220	0.37	10	9	24	23
lamella	279/265	0.48	13	14	27	29
sphere	147/509	0.19	15	14	46 (52)[a]	44

[a] For dodecahedron approximation according to Helfand[16b] (for bcc structure according to Ohta and Kawasaki[5]).

equilibrium values for the microdomain size and the interdomain distance based upon the theory of spherical and lamellar domains in asymmetric block copolymers for the strong segregation limit developed by Helfand and Wasserman.[16] In Table 2 we compare the measured and predicted domain properties for the series of PI−PMMA block copolymers. There is almost complete agreement between the theoretical and DET experimental results in terms of absolute values for lamellar and spherical microphase dimensions.

A comment is in order about the value of δ obtained from the DET experiments through use of eqs 1−4. Calculating δ from the confinement fraction ignores the details of the distribution of donors and acceptors across the interfacial profile. While δ represents a characteristic interfacial width, it is not rigorously defined in terms of contemporary theory of block copolymer morphology. Recent advances in the theory of energy transfer in restricted geometry[17] offer the possibility that in the near future it will be possible to reanalyze the data presented here in terms of theoretical profiles for the diblock copolymer interface.

Theory of the Block Copolymer Interface

Early efforts at the analysis of block copolymers led to the Helfand expression for the interface thickness in strongly segregated systems:[18]

$$\delta_0 = 2b/(6\chi)^{0.5} \tag{7}$$

To derive eq 7, one balances the unfavorable energy of mixing segments of the A- and B-polymers, described by the Flory−Huggins parameter χ, with the entropy lost upon minimization of the interfacial area, which leads to stretching of the polymer chains. Recently, Semenov[8a] proposed correction terms to the Helfand expression, leading to

$$\delta = \{[\delta_0(1 + 1.34/(N\chi)^{1/3}]^2 + (3v/b^2)\delta_0 \ln(R/\delta_0)\}^{0.5} \tag{8}$$

In eq 8, R is equal to the half-period of the lamellar structure. The physical meaning of the first term of eq 8 (chain end correction) is the ideal gas free energy of the junctions confined in the layer of thickness δ. The entropic penalty of localizing the joints in the interface does not depend on the chemical structure of the block copolymer and diminishes as the polymer gets longer. The second term takes into account thermal fluctuations of the concentration profiles of the junctions, which imparts a waviness to the interface. The contribution of the fluctuation correction depends on the molecular parameters through the mean molecular volume of a link (v) and the statistical length of a monomer (b). The interface thickness, according to this description, is nearly independent of the degree of polymerization N, since the end correction is a decreasing function of N, and the fluctuation term is an increasing function of N, which appears through the dependence of R upon the b-, N-, and χ-parameters.[8b]

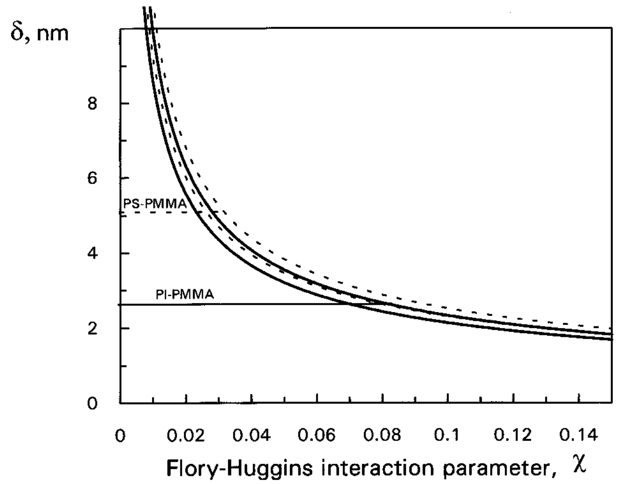

Figure 3. Dependence of the interface thickness δ upon the χ-parameter, calculated from eq 9, for the block copolymer films PS−PMMA (dashed line) and PI−PMMA (solid line). The upper line within each pair refers to N = 300; the lower line, to N = 800.

We wish to use the value of δ, determined by DET, to estimate the χ-parameter for the PI−PMMA block copolymer. Flory−Huggins parameters are commonly determined through cloud-point measurements, and calculated via a thermodynamic theory, or from scattering experiments on miscible blends, frequently of low molecular weight mixtures. Here the analysis involves the random phase approximation. The strengths of each approach and differences in values obtained by these different methods have been described in detail for PS−PMMA and PS−PI in a series of recent publications.[19−26] For the case of PI−PMMA, we know of no χ-parameter in the literature. Since the cohesive energy densities of PS and PMMA are similar, we might imagine that $\chi_{PI-PMMA}$ will be comparable in magnitude to χ_{PS-PI}, particularly since the value of δ we determine for PI−PMMA (26 Å) is only slightly larger than that reported for PS−PI (18 Å).

In the remaining portion of this paper we explore the possibility of using the values of δ to estimate χ. Application of eq 8 requires values for parameters (δ, N, f) that can be measured directly or calculated from experimental data, and in addition one needs values for other parameters (b, v) which are model dependent. Our main contribution to this discussion will be examination of the possibility that fluctuation effects make insignificant contributions to the DET experiment, because the DET experiment operates over such a short length scale (here ca. 35 Å). If this hypothesis is in fact valid, it means that the second term in eq 8, which contains the model-dependent parameters, will not be important in the analysis. Thus

$$\delta = 2b(6\chi)^{-0.5}[1 + 1.34/(\chi N)^{1/3}] \tag{9}$$

Determining χ from δ

The most convenient way to appreciate the dependence of δ upon χ is to plot δ vs χ for fixed values of N and b. We present this kind of plot in Figure 3 for systems representative of PS−PMMA (dashed line) and PI−PMMA (solid line), for values of N = 300 and 800. The larger value of N gives the line of smaller δ for comparable χ. In carrying out these calculations according to eq 9, we used values for the statistical lengths

Table 3. Flory–Huggins Interaction Parameters χ from Direct Energy Transfer Data

	structure	N	f	b, Å	δ_{exp}, Å	$\chi(\delta)$	(R/δ)	$\chi(R/\delta)$
PS–PMMA	lamella	300	0.50	6.8	51	0.032		
	lamella	810	0.50			0.027	3.65	0.028
PI–PMMA	sphere	193	0.08					
	lamella	305	0.43			0.083	3.24	0.077
	lamella	367	0.40	6.3	26	0.080	3.96	0.091
	lamella	544	0.51			0.075	5.76	0.074
	sphere	656	0.20					
	lamella	800	0.50			0.071		

(b) listed in Table 3. These represent average values calculated from those of the individual block copolymer components. One sees in Figure 3 that χ functions do not change strongly with the increasing degree of polymerization. To estimate the value of χ for the block copolymer, one can use the plot in Figure 3 to identify which value of χ corresponds to a given value of δ. The horizontal lines drawn in Figure 3 represent the values of $\delta = 51$ Å for PS–PMMA and 26 Å for PI–PMMA.

The difference in χ-parameter values (induced by the apparent dependence of the χ-parameter upon the degree of polymerization, see eq 9) is less then 10%, which is comparable with the experimental accuracy of the interface thickness measurements. In this way, we obtain for PS–PMMA a value of the χ-parameter of 0.029 ± 0.002. Since these samples were annealed initially at 70 °C followed by further annealing at 150 °C, we report this value at 70 °C. This choice is somewhat arbitrary because the samples were cooled to room temperature before the fluorescence decay measurements were carried out, but fortunately, here, the χ-parameter for PS–PMMA is not very sensitive to temperature. The value we obtain is very close the value 0.030 ($T = 70$ °C) calculated from the temperature dependence of χ obtained by SANS.[25,26] PS–PMMA is a system that has been studied extensively by Russell, and he has discussed the concordance between the experimental values of δ and the influence of thermal fluctuations of the concentration profiles of the junctions on its value.[27] The fact that similar values of χ are obtained from eq 9, which involved only a correction to the interface thickness because of the connectivity of blocks (end correction), is a reflection of the small contribution of the fluctuation term to δ in the case of PS–PMMA with a total degree of polymerization less than 800.

PI–PMMA is characterized by a more narrow interface. The smaller value of δ obtained here is a reflection of the stronger repulsion between dissimilar monomer units in the interface compared with PS–PMMA. Here the mean-squared displacement of the interface from its average position should be smaller than in the case of PS–PMMA because of the increased surface tension. From the value of 26 Å for the PI–PMMA interface, obtained by DET, we estimate from Figure 3 a value of the χ-parameter of 0.077 ± 0.004 for PI–PMMA. These samples were prepared at room temperature and subjected to only mild annealing (50 °C for 8 h), but the fluorescence decay profiles were measured at 22 °C. Because the T_g of the PI component is lower than room temperature, when we calculate χ-parameters in this system, we assume the values pertain to 22 °C. We note that for PI–PS, for which the interface thickness has been determined ($\delta = 18$ Å), the value of the χ-parameter (0.089) obtained by SAXS[22] is comparable with our value for PI–PMMA.

To test our assumption about the decreasing role of the thermal fluctuations in the case of strongly segregated systems, we have analyzed the total function for interface thickness described by eq 8 for PS–PI. The data of Figure 4 show the magnitude of the contribution of each term in eq 8 to the δ value. Using the approach mentioned above, we found that the fluctuation term leads to an incorrect value for χ, one which is much larger (>0.3) for both PI–PMMA and PI–PS than those obtained experimentally.

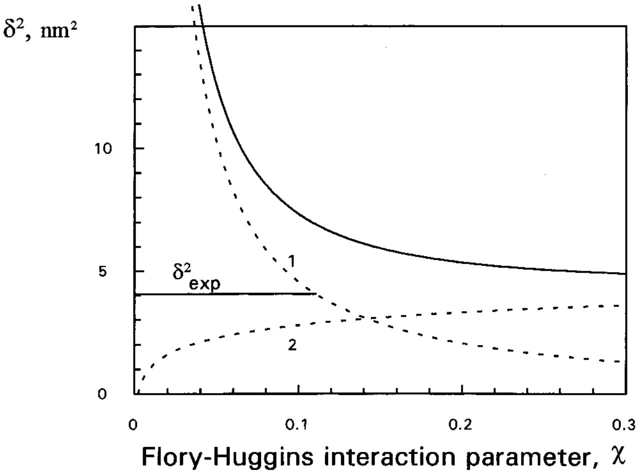

Figure 4. Dependence of the interface thickness δ upon the χ-parameter, calculated from eq 8, plotted as δ^2 vs χ, for PS–PI (solid line). Line 1 refers to values obtained by employing only the chain-end correction, and line 2, to values obtained by employing only the fluctuation term. (Parameters employed in the calculations include the mean volume of a link = 0.145 nm^3, statistical segment length = 0.63 nm, and polymerization index = 800.) The horizontal line represents the square of the mean experimental value of $\delta_{\mathrm{PS-PI}}$, which according to a recent review[31] is equal to 2.0 ± 0.5 nm.

Determining χ from R/δ

If we assume that the DET experiment is insensitive to fluctuations at the interface, we can use eq 9 to derive an expression for χ which eliminates or minimizes the need for model-dependent parameters. This approach rests on the measurements of the ratio R/δ, where R is the microdomain length (herein assumed to be lamellae). The parameter R/δ can be obtained directly from the fit of the donor decay profile in a DET experiment. According to the theory of block copolymer structure, the thickness of a lamellar microphase (R_B) varies with the molecular (N, b) and thermodynamic (χ) parameters of the block copolymer system according to the expression[8b,29,30]

$$R_{\mathrm{B}} = 4(24^{1/2}\pi^2)^{-1/3} b f_{\mathrm{B}} N^{2/3} \chi^{1/6} \tag{10}$$

where f_{B} has the same meaning as in eq 6. From eq 8 we obtain the following expression for the ratio R/δ:

$$R/\delta = (24/\pi^2)^{1/3} f(\chi N)^{2/3}[1 + 1.34/(\chi N)^{1/3}]^{-1} \tag{11}$$

All the parameters (R/δ, f, N) in eq 11 needed for estimating χ can be directly measured.

We can use the method mentioned above to examine the dependence of R/δ upon χ and to plot R/δ vs χ for fixed values of N. We present this kind of plot in Figure 5 for PI–PMMA for values of N = 544, 367, and 305. The larger values of N give lines of larger R/δ for comparable χ. To estimate the value of χ for the block copolymer, one can use the plot in Figure 5 to identify which value of χ corresponds to a given (experimentally obtained) value of R/δ (the horizontal lines drawn in

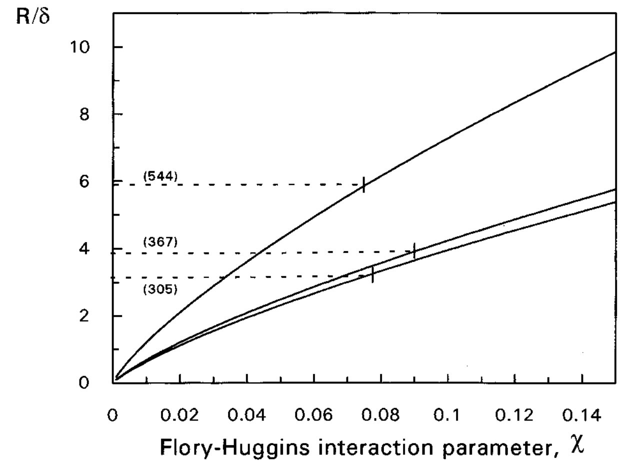

Figure 5. Plot of R/δ vs the Flory−Huggins interaction parameter χ, as calculated from eq 11, with parameters appropriate for PI−PMMA. The three lines (top-to-bottom) correspond to N = 544, 367, and 305. The values of the parameter $(R/\delta)_{\mathrm{exp}}$ used to obtain χ-parameters from this plot are listed in Table 3.

Figure 5). The values of R/δ obtained by the DET technique are collected in Table 3.

From a graphical analysis of eq 11 we obtain the values 0.028 ± 0.003 for $\chi_{\mathrm{PS-PMMA}}$ and 0.080 ± 0.007 for $\chi_{\mathrm{PI-PMMA}}$. For PS−PMMA, the χ value is calculated from two samples that form lamellar phases, and for PI−PMMA we have three samples that form lamellar phases (cf. Table 3). One can see that the magnitudes of the χ-parameters obtained by the two different methods of analyzing the DET data are in good agreement. It is important to note that for estimation of the χ-parameters from δ and R/δ we used different theories of block copolymer systems in the strong segregation limit. In spite of this, the results are in excellent agreement with one another.

The analysis of the block copolymer properties described above is based on the assumption that the χ-parameter is constant, independent of the composition of the block copolymer. There is some evidence that the effective χ-parameter for a real block copolymer system might be composition-dependent. The effect of composition dependence of the χ-parameter and its influence on the interface thickness has been analyzed for polymer blends.[8a,30] The discrepancy of the experimentally observed dependence of the critical χN value at the order−disorder transition on the copolymer composition with theoretical predictions was reported by Thomas.[21] Close examination of the χ-parameters we calculate from each of the different samples PI−PMMA indicates that the scatter in χ values (10%) is larger than the uncertainty in the fitting parameters used to calculate R/δ (3%). To examine whether there is a systematic change in χ with variation in copolymer composition, we plot calculated values of χ for each copolymer sample as a function of the mole fraction of isoprene units in the polymer. In Figure 6, we observe a monotonic decrease in χ with the increasing mole fraction of the minor PI component. More data and data of greater precision are needed before a firm conclusion can be drawn.

Summary

We have carried out DET experiments on a series of five polyisoprene−poly(methyl methacrylate) diblock copolymers with polyisoprene volume fractions ranging from 0.07 to 0.5. These experiments yield the ratio R/δ of the microdomain size R to the thickness of the domain−boundary interface δ as a function of the block copolymer overall chain length N. We find that the microdomain size varies as $N^{0.65}$, close to the $N^{2/3}$ predicted by theory, while the interfacial thickness δ (26 Å) is independent of N. We use the value of δ to estimate the Flory−Huggins interaction parameter χ for PI−PMMA and obtain a value of 0.077. When we apply our methodology to calculating χ from δ for PS−PMMA and for PI−PMMA, we obtain values in accord with those in the literature, providing that we neglect the fluctuation term in eq 8 for samples of narrow interface thicknesses. This may be a consequence of the relatively short chains we examine ($N \leq 800$) in our experiments.

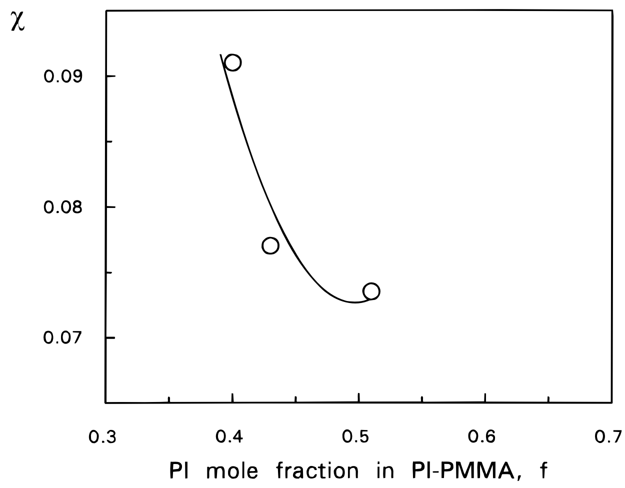

Figure 6. Dependence of the χ-parameter upon the mole fraction of the PI component in the PI−PMMA block copolymer films.

Acknowledgment. The authors thank NSERC Canada and the Ontario Centre for Materials Research for their support of this research. This work was also partially supported by U.S. DOE grant DE-FG05-95ER62070.

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MA950840B