Macromolecules **2003,** *36,* 4485−4491

Energy Transfer Study of the Interface Thickness in Symmetrical Isoprene−Methyl Methacrylate Diblock Copolymers

Jian Yang, Jianping Lu, Yahya Rharbi, Lan Cao, and Mitchell A. Winnik*

Department of Chemistry, University of Toronto, 80, St. George St.,
Toronto, Ontario, Canada M5S 3H6

Yuanming Zhang and Ulrich B. Wiesner

Department of Materials Science & Engineering, Cornell University, 329 Bard Hall,
Ithaca, New York 14853

Received January 6, 2003

ABSTRACT: We describe direct nonradiative energy transfer (DET) experiments on mixtures of two symmetrical poly(isoprene-*b*-methyl methacrylate) block copolymers of similar molar mass and composition, bearing different dyes at the junction. One polymer has a donor dye (9-phenanthrene) at the junction, and the other has an acceptor dye (2-anthracene). Small-angle X-ray scattering experiments show that films of the mixed diblock copolymers have a lamellar morphology with a spacing that varies with composition from 24 to 26 nm. Fluorescence decay profiles from these films were analyzed in terms of an energy transfer model that takes account of the distribution of junctions across the interface. On the basis of the value $R_0 = 2.3$ nm for the characteristic ET distance and an assumed value of $\langle \kappa^2 \rangle = 0.476$ for the preaveraged orientation parameter for randomly oriented immobile dipoles, we calculate an interface thickness of 1.6 ± 0.1 nm. This value is independent of the acceptor/donor ratio (i.e., the acceptor concentration) in the films.

Introduction

Diblock copolymers consist of two chemically distinct polymer chains that share a common junction. When the product of their chain length N and the Flory−Huggins interaction parameter χ_{FH} exceeds a critical value,[1] the components undergo microphase separation. When the two blocks (A and B) are nearly equal in length,[2] a spatially periodical lamellar morphology forms as an arrangement of A-rich and B-rich layers. Many experimental methods, such as electron microscopy,[3] small-angle X-ray scattering (SAXS),[4] small-angle neutron scattering (SANS),[5] and specular neutron reflectivity (SNR),[6,7] have been used to study the lamellar morphology of symmetric and nearly symmetric diblock copolymers. The interface between the two blocks is one of the most important features of the structure and also one of the most difficult aspects of the morphology to study. The most precise information is obtained by SNR. This technique involves measuring the intensity of neutrons reflected from a block copolymer film as a function of angle of incidence at small angles. The data are rich and can be fitted with high precision with computer models that simulate the data expected on the basis of a theoretical model of the polymer segment density profile across the interface. The major shortcoming of reflectivity techniques is that they cannot distinguish between diffuseness of the interface and waviness at the interface. For this reason, values of the apparent interface thickness (δ_{app}) have to be corrected. One normally employs a theory of capillary waves to impose this correction on the data.[8]

Our research group has been interested in developing an alternative approach to the study of block copolymer interfaces based upon direct nonradiative energy transfer (DET) experiments.[9−12] In this approach, we synthesize matched pairs of diblock copolymers containing a single dye at the junction. One polymer contains a dye such as phenanthrene (Phe), which can serve as the DET donor, and the other polymer contains a dye such as anthracene (An), which can serve as the acceptor. Because the dyes are covalently bound to the junction, they are confined to the interface. Thus, their local concentration is greater than their bulk-averaged concentration. The DET experiment is sensitive to the distribution of donors and acceptors. If the distance between junction points is comparable to the characteristic DET distance (the Förster radius R_0), the experiment provides information about the distribution of junctions in the interface. Because both polymers have similar molecular weights and compositions, mixtures of the two polymers will have the same morphology as that formed by the individual components. As a consequence, one can prepare a series of mixtures with different donor−acceptor dye ratios and carry out independent experiments in order to improve the precision in measurements of the interface structure.

With the aid of this method, we have examined the nature of the interfaces formed by poly(styrene-*b*-methyl methacrylate) (PS−PMMA)[9] and poly(isoprene-*b*-methyl methacrylate) (PI−PMMA)[10−12] diblock copolymers in the bulk state. These early experiments focused on localization of dyes in the interface, analyzing the results of fluorescence decay measurements in terms of the Zumhofen−Klafter−Blumen model[13−15] of reaction dynamics in restricted geometries. This approach, which provides very useful insights, does not take account of the shape of the junction distribution profile across the interface. More recently, these models have been extended to take explicit account of the distribution of both donors and acceptors within the dimensions of a confining space.[16−19] These models provide new theoretical tools for analyzing DET experiments in terms of the

---

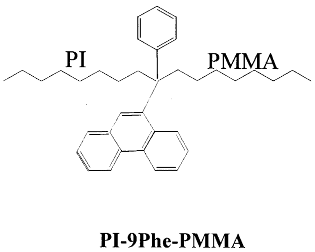
* To whom correspondence should be addressed.

10.1021/ma030005r CCC: $25.00

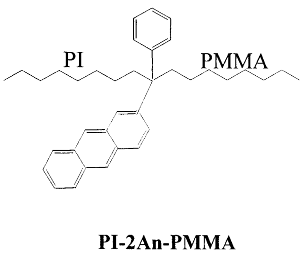
detailed structure of the interface between two adjacent blocks. Rharbi et al.[20] employed this theory to analyze the results of DET experiments on a PS−PMMA diblock copolymer annealed at 140 °C and obtained an interface thickness of 4.9 nm.

There are a number of important aspects of the Rharbi experiment that require further comment. First, polystyrene contributes a weak background fluorescence to the fluorescence decay signal. This background has to be subtracted before the fluorescence decay profiles can be analyzed. Second, the authors argue that the limited span of the DET experiment ($<2R_0$) is too small to be sensitive to capillary waves. Third, to compare their value of the interface thickness δ to the values obtained by SNR for PS−PMMA, one has to take account of the influence of chain deuteration (in the SNR experiment) on the magnitude of the Flory−Huggins χ parameter between PS and PMMA. Finally, they showed that the value of δ obtained from analysis of the DET data is very sensitive to the magnitude of R_0 between the donor and acceptor. This parameter has to be determined independently.

In this paper, we describe similar experiments on a pair of symmetric PI−PMMA block copolymers, whose structures are shown below. In the Phe-labeled polymer, the dye is linked through its 9-position to the junction of the two blocks. In the acceptor-labeled polymer, the An is linked through its 2-position. As in the case of PS−PMMA, we find a weak parasitic emission that must be subtracted from the measured donor decay profiles. Here the emission is only from the An-labeled polymer at a wavelength 350−355 nm where no anthracene emission occurs. Because of concerns that this emission might arise because of sample aging or because of the substantial amount of antioxidant added by Ni[10−12] to samples prepared previously in this laboratory, we prepared new samples, exercising care to ensure that the 2-substituted anthracene derivative used here was free of its 1-substituted isomer.[21] We refer to these samples as PI-9Phe-PMMA and PI-2An-PMMA, respectively. We carried out fluorescence decay measurements on samples consisting of mixtures of these polymers and interpreted the decay profiles in terms of the Yekta model[16,17] for energy transfer in restricted dimensions. This model takes explicit account of the distribution of donor and acceptor dyes in the block copolymer interface.



PI-9Phe-PMMA



PI-2An-PMMA

Experimental Section

Characterization. UV−vis absorption spectra were recorded on Perkin-Elmer Lambda 6 UV/vis spectrophotometer. Molecular weights (M) and molecular weight distributions (MWD) were determined by gel permeation chromatography (Waters GPC 515), using THF as the eluent and PMMA as molecular weight standards. Signals were collected using tandem fluorescence (FL) and refractive index (RI) detectors. For the FL detector, the excitation/emission wavelengths were 300 nm/399 nm for phenanthrene and 350 nm/450 nm for anthracene. Fluorescence spectra were measured with a Perkin-Elmer fluorescence spectrometer LS50B. Fluorescence decay profiles were measured by the single photon timing technique with a pulsed lamp (0.5 atm of D_2) as an excitation source. Small-angle X-ray scattering (SAXS) measurements for lamellar spacing of the symmetric diblock copolymer were performed on a NanoStar X-ray camera from Bruker AXS GmbH. It was operated with a Cu Kα line ($\lambda = 0.154$ nm) and a sample-to-detector distance of 62.85 mm. The scattering patterns were recorded with Hi-Star 2-D X-ray detector. Azimuthal integration from 0° to 360° was subsequently used to extract the q dependence of the scattering intensity.

Table 1. Characteristics of the Diblock Copolymers

polymers	M_n(GPC)[a]	M_n(UV)[b]	PDI[a]	V_{PI}:V_{PMMA}[c]
PI-9Phe-PMMA	32 600	32 300	1.17	51.5:48.5
PI-2An-PMMA	28 600	30 600	1.11	51.2:48.8

[a] Relative to PMMA standards. [b] Assuming diblock copolymers and their corresponding model compounds have the same molar extinction coefficient. [c] Calculation is based on ^{1}H NMR analysis.

Table 2. Mole Fractions of Phe and Concentrations of An in the Polymer Films

film no.	mole ratio Phe/An	mole fraction Phe (f_{Phe})[a]	concn of An, C_A^0 (mM)[b]
1	1:0	1	0
2	9.15:1	0.90	3.21
3	3.53:1	0.78	7.31
4	2.07:1	0.67	10.93
5	1.63:1	0.62	12.84
6	0.9:1	0.47	18.12
7	0:1	0	36.5

[a] Calculated from $f_{Phe} = m_{PI-9Phe-PMMA}/(m_{PI-9Phe-PMMA} + m_{PI-2An-PMMA})$, where m refers to the moles of sample. [b] The bulk-averaged An concentration, 36.5 mmol/L, in PI-2An-PMMA, was calculated with the aid of the densities of PMMA (1.19 g/cm^3) and PI (0.913 g/cm^3), the molar masses of the two copolymers, and the condition that there is only one dye per polymer chain.

Polymer Synthesis and Characterization. The synthesis and characterization of the An-substituted polymer examined here have been reported separately.[21] The Phe-labeled polymer was synthesized as described by Tcherkasskaya et al.[10] In both syntheses, isoprene was polymerized anionically in tetrahydrofuran and then end-capped with a 1-aryl-1-phenylethylene derivative. The anion formed was used subsequently to initiate MMA polymerization. For the Phe-labeled polymer, the aryl group was phenanthrene, attached to the double bond at the 9-position. For anthracene, the aryl group was anthracene attached via the 2-position. Comparable molecular weights obtained from GPC and UV experiments for both of the diblock copolymers are consistent with one dye molecule in each polymer chain. PI-2An-PMMA, which is free of dye isomers, was synthesized and characterized previously.[21] GPC analysis showed that this sample was free of unreacted dye monomer. The characteristics of the two diblock copolymers are shown in Table 1.

Sample Preparation. PI-9Phe-PMMA and PI-2An-PMMA were each dissolved in a mixture of tetrahydrofuran/cyclohexane (THF/CH: 9:1 v/v) to form 5 wt % solutions. These solutions were mixed to give solutions with different weight ratios of the two polymers. A gas-tight syringe was used to measure 0.2 mL of each solution and spread them onto quartz plates (2 cm × 2 cm). These samples were dried very slowly at room temperature, in a box equipped with a small release hole in the presence of a reservoir containing additional THF/CH (9:1) mixed solvent in order to minimize the drying rate. In this way we obtained smooth transparent films of essentially identical thickness. The mole ratios of Phe to An and the bulk-averaged An concentrations of these films are shown in Table 2. These films, after drying, were annealed overnight at 140 °C under nitrogen. The thickness of each film was about 20 μm; the optical density of the Phe absorption at the excitation wavelength (300 nm) was small enough that the intensity of its fluorescence was proportional to the dye concentration. Through careful placement of these optical quality films in a goniometer mounted in the sample chamber of the fluorescence decay instrument, we were able to subtract background fluorescence from the measured signal of the polymers.[20]

Fluorescence Decay Measurements. Fluorescence decay profiles were measured by the single photon timing technique[22] at room temperature. The samples were excited at $\lambda_{ex} = 300$ nm, and the phenanthrene fluorescence was detected at $\lambda_{em} = 350$ nm. A band-pass filter (350 ± 5 nm) was used to cut off emission from anthracene. Decay curves were also corrected for a weak background emission at 350 nm associated with the An-labeled polymer. For samples containing different amounts of this component, we subtracted weighted amounts of this background signal from the measured decay before proceeding with data analysis. The integrated area of this emission represented at most 3% of the area of the donor decay in the samples described here.[23] We refer to the decay profiles treated in this way as "corrected decays".

The mimic lamp profile, used for the convolution analysis,[19] was obtained by exciting a solution of *p*-terphenyl in de-aerated cyclohexane (lifetime: 0.96 ns). The films were mounted on a goniometer in the sample chamber of the fluorescence decay instrument, and the positions of films were controlled at 20 ± 1° from the excitation beam to eliminate the scattered light from the excitation beam. In each experiment, 10 000 counts were collected in the maximum channel; measurement times ranged from 15 to 90 min depending on the ratio of donor and acceptor concentrations in the films. Model decay profiles $I_D(t)$ were parametrized by convoluting trial decay functions with the instrument response time Lamp(t') determined by the Mimic technique [19] to find the best fit to the measured decay profile $I_{\text{meas}}(t)$.

$$I_{\text{meas}}(t) = I_0 \int I_D(t - t')\ \text{Lamp}(t')\ \mathrm{d}t' \tag{1}$$

Direct nonradiative energy transfer (DET) experiments take advantage of the distance dependence of the energy transfer rate $w(r)$, where r is the distance between the centers of the transition dipoles of the donor and acceptor.[24]

$$w(r) = \frac{3}{2}\kappa^2 \frac{R_0^6}{\tau_D r^6}\,\mathrm{d}\nu \tag{2}$$

The characteristic (Förster) energy transfer distance R_0 is related to the spectroscopic properties of the donor and acceptor in the medium.

$$R_0{}^6 = \frac{2}{3}\,\frac{9000(\ln 10)\phi_D}{128\pi^5 n^4 N_A}\int_0^\infty \frac{F_D(\nu)\,\epsilon_A(\nu)}{\nu^4} \tag{3}$$

Here N_A is Avogadro's number, Φ_D is the donor fluorescence quantum yield in the absence of acceptor, τ_D is the unquenched donor lifetime, $F_D(\nu)$ is the fluorescence intensity of the donor at the wavenumber ν normalized to unit area on the wavelength scale, and $\epsilon_A(\nu)$ is the extinction coefficient of the acceptor. The term κ^2 is a geometric orientation factor. In a coordinate system in which a donor is located at θ_d (polar angle), ϕ_d (azimuthal angle), and the acceptor at θ_a, ϕ_a, the orientation factor can be written[25]

$$\kappa^2 = (\sin\theta_a \sin\theta_d \cos(\phi_a - \phi_d) - 2\cos\theta_a \cos\theta_d)^2 \tag{4}$$

which takes the average value $\langle\kappa^2\rangle = {}^2/_3$ for rapidly reorienting dipoles in three-dimensional homogeneous media. Preaveraging over randomly oriented dipoles in three-dimensional rigid media leads to the value $\langle\kappa^2\rangle = 0.476$.[26] R_0 is calculated assuming rapid dipole orientation, and the factor ${}^3/_2$ in eq 1 is introduced to remove this term.[27] For the experiments described here we use the value of R_0 determined by Duhamel et al.[28]

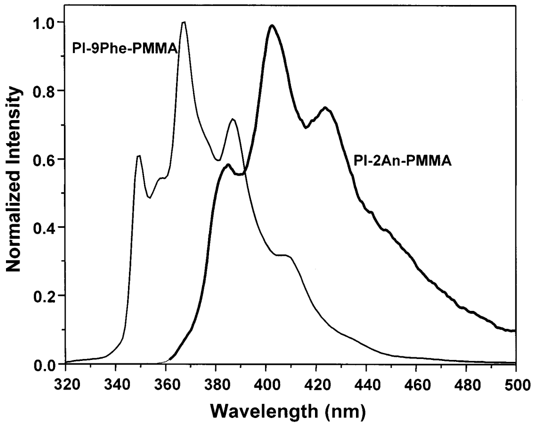


Figure 1. Fluorescence emission spectra of the diblock copolymer films: PI-9Phe-PMMA and PI-2An-PMMA.

For a random distribution of donors and acceptors in three dimensions, the donor decay function will have the stretched exponential form first derived by Förster.[29]

$$I_D(t) = \exp\left(-\frac{t}{\tau_D}\right)\exp\left[-P\left(\frac{t}{\tau_D}\right)^{0.5}\right] \tag{5}$$

The parameter P depends on the local concentration of acceptors and on the ensemble averaged magnitude of the orientation parameter $\langle\kappa^2\rangle$

$$P = \frac{4}{3}\pi^{3/2}\,C_A R_0{}^3\left(\frac{3\langle\kappa^2\rangle}{2}\right)^{1/2} \tag{6}$$

When the donors and acceptors are confined to the restricted geometry of a block copolymer interface, the form of $I_D(t)$ depends on the details of the distribution of donors and acceptors in the system. We discuss this topic in a later section of this paper.

Results and Discussion

Our data analysis depends on two characteristics of the fluorescence decay experiments—that the unquenched donor decay is exponential and in films containing donor plus acceptor that the donor decay is not contaminated with emission from the acceptor. We find that the Phe fluorescence decay in films of PI-9Phe-PMMA is exponential with $\tau_D = 44.8$ ns. The fit is excellent, with randomly distributed weighted residuals and a random autocorrelation of the residuals. In Figure 1 we show for film samples the fluorescence spectra of the Phe group of PI-9Phe-PMMA and the An group of PI-2An-PMMA. From these spectra we see that donor emission should be measured using a narrow band-pass filter limited to 350 ± 5 nm to minimize emission from the An group in the measured donor decay profiles.

A series of film samples were prepared containing different amounts of the Phe- and An-labeled polymers. We refer to these samples in terms of the fraction f_{Phe} of Phe-labeled polymer in the films as shown in Table 2. A series of fluorescence decay curves measured for those various samples are shown in Figure 2. We also show in Figure 2 the rapid decay obtained for a solution of *p*-terphenyl in aerated cyclohexane, which is used by the mimic technique[19] to calculate the instrument response time of the lamp profile, representing the pulsed source used to excite the samples at 300 nm.

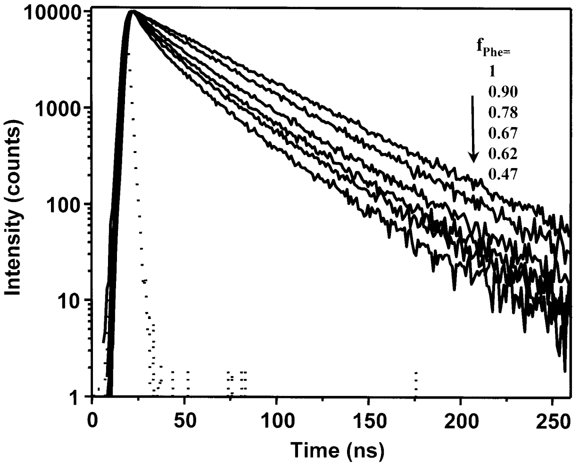


Figure 2. Normalized fluorescence decays from films of identical thickness (±4%) consisting of PI-9Phe-PMMA and PI-2An-PMMA copolymer mixtures. The values of f_{Phe} (see Table 1) are indicated on the graph. The dotted line is the mimic lamp profile, obtained by exciting a solution of *p*-terphenyl in de-aerated cyclohexane (lifetime: 0.96 ns).

Polymer Morphology and Dye Distribution in the Interface. Symmetric diblock copolymers undergo microphase separation to form periodic structures when the product of the Flory–Huggins interaction parameter and the overall chain length $\chi_{FH}N > 10.4$.[2] On the basis of earlier energy transfer experiments, we have estimated $\chi_{FH} \approx 0.08$ for PI–PMMA;[10–12] thus, for the samples we examine here $\chi_{FH}N > 20$. Symmetric samples of PI–PMMA are expected to form a periodic lamellar structure at equilibrium. Kim and Kressler[30] used transmission electron microscopy to examine several of the PI–PMMA samples prepared by Ni[10–12] in our group. They found that symmetrical samples formed a hexagonal phase consisting of PI cylinders surrounded by a PMMA matrix when the films were cast from THF solution. In contrast, a lamellar phase was formed when the polymer was slowly evaporated from a 90:10 (v/v) mixture of THF:cyclohexane. For this reason, we prepared our samples from this solvent mixture to ensure that we obtained a lamellar morphology.

Helfand and Tagami[31–33] developed a mean-field model to describe the segment density profile of polymers across the interface in diblock copolymers and binary polymer blends for strong segregation and the high molecular weight limit. For polymers of finite length, the block copolymers differ from the blends by an added term for the block copolymers that takes account of the entropy penalty for localization of the junction points in the interface.[34] While this term affects the magnitude of the interface thickness δ, it has a much smaller effect on the hyperbolic tangent form of the segment density profiles across the interface.[35,36]

$$\rho_{PMMA}(z) = \frac{1 + \tanh\left(\frac{2z}{\delta}\right)}{2}; \quad \rho_{PI}(z) = \frac{1 - \tanh\left(\frac{2z}{\delta}\right)}{2} \qquad (7)$$

where δ is the interface thickness and z is the distance normal to the plane of the interface, taken to be centered at $z = 0$. Under these circumstances, the junction distribution density $P_j(z)$ across the interface is given by

$$P_j(z) = \frac{2\pi}{\delta}\,\mathrm{sech}\left(\frac{2z}{\delta}\right) \qquad (8)$$

In the theory of energy transfer in restricted geometries, donor groups are excited with equal probability independent of their location in the matrix. For each excited donor, the probability of DET is described by integration over the distance dependence of $w(r)$ (eq 2) and the distribution of acceptors imposed by the geometry of the system.[13–15] Yekta et al.[16,17] used these ideas originally developed by Klafter and Blumen to derive expressions appropriate for donors and acceptors distributed along the z-axis normal to a dividing surface. In this model, the donor decay profile $I_D(t)$ can be expressed as

$$I_D(t) = I_0 \exp(-t/\tau_D)\int C_D(z) \exp[-g(z,t)]\, dz \qquad (9a)$$

$$g(z,t) = 2\pi\int_0^\infty \langle C_A(r,z)\rangle[1 - \exp(-tw(r))]r\, dr \qquad (9b)$$

$$\langle C_A(r,z)\rangle = N_A\int_{z-r}^{z+r} C_A(r')\, dr' \qquad (9c)$$

where I_0 is the intensity at $t = 0$. $C_D(z)$ and $C_A(z,r)$ describe the donor and acceptor distributions, respectively. Since the donor and acceptor dyes are attached to the junctions of the block copolymers, their distribution follows that of the junctions and

$$C_D(z) = C_D^0(z)\, P_j(z); \quad C_A(z) = C_A^0(z)\, P_j(z) \qquad (10)$$

where $C_D^0(z)$ and $C_A^0(z)$ refer respectively to the bulk-averaged molar concentration of donor and acceptor groups in the sample. From the molecular weights of the polymers and the densities of their components we calculate $C_D^0(z) = 32.2$ mM for PI-9Phe-PMMA and $C_A^0(z) = 36.5$ mM for PI-2An-PMMA.

The efficiency of energy transfer for donor–acceptor pairs is given by the expression[24]

$$\Phi_{ET} = 1 - \frac{\int_0^\infty I_D(t)\, dt}{\int_0^\infty I_D^0(t)\, dt} = 1 - \frac{\int_0^\infty I_D(t)\, dt}{\tau_D} \qquad (11)$$

where $I_D(t)$ is the normalized intensity of the donor–acceptor system at time t and $I_D^0(t)$ is the corresponding decay for a sample free of acceptor. When the $I_D^0(t)$ decay is exponential, the integral is equal to the unquenched donor lifetime τ_D. The efficiency of energy transfer calculated for PI-9Phe/2An-PMMA films is shown in Figure 3. One can see that these values are strongly enhanced compared to the values that would be predicted from eq 6 based on the bulk averaged concentrations $C_D^0(z)$ and $C_A^0(z)$. Mendelsohn et al.[37] have commented that even if the polymers were in a random disordered state, correlation effects would decrease the local dye concentrations over that predicted from bulk concentrations. The data in Figure 3 establish that attachment of the dyes to the block copolymer junctions confines them to domains with enhanced local concentrations.

Interface Thickness Determination Using Energy Transfer. In this section we determine the interface thickness based on Helfand–Tagami interface theory and the kinetics of energy transfer that take account of the distribution of donor and acceptor dyes.

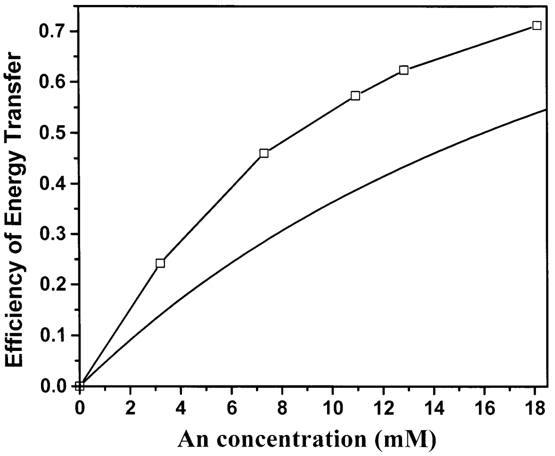


Figure 3. Efficiency of energy transfer as a function of the bulk-averaged acceptor concentration in diblock copolymer films. The efficiency for homogeneous system with the same R_0 and κ^2 (Förster equation, lower line) is also presented for comparison.

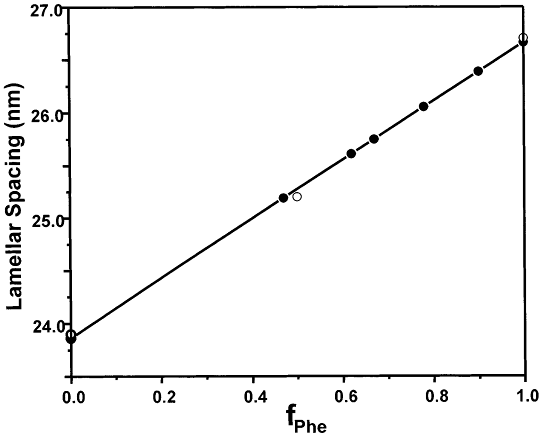


Figure 4. Plot of the lamellar spacing against f_{Phe}. The experimental results are shown as open circles. The solid line is the fitting based on Semenov's theory.[38] The filled points are the estimated lamellar spacing for the five different mixtures of PI−PMMA examined in this paper.

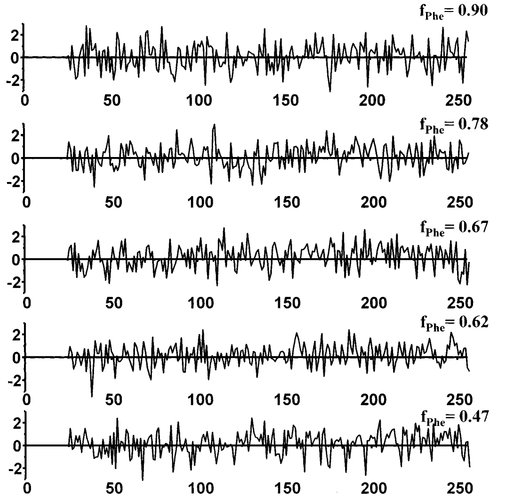


Figure 5. Weighted residuals from the fitting of experimental decay curves for all samples.

Our analysis of the interface of diblock copolymer is based upon a comparison of experimental and simulated donor decay curves using eqs 7−10, in which the interface thickness δ is the only variable to be optimized. For a given donor and acceptor concentration, Förster radius and lamellar spacing of diblock copolymer film, the value of the interface thickness was optimized by choosing the fluorescence decay curve which gave the best fitting (least-squares algorithm) with the experimental decay curve after convolution with the reference lamp profile.

In our data analysis, we determined independently the lamellar spacing of our diblock copolymers because the Phe- and An-labeled polymers have slightly different molecular weights. The lamellar spacing of each sample should therefore depend on the blend composition. To test this idea, we prepared three films in the same way as films for energy transfer experiments. One film consisted of pure PI-9Phe-PMMA, the second of PI-2An-PMMA, and the third of a 1:1 mixture. The lamellar spacings as calculated from the primary maximum of the SAXS profile define a straight line when plotted against composition, as shown in Figure 4. The experimental data are shown as open circles in the figure. According to Semenov's theory,[38] the lamellar spacing H and overall chain length N have the following relationship in the strong segregation limit, where a is the length of a monomer:

$$H \propto aN^{2/3}\chi_{\mathrm{FH}}^{1/6} \tag{12}$$

Equation 12 is asymptotically correct in the limit $\chi_{\mathrm{FH}}N \rightarrow \infty$. For the same diblock copolymer, the lamellar spacing is thus proportional to $N^{2/3}$. If we assume that eq 12 is still applicable in the range of molecular weights of our polymers, we can estimate the lamellar spacings expected for the samples we examine here, shown in Figure 4 as solid points.

In previous experiments in our laboratory,[27] an R_0 value of 2.3 nm for the phenanthrene−anthracene chromophore pair was obtained for the model compounds in 1,4-dioxane solution using the overlap integral method. This value is confirmed by more recent experiments by Roller in our laboratory, which will be described in a future publication.[39] The choice of the best value for the orientation parameter κ^2 is more subtle and will discussed below. In our previous work,[20] $\langle\kappa^2\rangle$ was chosen as 0.476, the number appropriate for preaveraged random dipole orientations for immobile donors and acceptors. In this paper, we use the values $R_0 = 2.3$ nm and $\langle\kappa^2\rangle = 0.476$ as input parameters to simulate fluorescence decay profiles expected for a diblock copolymer of known lamellar spacing, based upon the theory of energy transfer in restricted geometries. In Figure 5 we plot the weighted residuals for the best fits to the fluorescence decay curves shown in Figure 2 after correction for background fluorescence. In Figure 6, we show plots of the goodness-of-fit parameter χ^2 against the assumed value of the interface thickness δ used in the simulations. The χ^2 plots become steeper, and the experiment becomes more sensitive to the chosen value of the interface thickness, as the acceptor concentration increases in the system.

The best-fit interface thickness vs bulk-averaged An concentration is show in Figure 7. The interface thickness, 1.6 ± 0.1 nm, is almost independent of the individual An concentrations in the polymer films. This value is smaller than the value (2.6 nm) we obtained previously from DET experiments analyzed in terms of a model[10] that did not take account of the donor and acceptor distribution in the interface. Those experiments

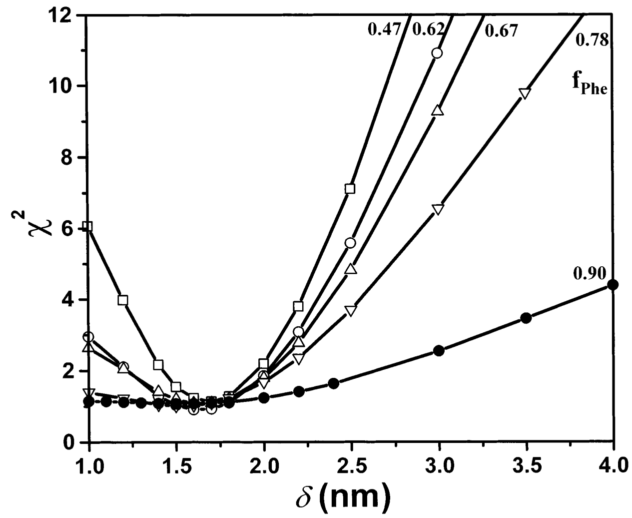


Figure 6. χ^2 surface as a function of the assumed interface thickness δ for all prepared samples. The values of the mole fraction of Phe for each curve are indicated in the figure.

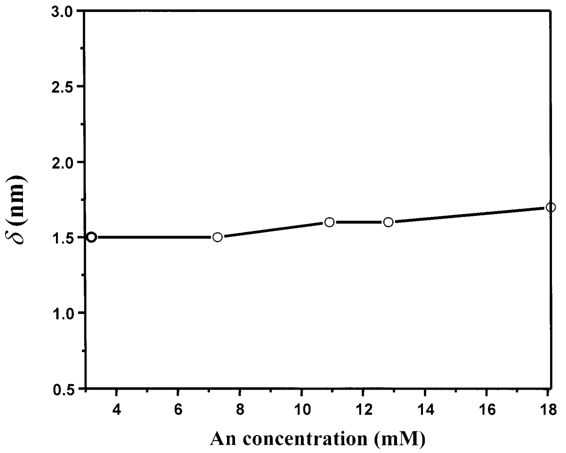


Figure 7. Plot of the optimum values of the interface thickness, taken from Figure 6, against the bulk An concentration in each sample.

also did not attempt to correct for background emission from the polymers and antioxidant additive. The value of δ we obtain is close to the value (1.8 nm) inferred by Hashimoto[3,40] from SAXS measurements on PS−PI.

In an earlier section, we referred to an earlier estimate of the magnitude of the Flory−Huggins interaction parameter χ_{FH} for PI and PMMA based upon an estimated interface thickness of 2.6 nm. The more rigorous experiments described here led to a δ value of 1.6 nm. The narrower interface implies a larger value of χ_{FH}. For block copolymers in strong segregation limit, the relationship between Flory−Huggins interaction parameter and interface thickness can be expressed as[34]

$$\delta = \frac{2b}{(6\chi_{FH})^{1/2}}(1 + 1.34/(N\chi_{FH})^{1/3}) \qquad (13)$$

where the second term inside the parentheses takes into account the entropy of localization of the joints in the interface for chains of finite length. Equation 13 does not take into account that copolymer chains in the strong segregation limit are elongated in the direction normal to the interface, nor does it account for thermal fluctuations that leads to waviness of the interface. Semonov has discussed the small effect of elongation on the interface calculation.[34] Capillary waves and other thermal fluctuations of the interface play an important role in scattering experiments,[41] and should not have an influence on our results, because the DET experiment operates over only a very short length scale. In evaluating eq 13, we set $b = 0.63$ nm as reasonable estimate of the statistical length of a monomer.[10] In this way, we calculate $\chi_{FH} = 0.18 \pm 0.02$. This value, which is nearly twice the value obtained for PI−PS by SAXS[42] (but see Vavasour and Whitmore[43]), does depend on our choice of a value of b to insert into eq 13.

The Orientation Factor κ^2. There are two features of the orientation factor that pose important scientific challenges to our understanding of block copolymer interfaces. The first and most difficult is whether chain stretching at the interface leads to an orientation preference for the chain backbone. If there is a preferred orientation of the polymer backbone at the interface, this can affect the range of orientations of the donor and acceptor dyes. This is a topic that can be addressed through molecular simulations of block copolymer structure or by developments in the theory of block copolymers. If appropriate simulations were available, they could be used to test the issues that we raise in this section. We know of no attempts in the polymer literature to address this matter.

The second feature concerns the validity of preaveraging the orientation parameter. In the definition of R_0 (eq 3), one treats the case of rapidly reorienting dipoles, for which one obtains a preaveraged value $\langle\kappa^2\rangle = {}^2/_3$. The preaveraged value for randomly oriented immobile transition dipoles in three dimensions, $\langle\kappa^2\rangle = 0.476$.[26] In the biochemical community, resonant energy transfer is used as a spectroscopic ruler[44] to measure distances between sites on biomacromolecules. For this type of application, where the distribution of distances is often narrow, there has been concern that preaveraging of κ^2 may lead to incorrect results when the dyes are immobile on the time scale of the fluorescence lifetime.[45,46] Individual values of κ^2 vary between 0 for orthogonal dipoles to 4 for aligned and parallel dipoles. There is a particular concern, for the case of a single donor/acceptor (D/A) in each molecule, whether there is a coupling between the distance between the dyes and the influence of κ^2 on the efficiency of energy transfer. For example, Wu and Brandt[25] carried out Monte Carlo calculations of the DET efficiency Φ_{ET} for a D/A pair separated by a fixed distance (r/R_0) with randomly selected orientations. They found a broader distribution of Φ_{ET} values for $R_0/r = 1.37$ (i.e., close pairs) than for $R_0/r \approx 1$ or $R_0/r = 0.64$. They also found that a substantial fraction of the pairs had Φ_{ET} values close to zero.

We raise this issue here because the interface thickness we find from our data analysis is smaller than the Förster energy transfer distance, $\delta/R_0 = 0.7$. The mean separation of D and A groups in our experiment depends on the shape of the junction distribution profile and varies with the ratio of acceptor-to-donor labeled polymer. As a test of the sensitivity of our data analysis to the mean separation between donor and acceptor chromophores, we plot values in Figure 7 of the optimum interface thickness against f_{Phe}, the fraction of donor-labeled polymer in the film. We find that δ is insensitive to this ratio. From this perspective, we conclude that employing a preaveraged orientation parameter leads to self-consistent results in our experiments.

It would be worthwhile, nevertheless, to carry out molecular simulations of a block copolymer lamella in such a way that the distance distributions between the junctions would be known. Then one could employ Monte Carlo or other statistical methods to evaluate how the energy transfer experiment is affected by the details of the junction distribution.

Summary

In this paper, we used direct nonradiative energy transfer as a tool to study the interface of symmetric PI−PMMA diblock copolymers. Each experiment examined a film consisting of a mixture of two polymers of similar chain length and composition, one containing a donor dye at the junction and the other an acceptor dye. Input parameters for the data analysis were the lamellar spacing determined by SAXS, the characteristic Förster ET distance R_0, and a preaveraged value of the dipole orientation parameter appropriate for randomly oriented immobile dipoles. On the basis of an analysis of the fluorescence decay profile that takes account of the junction distribution in the interface, we calculate an interface thickness of 1.6 ± 0.1 nm. On the basis of this value and the theory of Semenov, we estimate a value for the Flory−Huggins interaction parameter for the PI−PMMA diblock copolymer as 0.18 ± 0.02.

Acknowledgment. The authors thank NSERC Canada for their support of this research and John G. Spiro for fruitful discussions.

References and Notes

(1) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.
(2) Hamley, I. W. *The Physics of Block Copolymers*; Oxford Press: New York, 1998; Chapter 2.
(3) Hashimoto, T.; Fujimura, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1660.
(4) Sakura, S. *Trends Polym. Sci.* **1995**, *3*, 90.
(5) Bates, F.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(6) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys.* **1990**, *92*, 5677.
(7) Russell, T. P.; Menelle, A.; Hamilton, W. A.; Smith, G. S.; Satija, S. K.; Majkrzak, C. F. *Macromolecules* **1991**, *24*, 5721.
(8) Shull, K. R.; Mayes, A. M.; Russell, T. P. *Macromolecules* **1993**, *26*, 3929.
(9) Ni, S.; Zhang, P.; Wang, Y.; Winnik, M. A. *Macromolecules* **1994**, *27*, 5742.
(10) Tcherkasskaya, O.; Ni, S.; Winnik, M. A. *Macromolecules* **1996**, *29*, 610.
(11) Tcherkasskaya, O.; Ni, S.; Winnik, M. A. *Macromolecules* **1996**, *29*, 4241.
(12) Tcherkasskaya, O.; Spiro, J. G.; Ni, S.; Winnik, M. A. *J. Phys. Chem.* **1996**, *100*, 7114.
(13) Klafter, J.; Blumen, A. *J. Chem. Phys.* **1984**, *80*, 874.
(14) Klafter, J.; Drake, J. M. *Molecular Dynamics in Restricted Geometries*; Wiley: New York, 1989.
(15) Drake, J. M.; Klafter, J.; Levitz, P. *Science* **1991**, *251*, 1574.
(16) Yekta, A.; Duhamel, J.; Winnik, M. A. *Chem. Phys. Lett.* **1995**, *235*, 119.
(17) Yekta, A.; Winnik, M. A.; Farinha, J. P. S.; Martinho, J. M. G. *J. Phys. Chem. A* **1997**, *101*, 1787.
(18) Farinha, J. P. S.; Martinho, J. M. G.; Kawaguchi, S.; Yekta, A.; Winnik, M. A. *J. Phys. Chem.* **1996**, *100*, 12552.
(19) Yekta, A.; Spiro, J. G.; Winnik, M. A. *J. Phys. Chem. B* **1998**, *102*, 7960.
(20) Rharbi, Y.; Winnik, W. A. *Macromolecules* **2001**, *34*, 5238.
(21) Yang, J.; Lu, J.; Winnik, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1225.
(22) Phillips, D.; O'Connor, D. V. *Time Correlated Single Photon Counting*; Academic Press: London, 1984.
(23) GPC analysis with fluorescence detection show that the impurity emission is associated with the polymer. Samples of **PI-2An-PMMA** synthesized 5 years ago by Ni[10−12] show the same results.
(24) Lakowicz, J. R., Ed. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; Vol. 10.
(25) Wu, P.; Brand, L. *Biochemistry* **1992**, *31*, 7939.
(26) Baumann, J.; Fayer, M. D. *J. Chem. Phys.* **1986**, *85*, 4087.
(27) Farinha, J. P. S.; Spiro, J. G.; Winnik, W. A. *J. Phys. Chem. B* **2001**, *105*, 4879.
(28) Duhamel, J.; Yekta, A.; Ni. S.; Khaykin, Y.; Winnik, M. A. *Macromolecules* **1993**, *26*, 6255.
(29) Förster, Th. *Ann. Phys. (Leipzig)* **1948**, *2*, 55. Förster, Th. *Z. Naturforsch.* **1949**, *4A*, 321.
(30) Kim, Y. Diplomarbeit in University of Freiburg, 1997.
(31) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56*, 3592.
(32) Helfand, E. *Macromolecules* **1975**, *8*, 552.
(33) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1980**, *13*, 994.
(34) Semenov, A. N. *Macromolecules* **1993**, *26*, 6617.
(35) Matsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29*, 1091.
(36) Kikuchi, M.; Binder, K. *J. Chem. Phys.* **1994**, *101*, 3367.
(37) Mendelsohn, A. S.; Delacruz, M. O.; Torkelson, J. M. *Macromolecules* **1993**, *26*, 6789.
(38) Semenov, A. N. *Sov. Phys. JEPT* **1985**, *61*, 733.
(39) Roller, R.; Winnik, M. A., unpublished results.
(40) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.
(41) This term describing waviness is important in neutron scattering or reflectivity experiments, because the coherent radius in such kinds of experiments is typically much larger than the periodic spacing. As a consequence, the apparent segment profile across the interface sampled by the experiment is broader than the profile one would obtain with a flat interface.
(42) Hashimoto, T.; Ijichi, Y.; Fetters, L. J. *J. Chem. Phys.* **1988**, *89*, 2463.
(43) Vavasour, J. D.; Whitmore, M. D. *Macromolecules* **2001**, *34*, 3471.
(44) Stryer, L. *Annu. Rev. Biochem.* **1978**, *47*, 819.
(45) Dale, R. E.; Eisinger, J.; Blumber, W. E. *Biophys. J.* **1979**, *26*, 161.
(46) Cundall, R. B., Dale, R. B., Eds. *Time-Resolved Fluorescence Spectroscopy in Biochemistry and Biology*; Plenum Press: New York, 1983; Vol. 69, p 411.

MA030005R