Energy Transfer Study of Symmetric Polyisoprene−Poly(methyl methacrylate) Diblock Copolymers Bearing Dyes at the Junctions: Dye Orientation

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ABSTRACT: Direct nonradiative energy transfer experiments are described for the lamellar structures formed in films of poly(isoprene-*b*-methyl methacrylate) in which individual polymers are labeled at the junction with a single dye molecule. The donor was 9-phenanthryl (9Phe), and we compare two acceptors (1-anthryl (1An) and 2-anthryl (2An)) which differ in the orientation of their transition moments with respect to the polymer backbone. Experiments on the lamellar structures formed in films of PI-9Phe-PMMA/PI-1An-PMMA and PI-9Phe-PMMA/PI-2An-PMMA provide identical values of the interface thickness (1.1 ± 0.2 nm) between the PI and PMMA domains. The fact that a common value is obtained for the two sets of experiments indicates that the orientation parameter κ^2 for the energy transfer process in this rigid system makes an identical contribution to both sets of experiments. We take these results as justification for using an averaged value of the orientation parameter $\langle|\kappa|\rangle^2$ in fitting experimental data to the underlying theory of energy transfer. We find that in our experiments the local correlation in orientation of the polymer chains in the region of the interface is too small to be detected.

Introduction

Immiscible polymer blends form separate phases in the bulk state. Block copolymers with the same constituents undergo microphase separation, forming periodic structures if the molar mass distribution is sufficiently narrow.[1] In either case, the two types of domains are separated by an interface with a width that is normally larger than the size of a monomer unit but much smaller than the radius of gyration of either of the chains. Polymer blends and block copolymers are expected to have similar interface composition profiles, in which the interfacial thickness depends on the thermodynamic interaction parameter (χ_{FH}) between the two components, the chain lengths of the components, and, for block copolymers, an entropy term for localization of the junctions in the interface. Polymer interfaces are very difficult to characterize.

Symmetric block copolymers form lamellar structures in the bulk state. For these systems, if one of the blocks is deuterated, specular neutron reflectivity (SNR) measurements provide excellent quantitative raw data related to the width of the interface.[2,3] The challenge in interpreting these data is to separate the interface width, which measures the diffuse distribution of monomer units of the two components across the dividing surface between the two microdomains, from the waviness of the dividing surface.[4]

We have been interested in using direct nonradiative energy transfer (DET) experiments to probe the width of the interface in block copolymer systems.[5−7] In this type of experiment, one synthesizes pairs of block copolymers containing a single dye at the junction. One polymer contains a donor chromophore (D) at the junction, the other an acceptor (A). One of the attractive features of this experiment is that the junctions define the interface. By carrying out experiments which monitor DET between D-groups at the junction to A-groups at the junction, one obtains information about the spatial distribution of junctions in the interface. Another important feature of the interface is that the range of the energy transfer step is so short that the experiment becomes insensitive to waviness of the dividing surface between the domains.[7,8] Finally, the DET experiment can be carried out in systems with cylindrical or spherical morphologies, where the SNR experiment fails. We have shown that, in a properly executed series of experiments, the *precision* in the data from which inferences about the interface thickness are drawn is comparable to that for the data in an SNR experiment.[8]

Proper data interpretation in DET experiments on block copolymer melts requires that three parameters be known independently. The first is the repeat length of the periodic structure. This information is available from small-angle X-ray scattering (SAXS) measurements. The second parameter is the characteristic energy transfer distance (the Förster radius R_0). Finally, one needs a value for the orientation parameter κ^2 that characterizes the relative orientation of transition dipoles of the D- and A-groups in the system. Roller in our group has carried out a careful determination of R_0 values for the types of donors (e.g., phenanthrene, Phe) and acceptors (e.g., anthracene, An) that we have found to be useful for these DET experiments.[9] While his detailed analysis of this measurement will be reported elsewhere, we describe in a later section of this paper the determination of the R_0 values important for interpreting the experiments described here.

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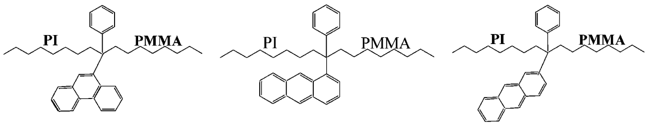
Chart 1



PI-9Phe-PMMA **PI-1An-PMMA** **PI-2An-PMMA**

Here we are interested in the influence of the orientation parameter on DET experiments involving the interface of symmetrical poly(isoprene-*b*-methyl methacrylate) (PI−PMMA) block copolymers.[6,7] We designed a system in which we use two different acceptor-labeled polymers. Both polymers have an An group attached to the junction, but the point of attachment is different. In one polymer, the anthracene is attached through its 1-position (PI-1An-PMMA). In the other, it is attached through its 2-position (PI-2An-PMMA).[10] The donor-labeled polymer has a phenanthrene chromophore attached via its 9-position (PI-9Phe-PMMA). The structures of these polymers are shown in Chart 1. The polymers form lamellar structures whose periods were determined by SAXS measurements. One set of experiments involves lamellae formed from the PI-9Phe-PMMA/PI-1An-PMMA block copolymer pair. The other set of experiments involves the PI-9Phe-PMMA/PI-2An-PMMA pair. Because of the differences in the positions of attachment of the dyes, the transition moments of the chromophores have different orientations relative to the backbones of their respective polymers. This difference is depicted in Figure 1. We imagine that if dye orientation is significant in these self-assembled structures, or if dye orientation were coupled in some significant way to the donor/acceptor separation distance, then the orientation parameter for the 9Phe/1An pair would be different from that for experiments involving the 9Phe/2An pair. Our experiments show that there is no major difference in the magnitude of the orientation parameter for these two sets of donor/acceptor pairs.

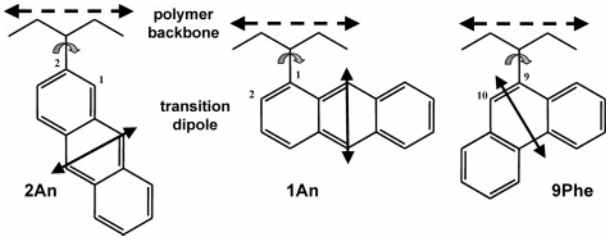


Figure 1. Schematic representation of the An chromophore and the Phe chromophore attached at the junction of a diblock copolymer. The position of attachment (1, 2, or 9) and the direction of the transition dipoles (solid arrows) are indicated in the figure. The dashed arrows stand for the orientations of the polymer backbone at the junction. Note that rotation of the chromophore about the bond connecting it to the polymer backbone (curved arrow) provides a limited range of relative orientations between the transition moment and the backbone vector at the junction.

Experimental Section

Instrumentation. UV−vis absorption spectra were recorded on a Perkin-Elmer Lambda 6 UV−vis spectrophotometer. Steady-state fluorescence spectra were measured with a Fluorolog 3 luminescence spectrometer from JY Horiba. SAXS measurements of the lamellar period of the symmetric diblock copolymer were performed using Cu Kα radiation ($\lambda = 0.154$ nm) through a pinhole collimation, and a 2D position-sensitive detector (Bruker) was used. Measurements were performed at room temperature. The recorded scattering intensity distributions were integrated over the azimuthal angle and are presented as functions of the scattering vector ($\mathbf{q} = 4\pi(\sin\theta)/\lambda$, where 2θ is the scattering angle). Fluorescence decay profiles were measured using the single-photon timing technique[11] following the procedure described previously.[7] These experiments employed a spark discharge in 0.5 atm of D_2 as the excitation source. Phenanthrene was excited selectively at 300 nm.

Synthesis and Characterization. The syntheses and characterization of the Phe and An model compounds[10,12] and the Phe- and An-labeled diblock copolymers have been reported previously.[7,10] The model compounds were used as standards both in the characterization of the dye content for the junction-labeled diblock copolymers and for the determination of the Förster radii. In all of the polymer 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 donor-labeled polymer, the aryl group was 9-phenanthryl (9Phe). For the acceptor-labeled polymer, the aryl group was anthracene attached via either the 1-position (1An) or the 2-position (2An). The molecular weights of the dye-labeled polymers and the analysis of the fraction of polymers containing the dye were carried out with a combination of gel permeation chromatography (GPC) and UV methods as described in ref 10.

Determination of Förster Radii of Phe−An Pairs in a PMMA Substrate. The Förster radii were determined by the spectral overlap method in which the magnitude of each of the terms in the definition of R_0 was measured individually:[13]

$$R_0^{\,6} = \frac{2}{3}\,\frac{9000(\ln 10)\Phi_f}{128\pi^5 N n^4}\,\frac{\int_0^\infty F_D(\lambda)\,\epsilon_A(\lambda)\,\lambda^4\,d\lambda}{\int_0^\infty F_D(\lambda)\,d\lambda} = 0.353\Phi_f J/Nn^4 \tag{1}$$

where N is Avogadro's constant. The integral in this equation, known as the spectral overlap integral (J), consists of three parts, the fluorescence spectrum of the donor, $F_D(\lambda)$, the extinction coefficient spectrum of the acceptor $\epsilon_A(\lambda)$ ($M^{-1}\,cm^{-1}$), and the wavelength, λ (nm). Φ_f is the donor fluorescence quantum yield in the absence of the acceptor, and n is the refractive index of the medium in the wavelength range of the spectral overlap. The corrected fluorescence spectrum $F_D(\lambda)$ was measured for 9-PheM dissolved in a PMMA matrix mounted on a quartz substrate. The spectrum $\epsilon_A(\lambda)$ was established by acquiring a series of absorption spectra on PMMA films containing a constant concentration of 1-AnM (4.90×10^{-3} M) or 2-AnM (5.11×10^{-3} M) with thicknesses ranging from 70 to 500 μm. Next, the extinction coefficient was determined from the slope of the Beer's law plot of absorbance vs thickness at the three wavelengths corresponding to the maxima of the three lowest energy vibronic transitions, and these values were used to scale the absorption spectrum to $\epsilon_A(\lambda)$. Corrections of $F_D(\lambda)$ for background fluorescence and $\epsilon_A(\lambda)$ for background absorbance originating from impurities in the PMMA matrix were carried out as described in ref 9.

The quantum yield determination was performed through area integration of the corrected fluorescence spectra of four samples of optical density varying from 0.01 to 0.04 in ethyl acetate solution. These were measured against the secondary reference standards 2-aminopyridine in 0.1 N H_2SO_4 ($\Phi_{Rf} = 0.60 \pm 0.05$) and naphthalene in cyclohexane ($\Phi_{Rf} = 0.23 \pm 0.02$). The yield in ethyl acetate (Φ_f^{EtAc}) was taken to be the linear extrapolation of these four quantum yields to zero optical density. The predicted quantum yield of fluorescence in PMMA (Φ_f^{PMMA}) was then calculated according to the equation

$$\frac{\Phi_f^{\,PMMA}}{\Phi_f^{\,EtAc}} = \frac{n_{PMMA}^{\;2}\tau_D^{\;PMMA}}{n_{EtAc}^{\;2}\tau_D^{\;EtAc}} \tag{2}$$

where τ_D^X is the fluorescence lifetime of 9PheM in medium X as obtained by time-correlated single-photon timing. As well, n_X is the tabulated refractive index of X at 25 °C, i.e., 1.437 for ethyl acetate and 1.492 for PMMA. The latter value was also employed for n in eq 1.

In the calculation of R_0^6 with eq 1, we follow the common practice of using the value of κ^2 (=2/3) preaveraged for the case of mobile chromophores in solution with rapidly rotating transition dipoles. In our system, the chromophores are immobile on the nanosecond time scale. For this system, the DET experiment (see below) considers an effective energy transfer distance ($R_{\text{eff}}^6 = (3/2)\langle|\kappa|\rangle^2 R_0^6$) in which the value of the orientation factor is that appropriate for the conditions of the experiment. For donor and acceptor transition dipole moments that are randomly oriented and immobile on the time scale of donor fluorescence, the orientation factor $\langle|\kappa|\rangle^2$ has the value 0.476.[14] Our two sets of diblock copolymer systems have different acceptor dipole orientations (for 1An and 2An) relative to the polymer backbone. One aspect of the experiment we wish to examine is whether the preaveraged orientation factor, 0.476, is still appropriate for our DET experiments (see below). The two sets of diblock copolymer lamellae should have very similar interface thicknesses, and thus very similar spatial distributions of donor and acceptor dyes. Any difference in the apparent distance distribution for the two systems obtained from analysis of our data would be an indication of the inappropriate use of a preaveraged orientation factor.

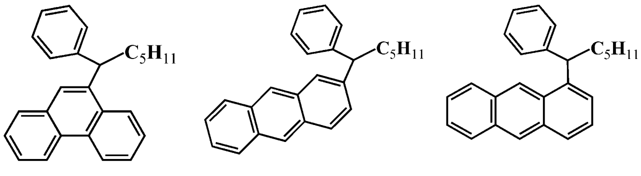
Sample Preparation for Fluorescence DET Experiments. (a) Polymer Films. PI-9Phe-PMMA and PI-1An-PMMA (or PI-2An-PMMA) were each dissolved in tetrahydrofuran (reagent grade, Aldrich) to form 5 wt % solutions. These solutions were mixed to give solutions with different weight ratios of the two polymers (PI-9Phe-PMMA/PI-1An-PMMA or PI-9Phe-PMMA/PI-2An-PMMA). A micropipet was used to measure 140 μL of each solution and spread it onto a quartz plate (1 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 solvent to minimize the drying rate. In this way we obtained smooth transparent films of essentially identical thickness. Three different molar ratios of 9Phe to 2An (or 1An) were prepared for the energy transfer study. For SAXS measurements, only films of the three neat diblock copolymers were prepared following the same procedure mentioned above. After drying, the samples were annealed in a vacuum for 5 h at 110 °C, then 5 h at 130 °C, and finally overnight at 150 °C. SAXS and DET measurements were performed at room temperature right after each annealing step.

(b) Energy Transfer Measurements. Fluorescence decays from the donor-labeled diblock copolymer were measured in the absence and in the presence of acceptor-labeled diblock copolymers. In each experiment, 10000 counts were collected in the maximum channel. The fluorescence decays were corrected by subtracting as background emission the signal obtained from a film of the neat acceptor-labeled diblock copolymers in the wavelength range (350−355 nm) where Phe emission is normally detected and where emission from the An group is negligible. The background-corrected decays were then analyzed using the reconvolution method, which involves comparing the experimental decay curves to the DET models convoluted with a mimic lamp profile.[15] All of the parameters with physical meaning in the DET models were recovered from the best fit to the experimental decay curves.

Results and Discussion

Polymer Synthesis and Characterization. We have previously presented a detailed description of the syntheses of the junction-labeled polymer and its characterization.[10] To interpret the experiments described below, we need to look closely at the efficiency of dye incorporation into each polymer. This efficiency is determined with the help of the model compounds whose structures are shown in Chart 2. These model compounds, whose synthesis and characterization are described in ref 10, were designed to capture the essential features of the chromophores at the block junction, and they have very similar absorption and emission spectra. To proceed with the analysis, we measured the UV absorption of solutions of each block copolymer at wavelengths characteristic for each chromophore and used the absorbance values to calculate apparent molecular weights ($M_{\text{n,app}}$) of the three diblock copolymers. These values were compared to molecular weights determined by gel permeation chromatography (GPC). Table 1 shows the molecular weights of diblock copolymers from GPC results. The dye attachment efficiencies were calculated by assuming that the model compound and the dye attached to the block copolymer have the same extinction coefficients. This type of assumption has served us well in characterizing samples of PS-9Phe-PMMA and PS-2An-PMMA[5] (PS is polystyrene), as well as in previous syntheses of PI-9Phe-PMMA and PI-2An-PMMA samples.[6]

Chart 2



9Phe-M 2An-M 1An-M

Table 1. Characteristics of the Diblock Copolymers

polymer	M_n(GPC)[a]	dye attached fraction (x_{dye})[b]	PDI[a]	V_{PI}:V_{PMMA}[c]
PI-9Phe-PMMA	32600	1.0	1.17	51.5:48.5
PI-2An-PMMA	28600	0.93	1.11	51.2:48.8
PI-1An-PMMA	32300	0.61	1.16	51.7:48.3

[a] Relative to PMMA standards. [b] The fraction of polymer labeled with dye, assuming diblock copolymers and their corresponding model compounds have the same molar extinction coefficient. [c] Calculation based on ^{1}H NMR analysis.

As shown in Table 1, PI-9Phe-PMMA and PI-2An-PMMA have high dye attachment efficiencies. But the dye content of PI-1An-PMMA is significantly smaller (61%).[16a] We use the parameter x_{dye} to denote the fraction of chains in the sample that contain a dye at the junction.[16b] For PI-9Phe-PMMA, $x_{\text{Phe}} = 1.0$. For PI-2An-PMMA, $x_{\text{An}} = 0.93$, but for PI-1An-PMMA, $x_{\text{An}} = 0.61$ (see Table 1).

Förster Radius Determination. The value of Φ_f^{EtAc} was determined to be 0.19 ± 0.02, and on the basis of this value, we calculated a value of $\Phi_f^{\text{PMMA}} = 0.21 \pm 0.02$ following the procedure outlined in the Experimental Section. The emission spectrum of 9PheM and the extinction coefficient spectra of 1AnM and 2AnM in PMMA films are shown in Figure 2. The magnitudes of the spectral overlap integrals for samples in both EtAc and PMMA as well as the corresponding effective energy transfer distance (R_{eff}) for 9PheM as donor with each of 1AnM and 2AnM as acceptor, as determined from eq 1, are given in Table 2. The environment of the dyes in a PMMA matrix is similar to that in our lamellar PI−PMMA diblock copolymer films. Consequently, we use the Förster radii obtained from PMMA films in the calculation of the interface thickness of PI−PMMA diblock copolymer lamellae.

Effect of Temperature on the Lamellar Period. Symmetric PI−PMMA diblock copolymers form lamellar

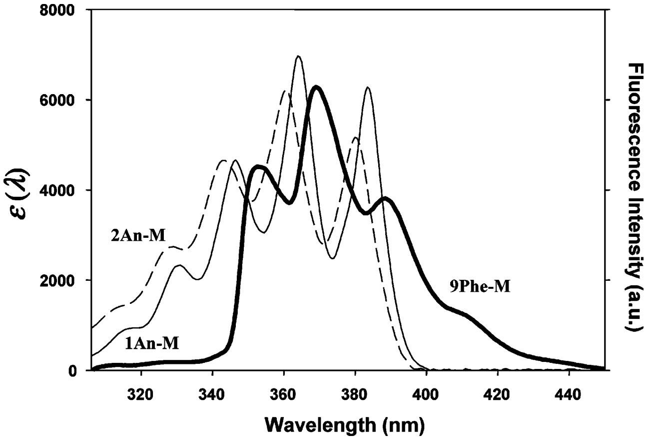


Figure 2. Fluorescence emission spectrum of 9PheM in PMMA (solid bold line) and extinction coefficient spectra of 1AnM (solid line) and 2AnM (dashed line) in a PMMA matrix as the solvent.

Table 2. Förster Radii[a] (R_0) and Effective DET Distances[b] (R_{eff}) for the Anthracene Chromophore (9-Phenathryl Group as Donor)

	EtAc			PMMA		
acceptor	J ($M^{-1}\,cm^{-1}\,nm^4$)	R_0 (Å)	R_{eff} (Å)	J ($M^{-1}\,cm^{-1}\,nm^4$)	R_0 (Å)	R_{eff} (Å)
1AnM	6.74	24.3	24.3	6.12	23.2	21.9
2AnM	5.50	23.5	23.5	5.75	22.8	21.6

[a] R_0 values are calculated with the assumption of rapid rotation of the transition dipoles ($\langle\kappa^2\rangle = 2/3$). [b] $R_{\text{eff}}^6 = (3/2)\langle\kappa^2\rangle R_0^6$. $\langle\kappa^2\rangle$ is assumed to be 2/3 in EtAc and 0.476 in PMMA.

morphologies due to the strong repulsive interaction between the two blocks.[6,7] Because of the high glass transition temperature of PMMA, there is always a concern about whether the samples reach their equilibrium dimensions. To provide sufficient mobility to the system, films were prepared by casting from a common good solvent (THF) followed by very slow (1 week) solvent evaporation. The films were then annealed at a series of increasing temperatures. We carried out SAXS measurements (at room temperature) on the as-prepared samples and then on these samples after they were annealed at successively higher temperatures. Sample SAXS scattering curves are shown in the inset of Figure 3. Well-ordered (1:2:3...) scattering peaks of PI−PMMA were clearly observed. The lamellar period, which was calculated from the first peak of the scattering curve, increased with annealing temperature as shown in Figure 3. The changes are small for any one individual sample annealed at 100, 130, and 150 °C, but outside of experimental error. From this result we infer that there is greater likelihood of the samples annealed overnight at 150 °C being close to equilibrium than those annealed for 5 h at 130 °C.

There are larger differences among the individual samples themselves. This result is a reflection of the small differences in molar mass among the samples. In ref 7 we described SAXS measurements on two of the polymers examined here, PI-Phe9-PMMA and PI-An2-PMMA, as well as a 1:1 mixture. The lamellar period H for the blend of these very similar polymers was in accord with the prediction of the Semenov model[17] for strongly segregated systems that H is proportional to $N^{2/3}$, where N refers to the mean chain length of the sample. In the experiments described below, involving energy transfer experiments on blends of donor- and acceptor-labeled PI−PMMA block copolymers, we assume that this relationship is applicable and use it to calculate the lamellar period for each of the blends we examined.

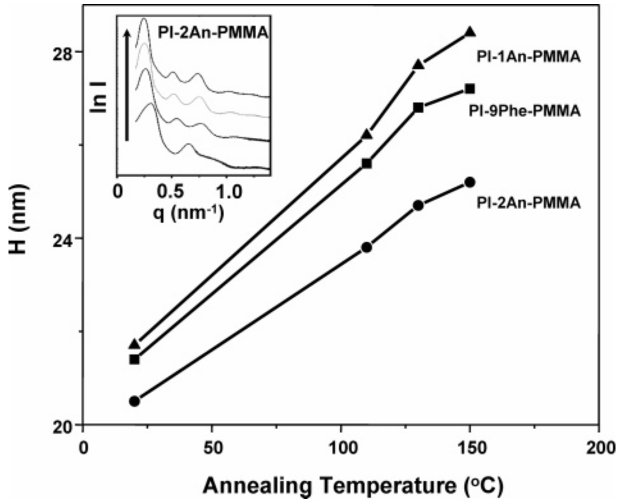


Figure 3. Relationship between the lamellar period determined by SAXS and the annealing temperature for different PI−PMMA diblock copolymers, as indicated in the figure. The lamellar periods were measured in a sequence of experiments for samples annealed at increasing temperatures as described in the Experimental Section. Inset: SAXS scattering curves for PI-2An-PMMA after annealing at different temperatures. The curves are offset vertically for clarity, and the arrow indicates the increase of temperature. The temperatures are, from bottom to top, room temperature, 110 °C, 130 °C, and 150 °C.

One other comment is in order about the results reported here and those described in ref 7 for the PI-Phe9-PMMA and PI-An2-PMMA samples. The values of H shown in Figure 3 for samples annealed overnight at 150 °C are slightly larger than those reported in ref 7 for the same samples annealed for a similar time at 140 °C.[18] We will see below that the higher annealing temperature also has an effect on the measured value of the interface thickness.

Energy Transfer and Interface Thickness in the Bulk State. (a) Theoretical Considerations. To obtain information about the interface thickness in the bulk state for block copolymers containing donor and acceptor dyes at the junction, we combine the Helfand and Tagami mean field model for the structure of diblock copolymers[19−21] with the theory for DET kinetics in lamellar structures.[15] This theory is based on the Klafter and Blumen model for DET in restricted geometries.[22] We have described the technical details of these calculations previously.[7] A brief summary can be given as follows. The junction distribution density $P_j(z)$ in diblock copolymer lamellae can be expressed as

$$P_j(z) = \frac{2\pi}{\delta}\,\text{sech}\left(\frac{2z}{\delta}\right) \tag{3}$$

where δ is the interface thickness and z is the distance normal to the plane of the interface, taken to be centered at $z = 0$. Equation 3 also represents the spatial distribution of junction-bound dye molecules across the interface in diblock copolymer lamellae. DET experiments take advantage of the distance dependence of the energy transfer rate $w(r)$:[13]

$$w(r) = \frac{{R_{\mathrm{eff}}}^6}{\tau_{\mathrm{D}} r^6} = \frac{3}{2}\kappa^2 \frac{{R_0}^6}{\tau_{\mathrm{D}} r^6} \qquad (4)$$

where r is the distance between the centers of the transition dipoles of the donor and acceptor and κ^2 is the orientation factor for the coupling of donor and acceptor dipoles. 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 $w(r)$ and the distribution of acceptors imposed by the geometry of the system. For donors and acceptors distributed along the z-axis normal to a dividing surface, the donor decay profile $I_{\mathrm{D}}(t)$ can be expressed as[22]

$$I_{\mathrm{D}}(t) = I_0 \exp(-t/\tau_{\mathrm{D}}) \int C_{\mathrm{D}}(z) \exp[-g(z,t)]\, \mathrm{d}z \qquad (5a)$$

$$g(z,t) = 2\pi \int_0^{\infty} \langle C_{\mathrm{A}}(r,z)\rangle [1 - \exp(-tw(r))] r\, \mathrm{d}r \qquad (5b)$$

$$\langle C_{\mathrm{A}}(r,z)\rangle = N_{\mathrm{A}} \int_{z-r}^{z+r} C_{\mathrm{A}}(r')\, \mathrm{d}r' \qquad (5c)$$

where I_0 is the intensity at $t = 0$. $C_{\mathrm{D}}(z)$ and $C_{\mathrm{A}}(r,z)$ 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

$$C_{\mathrm{D}}(z) = {C_{\mathrm{D}}}^0(z)\, P_j(z); \qquad C_{\mathrm{A}}(z) = {C_{\mathrm{A}}}^0(z)\, P_j(z) \qquad (6)$$

where $C_{\mathrm{D}}{}^0(z)$ and $C_{\mathrm{A}}{}^0(z)$ refer, respectively, to the bulk-averaged molar concentration of donor and acceptor groups in the sample. The efficiency of energy transfer (Φ_{ET}) for donor/acceptor pairs is given by the expression[13]

$$\Phi_{\mathrm{ET}} = 1 - \frac{\int_0^{\infty} I_{\mathrm{D}}(t)\, \mathrm{d}t}{\int_0^{\infty} {I_{\mathrm{D}}}^0(t)\, \mathrm{d}t} = 1 - \frac{\int_0^{\infty} I_{\mathrm{D}}(t)\, \mathrm{d}t}{\tau_{\mathrm{D}}} \qquad (7)$$

where $I_{\mathrm{D}}(t)$ is the normalized intensity of the donor/acceptor system at time t and $I_{\mathrm{D}}{}^0(t)$ 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}.

(b) Experimental Results. We prepared films of two comparable block copolymer mixtures, PI-9Phe-PMMA/PI-1An-PMMA and PI-9Phe-PMMA/PI-2An-PMMA. Table 3 provides information about the two systems. The lamellar period for each blend was calculated as described above. The neat PI-9Phe-PMMA diblock copolymer gave an unquenched lifetime of 44.9 ns. By fitting the experimental fluorescence decay curves to eqs 3−6, we were able to retrieve the interface thickness of the two diblock copolymer systems as shown in Figure 4. The interface thicknesses of the two diblock copolymer systems are very similar for all of the annealing temperatures except the small difference at lower temperatures. The decrease of interface thickness with increasing temperature[23] indicates that the diblock copolymers formed more sharply defined lamellar structures as the samples were subjected to further annealing at elevated temperatures.

For the as-prepared sample and the samples annealed at 110 °C, the experimentally determined values of the interface thickness are likely to reflect the history of sample preparation. What is more surprising is that the interface thickness narrows for samples annealed overnight at 150 °C compared to the samples annealed for 5 h at 130 °C. While the error bars on the two pairs of data points in Figure 4 indicate that the mean values are within 1 standard deviation of one another, we found a decrease in the fitted value of δ for each individual sample following annealing at the higher temperature.

To examine the validity of the conclusion that the interface narrows with annealing at higher temperature, we take another approach to data analysis that does not depend on a model for the distribution of junctions in the interface. We use eq 7 to calculate the quantum efficiency of ET for each of the films as a function of their thermal history. Any factor that leads to sharpening of the interface between the PI and PMMA domains will increase the local concentration of Phe and An groups and lead to an increase in Φ_{ET}. The results in Figure 5 show that Φ_{ET} values increase, as expected, with increasing bulk-averaged acceptor concentration C_{An} in the sample. The data show that these

Table 3. Mole Fractions of Phe and Concentrations of An in the Polymer Films

system	film no.	molar fraction of Phe, $f_{\mathrm{Phe}}{}^a$	concn of An, $C_{\mathrm{A}}{}^{0\,b}$ (mM)
PI-9Phe-PMMA/PI-1An-PMMA	1	0.72	7.72
	2	0.90	3.24
	3	0.94	1.88
PI-9Phe-PMMA/PI-2An-PMMA	1	0.50	16.45
	2	0.73	8.75
	3	0.86	4.43

[a] Calculated from $f_{\mathrm{Phe}} = m_{\mathrm{PI\text{-}9Phe\text{-}PMMA}}/(m_{\mathrm{PI\text{-}9Phe\text{-}PMMA}} + x_{\mathrm{An}} m_{\mathrm{PI\text{-}An\text{-}PMMA}})$, where m refers to the number of moles of each component and x_{An} is the fraction of chains bearing An groups for the An-labeled diblock copolymer samples. [b] Calculated from the mole number of An ($m_{\mathrm{PI\text{-}An\text{-}PMMA}}$), the degree of labeling (x_{An}), the mean number-averaged molecular weight of the polymer (M_{n}), and the polymer density (ρ), $C_{\mathrm{A}}{}^0 = x_{\mathrm{An}} m_{\mathrm{PI\text{-}An\text{-}PMMA}}/(M_{\mathrm{n}}\rho)$.

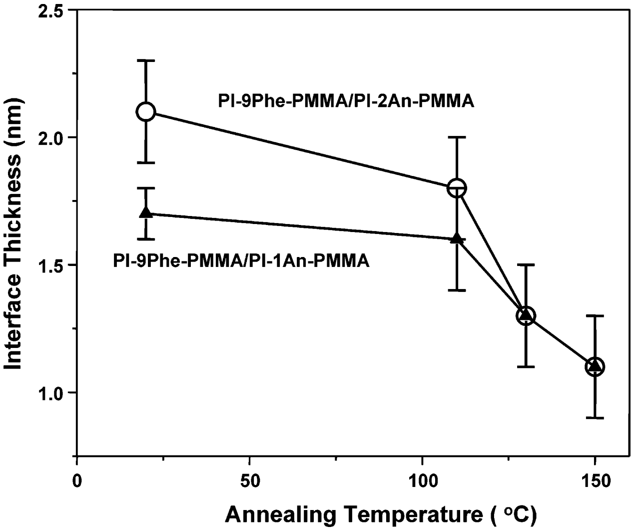


Figure 4. Best-fit values of the interface thickness of two diblock copolymer lamellae (PI-Phe-PMMA/PI-1An-PMMA and PI-Phe-PMMA/PI-2An-PMMA) for samples annealed at different temperatures. The thickness is recovered from the best fitting of eqs 1−4 to the experimental decays ($\chi^2 \leq 1.20$). For each data point, the mean value and error bar (1 standard deviation) are determined from measurements of samples with three different An concentrations.

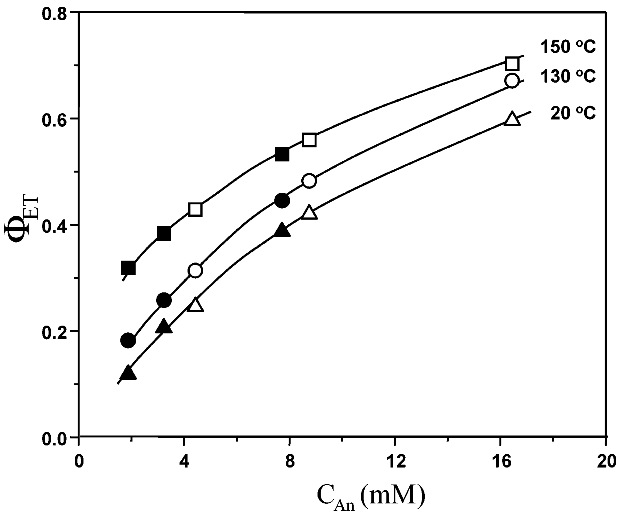


Figure 5. Efficiencies of energy transfer (Φ_{ET}) for PI-9Phe-PMMA/PI-1An-PMMA (filled symbols) and PI-9Phe-PMMA/PI-2An-PMMA (open symbols) as a function of the bulk-averaged An concentration. Φ_{ET} values were calculated using eqs 3−7 on the basis of the best fit values from the experimental decay curves. The samples were annealed at the temperatures indicated in the figure. For clarity, we do not show the results at 110 °C. The lines serve as guides for the eye.

values for individual samples are higher following annealing at higher temperature.

The interface thickness determined for the samples annealed at 150 °C ($\delta = 1.1 \pm 0.2$ nm) is slightly smaller than the value reported in ref 7 ($\delta = 1.6 \pm 0.1$ nm at 140°C) for the PI-9Phe-PMMA/PI-2An-PMMA pair. The difference in these two values arises from our data analysis in ref 7, in which we treated the PI-2An-PMMA as though all polymer chains bore a dye at the junction. Subsequent experiments have given us much more confidence in the idea that the extinction coefficients of the dyes attached to the polymer are the same as those of the model compounds. Here we take into account the result that 7% of the PI-2An-PMMA chains are missing an An group at the junction, which changes the value of the An concentration that we introduced into the calculation of δ.

(c) Orientation Factor. In fluid media, where the dyes undergo rapid rotation prior to energy transfer, the orientation term takes its average value for each pair of chromophores, and $\langle \kappa^2 \rangle = 2/3$ can be factored outside the integral in eq 5b. For rigid media, the orientation term is distinct for each pair of chromophores. The absolute value of the orientation parameter for a given donor/acceptor pair is given by the expression

$$|\kappa| = |\vec{D}\cdot\vec{A} - \frac{3}{|\vec{r}|^2}(\vec{D}\cdot\vec{r})(\vec{A}\cdot\vec{r})| \qquad (8)$$

where $\vec{D}$ and $\vec{A}$ are unit vectors representing the transition dipoles of the donor and acceptor, respectively, and $\vec{r}$ is the vector connecting their centers. Data analysis for experiments on dyes in rigid media require either a theory relating κ to r or an appropriate average value of $|\kappa|$ that can be extracted from the integral in eq 5b. For randomly oriented immobile dipoles in three-dimensional homogeneous media, $\langle|\kappa|\rangle^2 = 0.476$.[14,24] Baumann and Fayer[25] have calculated preaveraged values for other donor/acceptor distributions.

Wu and Brand[26] have examined the influence of the orientation parameter in static systems characterized by a single donor transferring energy to a single acceptor, such as a donor and an acceptor attached to two specific sites on a protein. In this type of experiment, one is interested in determining the average distance between two sites on the macromolecule. In this case they find that when the distance r separating the chromophores is larger than R_0, $\langle|\kappa|\rangle^2$ approaches 2/3, and the distance distribution can be recovered. When $r \leq R_0$, the orientation parameter and distance are coupled in their contribution to energy transfer. Under these circumstances, the apparent distance distribution that one obtains in the experiment may in fact reflect distributions in both the dipole orientation and the distance between the chromophores.

In the PI−PMMA block copolymer system, the fact that the interface thickness is on the order of 1 nm tells us that the mean separation between donors and acceptors is less than R_0. Our experiment differs in a fundamental way from those experiments intended to measure mean distances between pairs of sites in biological molecules. Our system is characterized by a large number of donors and acceptors, with a distance distribution dictated by the width of the interface. We designed our experiment with two different donor/acceptor pairs to examine whether the differences in dipole orientation in the two systems would lead to a difference in the apparent donor/acceptor distance distribution.

The data in Figure 4 indicate that the interface thickness calculated for the system containing PI-2An-PMMA and that for the system containing PI-1An-PMMA are virtually identical. These results were obtained using values of the lamellar period calculated from the measured values for the pure components, and with experimentally determined values of the characteristic energy transfer distance R_0, which turned out to be the same for both pairs of chromophores. In addition, we assumed that both systems could be described with a common mean orientation factor of $\langle|\kappa|\rangle^2 = 0.476$. If there were a pronounced coupling of distance and orientation for the dyes at the block junction, we would expect that preaveraging would be inappropriate. The experiments described here provide one test of whether preaveraging is appropriate to our experiment. Our finding of identical values of the interface thickness for the 1- and 2-substituted An derivatives supports the validity of preaveraging of the orientation factor.

The next question one can ask is whether these experimental results about the dye orientation can provide information about the tendency, if any, for polymer chains in the diblock copolymer interface to align perpendicular to the interface plane. There is evidence from neutron scattering[27] that, in strongly segregated block copolymers, the chains become elongated in the direction perpendicular to the interface and have contracted dimensions in the parallel direction. We are not aware of any experiments that examine chain conformation in the vicinity of the interface.

PI−PMMA is a strongly segregated system. But drawing a connection between dye orientation and polymer orientation from our experimental data is a difficult task. Because of rotation about the bond connecting the chromophore to the polymer backbone and rotation about the polymer backbone itself, each donor/acceptor pair can have a range of relative orientations of their transition dipoles. We depict this situation in

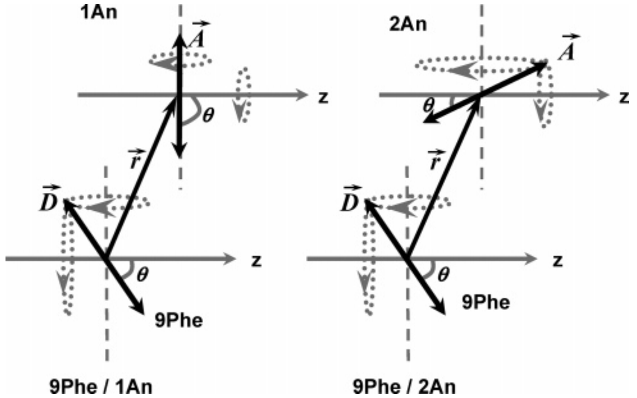


Figure 6. Schematic representation of the orientation of the transition dipoles in the two donor/acceptor systems PI-9Phe-PMMA/PI-1An-PMMA and PI-9Phe-PMMA/PI-2An-PMMA. The vectors $\vec{D}$ and $\vec{A}$ representing the transition dipoles are indicated by the double-headed arrows in black, and the vector $\vec{r}$ connecting the centers of the transition dipoles is indicated by the single-headed black arrow. The gray horizontal arrows along the z-axis represent the vector defining the direction of the polymer backbone at the interface. We assume the polymer backbones are highly oriented along the z-axis in the region of the interface. The diblock copolymer lamellar interface is perpendicular to the z-axis, and its position is indicated by the vertical dashed gray line. The dashed circular arrows at the ends of the transition dipoles define the possible rotations of the $\vec{D}$ and $\vec{A}$ dipoles around both the polymer backbone and the covalent bond connecting the chromophore to the polymer backbone. θ is the angle between the dipole ($\vec{D}$ or $\vec{A}$) and the polymer backbone, whereas ϕ (not shown in the figure) is the azimuthal angle between the projection of the dipole on the interface and the x-axis (arbitrarily selected in the interface plane).

Figure 6. Under these circumstances, even if the polymer backbone were strongly oriented, the difference in magnitude of $\langle|\kappa|\rangle^2$ for the 9Phe/1An pair might not be very different from that for the 9Phe/2An pair. Thus, the experiments described here might not be able to provide quantitative information about the tendency for the polymer chains to become oriented in the vicinity of the interface.

One way to test this idea is to calculate the magnitude of $\langle|\kappa|\rangle^2$ for the two donor/acceptor pairs assuming that the polymer backbone is highly oriented. To pursue this idea, we examine a simple model system, in which all of the polymer chains are strictly parallel. There are two limiting cases for this model. The first is a diffuse three-dimensional model (3D), with the dyes homogeneously distributed in space. The second is a much more restricted 2D model in which the interface is confined to a plane, and the dyes are located in the two dimensions of the interface plane. We allow the distance between the chains to vary, keeping in mind that the orientation parameter does not depend on the magnitude of the vector $\vec{r}$ connecting the centers of the transition dipoles, but on the ratio $\vec{r}/|\vec{r}|$. We consider the spherical coordinates θ and ϕ for the dipole orientation related to the polymer backbone (z-axis), where θ ($0° \leq \theta \leq 180°$) is the polar angle (the angle between the transition dipole and the z-axis shown in Figure 6) and ϕ ($0° \leq \phi < 360°$) is the azimuthal angle (the angle between the projection of the dipole on the interface plane (x,y plane) in the laboratory coordinates). Considering the possible rotations of the dye molecule, we calculate the distribution range related to the polymer backbone of the three diblock copolymers: $60° \leq \theta \leq 120°$ for 9Phe; $30° \leq \theta \leq 150°$ for 2An; $\theta = 90°$ for 1An. There is no confinement for ϕ for the three diblock copolymers. This model neglects any restriction on the dye orientation caused by local steric interactions with substituents on the chain backbone.

We used a Monte Carlo procedure to calculate the average orientation factor $\langle|\kappa|\rangle^2$ for the two systems PI-9Phe-PMMA/PI-1An-PMMA and PI-9Phe-PMMA/PI-2An-PMMA. For both the 3D model and the 2D model, we randomly picked two coordinate points for one donor/acceptor pair to generate $\vec{r}/|\vec{r}|$, and then randomly chose the dipole orientation 3-dimensionally within the distribution range mentioned above. For each system, we chose 10^8 donor/acceptor pairs to calculate the average values. As a test of the model, we also considered the case of random orientations in two and three dimensions in which we relax the restrictions on θ. Here we recover the known result[24,25] that $\langle|\kappa|\rangle^2 = 0.48$ for both two and three dimensions.

For the 3D case, we find only a small difference in the magnitude of the orientation parameter for the two different donor/acceptor pairs (in 3D, $\langle|\kappa|\rangle^2 = 0.50$ for 9Phe/1An vs 0.48 for 9Phe/2An), even when the polymer backbones in the interface are highly oriented. For the extreme and unrealistic case of the 2D interface, the difference between the two donor/acceptor pairs is larger, but the magnitude of $\langle|\kappa|\rangle^2$ is also very large.[28] Our block copolymer system, with an interface thickness of 1.1 nm, lies between these two limits. The calculation for the 3D case suggests that the type of experiment reported here is not very sensitive to the orientation of polymer chains at the interface. If, because of the narrow interface, there were sensitivity to the polymer backbone orientation, our results would support the idea that this net orientation is too small to be measured.

To delve more deeply into this question, one has to carry out mathematical modeling of block copolymer lamellae and investigate directly issues of polymer orientation and backbone orientation in the interface. We have carried out Monte Carlo calculations, to be reported elsewhere,[29] on the basis of Pakula's cooperative motion algorithm.[30-32] For a dense but strongly segregated system consisting of 35 beads of polymer A connected to 35 beads of polymer B, we found a modest tendency for the block copolymers to orient themselves with their end-to-end vector perpendicular to the plane of the lamellar interface. This orientation correlation observed on the size scale of the whole chains becomes very weak on the length scale of segments at the interface because of two effects: (1) weak coupling of local backbone correlation with the end-to-end vector for flexible polymers and (2) high composition fluctuations within the interface. As a consequence, there is no discernible preferred orientation of the local backbone vector at the junction. On this basis, the use of a preaveraged orientation factor in interpreting these kinds of DET experiments is put on a much firmer basis.

Summary

Direct nonradiative energy transfer experiments on the lamellar structures formed in films of PI-9Phe-PMMA/PI-1An-PMMA and PI-9Phe-PMMA/PI-2An-PMMA provide identical values of the interface thickness $\delta = 1.1 \pm 0.2$ nm at 150 °C. The fact that a common value was obtained for the two sets of experiments in which the transition moment of the anthracene chromophore has a different orientation to the polymer backbone indicates that there is no significant orientation of dyes attached to the block copolymer junction when the polymers self-assemble into lamellae. From the results of our experiments, we conclude that preaveraging of the orientation term provides a reasonable description of nonradiative energy transfer in these systems.

We can draw further information from the experiments, on the basis of the idea that all of the diblock copolymer samples have the same very narrow molar mass distribution, and their lamellar structures should have interfaces of identical thickness. If we assume that the interface is exactly 1.1 nm thick at 150 °C and that R_0 is known accurately, then the error of 0.2 nm in δ is due entirely to the uncertainty in $\langle|\kappa|\rangle^2$. We can reanalyze our data to find the best preaveraged orientation factor for every sample at that temperature through the best fit of the experimental decay curves. This analysis gives $\langle|\kappa|\rangle^2 = 0.483 \pm 0.044$. Thus, if the samples have identical interface thicknesses, our methodology leads to an orientation parameter with an uncertainty of about 9%.

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Supporting Information Available: To make the experimental fluorescence decay curves accessible to the reader, we fitted all of the decay curves to a stretched exponential decay function. All of the fitting parameters are presented in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bates, F.; Fredrickson, G. H. *Annu. Rev. Phys. Chem*. **1990**, *41*, 525.

(2) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys.* **1990**, *92*, 5677.

(3) Russell, T. P.; Menelle, A.; Hamilton, W. A.; Smith, G. S.; Satija, S. K.; Majkrzak, C. F. *Macromolecules* **1991**, *24*, 5721.

(4) Shull, K. R.; Mayes, A. M.; Russell, T. P. *Macromolecules* **1993**, *26*, 3929.

(5) Ni, S.; Zhang, P.; Wang Y.; Winnik, M. A. *Macromolecules* **1994**, *27*, 5742.

(6) Tcherkasskaya, O.; Ni, S.; Winnik, M. A *Macromolecules* **1996**, *29*, 610.

(7) Yang J., Lu, J., Rharbi, Y., Cao L, Winnik M. A., Zhang, Y., Wiesner U. B., *Macromolecules* **2003**, *36*, 4485.

(8) Rharbi, Y.; Winnik, M. A. *Macromolecules* **2001**, *34*, 5238.

(9) Roller, R. S. M.Sc. Thesis, University of Toronto, 2004.

(10) Yang J.; Lu, J.; Winnik M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1225.

(11) Phillips, D.; O'Connor, D. V. *Time Correlated Single Photon Counting*; Academic Press: London, 1984.

(12) Hruska, Z.; Vuillemin, B.; Riess, G.; Katz, A.; Winnik, M. A. *Makromol. Chem.* **1992**, *193*, 1987.

(13) Lakowicz, J. R., Ed. *Principles of Fluorescence Spectroscopy*; 2nd ed.; Plenum Press: New York, 1999.

(14) Steinberg, I. Z. *J. Chem. Phys*. **1968**, *48* (6) 2411−2413.

(15) Yekta, A.; Spiro, J. G.; Winnik, M. A. *J. Phys. Chem. B* **1998**, *102*, 7960.

(16) (a) The low dye content occurs presumably because of steric effects in the reaction of 1-(1-anthryl)-1-phenylethylene with the terminal carbanion of the living PI polymer. Thus, part of the living PI blocks were not capped by the 1-anthryl group, but the polymerization of these living anions continued when MMA monomer was added to the reaction. (b) The mole number of An groups in the dye-containing system is equal to the number of moles of "as-synthesized" An-labeled diblock copolymer times the fraction of polymer (x_{An}) that contains An groups.

(17) Semenov, A. N. *Sov. Phys. JEPT* **1985**, *61*, 733.

(18) For PI-9Phe-PMMA, $H = 27.2$ nm (150 °C) and 26.7 nm (140 °C).[7] For PI-2An-PMMA, $H = 25.2$ nm (150 °C) and 23.9 nm (140 °C).[7]

(19) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1971**, *56*, 3592.

(20) Helfand, E. *Macromolecules* **1975**, *8*, 552.

(21) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1980**, *13*, 994.

(22) Klafter, J.; Blumen, A. *J. Chem. Phys.* **1984**, *80*, 874. Klafter, J.; Drake, J. M. *Molecular dynamics in restricted geometries*; Wiley: New York, 1989. Drake, J. M.; Klafter, J.; Levitz, P. *Science* **1991**, *251*, 1574.

(23) Although the standard deviation of the interface thickness (±0.2 nm) is comparable with the change of thickness, the individual values for the same sample (same concentration) do decrease with increasing temperature.

(24) Dale, R. E.; Eisinger, J.; Blumberg, W. E. *Biophys. J.* **1979**, *26*, 161.

(25) Baumann, J.; Fayer, M. D. *J. Chem. Phys.* **1986**, *85*, 4087.

(26) Wu, P.; Brand, L. *Biochemistry* **1992**, *31*, 7939.

(27) Matsushita, Y.; Mori, K.; Mori, Y.; Saguchi, R.; Noda, I.; Nagasawa, M.; Chang, T.; Glinka, C. J.; Han, C. C. *Macromolecules* **1990**, *23*, 4317.

(28) In 2D, we calculate $\langle|\kappa|\rangle^2 = 0.87$ for 9Phe/1An and 0.62 for 9Phe/2An.

(29) Yang, J.; Winnik M. A.; Pakula, T. *Macromol. Theory Simul.* **2005**, *14*, 9.

(30) Pakula, T. *Macromolecules* **1987**, *20*, 679.

(31) Pakula, T.; Geyler, S. *Macromolecules* **1987**, *20*, 2909.

(32) Pakula, T.; Karatasos, K.; Anastasiadis, S. H.; Fytas, G. *Macromolecules* **1997**, *30*, 8463.

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