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Effective Volume per Junction in Block Copolymer Interfaces Probed by Direct Energy Transfer

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ABSTRACT: Direct nonradiative energy transfer (DET) experiments were carried out on a series of labeled polyisoprene−poly(methyl methacrylate) (PI−PMMA) and polystyrene−poly(methyl methacrylate) (PS−PMMA) diblock copolymers spanning a range of molecular weights and compositions. In all samples with spherical or cylindrical morphology, PMMA represents the major component, with PI or PS microdomains dispersed within the PMMA phase. These DET experiments yield the ratio of the microdomain size R to the interface thickness δ. We relate the R/δ ratio to the volume per junction v_j at the block copolymer interface and show that v_j does not depend upon the microdomain geometry or the overall block copolymer molecular weight, but only on the length N_B of the shorter component. We derive an expression which accommodates the observed dependence of v_j on $N_B^{1/3}$.

Introduction

Diblock copolymers are composed of two different polymers, A and B, connected at a junction point. In the experiments to be described here, each chain contains a single dye at this junction. We prepared matched pairs of polymers, nearly identical in chain length and composition, one labeled at the junction with phenanthrene (Phe), the other, with anthracene (An). These are the donor and acceptor dyes, respectively, for direct nonradiative energy transfer (DET) experiments. These polymers phase separate in bulk to form periodic structures. Since the morphology of the system formed by diblock copolymers in the bulk state depends only upon chain length and composition, we can vary the acceptor-to-donor ratio and maintain the morphology of the system by preparing various mixtures of these Phe- and An-labeled polymers.

In recent experiments, we have shown how DET measurements on diblock copolymers labeled at the junction point can be used to obtain information about the thickness δ of the interface between the A-rich and B-rich polymer phases.[1−3] Because the dyes are attached to the block copolymer junction, they become localized in the interface between the two polymer domains. DET occurs between pairs of dyes confined to the interface. The simplest way to think about how information is obtained is that the experiment measures the local concentration of dyes within the interface. Data analysis provides quantitative information about the interface thickness[1−3] through the term R_B/δ, where R_B refers to the size of B-rich microdomains.

This paper addresses two independent issues related to diblock copolymers in bulk as studied by DET. The first, pertinent to the structure of the block copolymer system, concerns the effective volume per junction for each chain at the boundary between the microdomains. We show, for example, that the magnitude of this volume does not depend upon whether the system self-assembles into spheres, cylinders, or lamellae, but does depend upon the length of the minor chain in the block copolymer. The second, related to the theory of energy transfer in restricted dimensions, examines the consequence on the energy transfer kinetics of confining the donor and acceptor dyes to interface volumes of different sizes. While we obtain both sets of information from the same type of experiment, we find that information about the effective volume per junction is obtained for samples in which the acceptor-to-donor concentration ratio is greater than unity and that new insights into the energy transfer process itself come from samples in which the acceptor-to-donor ratio is less than unity.

Interface Volume per Junction. Among the most important parameters characterizing the structure of a block copolymer system are the number of the chains $\tilde{N}$ per microdomain, the interface thickness δ, the interfacial area σ occupied by a single chain at the domain boundary, and the interface volume v_j per junction. These parameters, which depend upon the interfacial free energy, can be very sensitive to morphological rearrangements induced by changes in temperature, by external fields, by varying the chain length or compositional polydispersity of the block copolymer sample, or by the addition of homopolymer or small molecules to the sample.[4−8] The magnitude of these parameters is usually estimated from the size of the microdomains or from the interdomain distance (i.e., the lattice constant), as determined from transmission electron microscopy (TEM) or from small-angle scattering (SAXS, SANS) or specular neutron reflectivity (SNR) experiments. One normally treats the data under the assumption that the interface thickness is much smaller than the microdomain size. Under these circumstances, each single block is considered to be grafted to the surface of the microdomain.

Since these are fundamental parameters characterizing block copolymer systems at the molecular level, new experimental techniques which provide alternative methods to determine their magnitude will serve a valuable function. This will be particularly true if the assumptions made in analyzing these data are different from those made in obtaining these values from TEM and scattering experiments.

We are interested in the relationship between v_j or σ and the molecular characteristics of the polymer chains as well as the morphology of the system. To proceed, we arbitrarily take the B-chain as the shorter block and assume that the number of B-chains comprising a microdomain is equal to the ratio of the microdomain volume V_{domain} to the molecular volume of a B-chain, v_B. Then, the area σ at the surface of the microdomain

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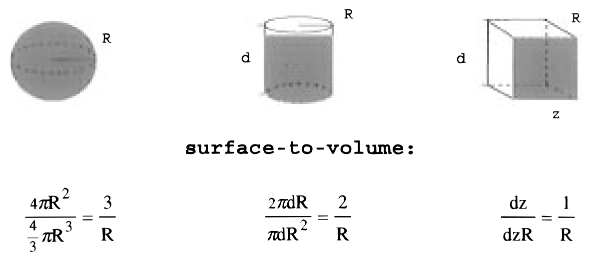

Figure 1. Drawings indicating the relationships between the surface area and the volume of spheres, cylinders, and lamellar solids.

occupied by a single block copolymer chain is given by

$$\sigma = v_B \frac{S_{domain}}{V_{domain}} \tag{1}$$

where S_{domain} is the microdomain surface separating the phases rich in A- and B-polymers.

For typical microdomains arising from the block copolymer self-assembly (spheres, cylinders, lamellae), one can show (Figure 1) that the surface-to-volume ratio[23] is related to the microdomain size R_B (the radius of the sphere or cylinder, or the half-length of the B-lamella) through a single expression in which changes in morphology affect only the magnitude of a numerical coefficient α. From geometrical considerations, eq 1 can be rewritten as

$$\sigma = \alpha \frac{v_B}{R_B} \tag{2}$$

with α = 1, 2, 3 for lamellar, cylindrical, and spherical microdomains, respectively (see Figure 1).

We define the effective volume v_j per junction at the interface as $\sigma\delta$, where δ is the interface thickness. Then, the expression relating the v_j to the length of the B-chain and the morphology of the system is given by

$$v_j = \sigma\delta = \alpha v_B \left(\frac{\delta}{R_B}\right) \tag{3}$$

Equation 3 is important to us because the ratio (δ/R_B) is obtained directly from DET experiments, allowing direct calculation of v_j. In strongly seggregated systems, where δ can be considered to be invariant with a change in morphology, eq 3 also allows us to obtain σ once the value for δ is known. One needs a value for α, thus information on sample morphology is also required.

Morphologies can be determined experimentally by TEM, SAXS, or SANS. If this evidence is not at hand, morphology can often be inferred from the composition of the block copolymers. The parameter of greatest uncertainty in eq 3 is the molecular volume v_B of a single B-chain in its microdomain. This parameter is usually estimated from the molar mass M_B of the B-chain under the assumption that the density of the polymer ρ_B inside the microdomain is equal to the density of the B-homopolymer in the bulk state

$$v_B = \frac{M_B}{\rho_B N_{Av}} \tag{4}$$

where N_{Av} is Avogadro's number. This implies equal packing coefficients of the polymer chains in microdomains of different geometry. In the general case, there is little evidence for this assumption. Thus, the concept of the molecular volume per chain is still a model parameter that depends upon assumptions about the system.

Fluorescence Decay Analysis. To analyze the fluorescence decay profiles, we rely on developments in the area of reaction dynamics in restricted geometry (in this case, the block copolymer interface) and fit the donor decay profile $I_D(t)$ to the Klafter–Blumen equation[9–11]

$$I_D(t) = A_1 \exp\{-(t/\tau_D) - P(t/\tau_D)^{\beta}\} + A_2 \exp(-t/\tau_D) \tag{5}$$

Here, the A_1 term represents the contribution of DET to the donor decay, and the A_2 term represents the independent fluorescence of donors located outside of the interface. The lifetime of the donor in the absence of the acceptor τ_D is obtained from independent experiments in which no acceptor-labeled polymer is present. The most difficult parameter in this expression to understand is the term β. It is a concentration-independent parameter sensitive to the details of the local geometry of the donor–acceptor distribution. In the case of DET on fractal lattices, 6β is equal to the fractal or Hausdorff dimension of the lattice. In restricted geometries, which by definition do not conform to self-similarity, β loses this meaning. Within the jargon of the field, 6β is sometimes referred to as the "apparent dimension" of a system. Simulations suggest that the magnitude of β is sensitive to edge effects in the restricted geometry. One contribution of this work is to examine in detail a crossover in β observed as the ratio of acceptor-to-donor becomes less than unity.[3]

In the context of the Klafter–Blumen model, the term P is proportional to the global acceptor concentration $C_{A,0}$

$$P = \frac{4\pi R_0^{\,3} N_{Av}}{3\lambda\Phi_B} g^{\beta}\Gamma(1-\beta)C_{A,0} \tag{6}$$

where R_0 is the characteristic (Förster) distance of the DET for the donor–acceptor pair chosen for the experiment, Φ_B is the volume fraction of the minor phase, $\Gamma(1-\beta)$ is the complete gamma function, and g is the orientation factor, which for a random orientation of immobile dyes takes the value of 0.711.[1]

The parameter of greatest interest is the ratio of the volume of the interphase to that of the minor phase. This parameter, denoted as λ, is related to the R_B/δ ratio

$$\lambda = \left(1 + \frac{\delta}{R_B}\right)^{\alpha} - 1 \tag{7}$$

where α has the same meaning as in eq 2.

To obtain R_B/δ, we prepare a series of samples comprised of different mixtures of donor- and acceptor-labeled polymers of the same chain length and composition. By analyzing their fluorescence decay curves, we obtain values of P, which are then plotted as a function of $C_{A,0}$. These plots should be linear and pass through the origin. For each set of samples, we obtain λ from the slope of the plot and then calculate R_B/δ by means of eq 7. By reference to the theory of Ohta and Kawasaki,[12] we can obtain values of the interface thickness δ directly from the fluorescence decay data. Experiments of this type, applied to PS–PMMA and PI–PMMA have recently been reported.[1–3] Now we

Table 1. Molecular and Morphological Characteristics for PI−PMMA and PS−PMMA Diblock Copolymers

sample	structure	N	N_B/N_{PMMA}	f_B[a]	R_B/δ	v_B[b] (nm^3)	v_j (nm^3)
PI−PMMA	sphere	193	15/178	0.07	1.12	1.8	4.9
	lamella	304	132/172	0.43	1.62	16.4	10.1
	lamella	367	147/220	0.40	1.98	18.2	9.2
	lamella	544	279/265	0.51	2.88	34.6	12.0
	sphere	656	147/509	0.21	6.04	18.2	9.0
PS-PMMA	sphere	319	29/290	0.09	0.94	4.7	14.9
	cylinder	366	106/260	0.29	1.42	17.2	24.2
	cylinder	536	106/430	0.25	1.51	17.2	22.9
	lamella	794	394/400	0.50	1.72	64.2	37.3
	sphere	1005	96/909	0.096	2.43	15.7	19.4
	cylinder	1543	394/1149	0.26	3.47	64.2	37.0
	sphere	1623	115/1508	0.07	2.63	18.8	21.4

[a] f_B = mole fraction of the minor B-component (B: PI or PS). [b] The molecular volume of the B-chain was calculated with densities $\rho_{PI} = 0.913$ g/cm^3 and $\rho_{PS} = 1.06$ g/cm^3.

carry out a reanalysis of the DET data obtained for these block copolymers to estimate the volume per junction at the block copolymer interfaces and to analyze its dependence upon the chemical structure of the block copolymer.

Experimental Section

Polymer Synthesis and Characterization. The synthesis of the labeled diblock copolymers, the fluorescence measurements, and the data analysis have already been described.[1−3] Here we briefly repeat the most important experimental information. Both block copolymers PI−PMMA and PS−PMMA were synthesized by anionic polymerization. The microstructure of the PI block was formed largely through 1,2 (40%) and 3,4 (55%) additions. In these polymers, the PS or PI minor component varies from 7 to 50 vol %. Sample morphology (spheres, cylinders, lamellae) was inferred from the composition of the block copolymer, although in three samples, confirming evidence for the morphology was obtained by SAXS measurements in the laboratory of T. Hashimoto in Japan. The molecular and morphological characteristics of the block copolymers are listed in Table 1.

Block copolymer films were prepared by casting solutions (1−3 wt %) in toluene onto quartz plates. The films were air-dried at room temperature and then dried under vacuum for 8 h at 50 °C for PI−PMMA and at 100 °C for PS−PMMA. Film thickness was typically 3−6 μm. Films were prepared from various mixtures of phenanthrene- and anthracene-labeled block copolymers of nearly identical composition and chain length. The acceptor-to-donor composition ratio ranged from 0 to 3.

Fluorescence decay profiles were obtained by the single photon timing technique,[13] as described previously.[3] According to our estimates, the uncertainty of the fitting parameters for each individual donor decay was less than 2%. The uncertainty in R_B/δ (obtained from the linear dependence of P on $C_{A,0}$) was in most cases less than 3−5%.

Results and Discussion

The key feature of data analysis of DET experiments based upon the Klafter−Blumen model of energy transfer in restricted geometry is the separation of the variables P and β. The parameter P is predicted to be proportional to the global acceptor concentration $C_{A,0}$, and β is predicted to be independent of concentration. Indeed, for all experiments with acceptor-to-donor compositions of $[C_A/C_D] > 1$, β is independent of $C_{A,0}$, P is proportional to $C_{A,0}$, and the plots of P vs $C_{A,0}$ all pass through the origin. Thus, the general features of the Klafter−Blumen model for DET in restricted geometry are satisfied, and from the slope of the experimental dependence of P on $C_{A,0}$, we can determine the ratio R_B/δ. Two examples of the experimental dependence of P and β upon the global acceptor concentration, for spherical and lamellar PI domains in a PMMA matrix, are presented in Figure 2. An unusual feature of this data, the crossover in β observed in the transition from $[C_A/C_D] < 1$ to $[C_A/C_D] > 1$, will be examined in more detail below.

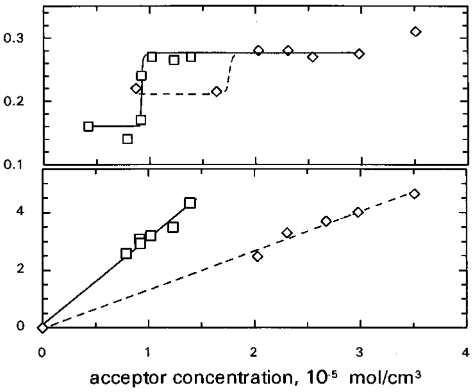

Figure 2. Variation of the fitting parameter P, and the exponent β versus $C_{A,0}$ for two block copolymer samples with spherical (□) and lamellar (◇) microdomain morphology. The samples are of PI−PMMA labeled at the junction with phenanthrene (donor) and anthracene (acceptor) and with degrees of polymerization $N = 656$ (spherical) and 305 (lamellar).

Interface thickness values were obtained from these various samples by reference to the molecular weight dependence of R_B/δ as predicted by the theory of Ohta and Kawasaki.[12] In this way, we obtained values of interface thickness of 5.1 nm for PS−PMMA[1] (compared to the value of 5.0 nm obtained by SNR[14]) and 2.6 nm for PI−PMMA.[2] The uncertainty in interface thickness determination was estimated to be on the order of 10%.

Values of the interface volume per junction v_j were evaluated from eq 3. This calculation requires knowledge of the molecular volume v_B of a single B-chain (i.e., for the PI or PS block). Here we assume (cf. eq 4) that the density of a polymer microdomain is similar to the density of PI or PS homopolymer, with values of 0.913 and 1.06 g/cm^3, respectively. Calculated parameters for PI−PMMA and PS−PMMA are presented in Table 1. Much of the remainder of this paper will be devoted to establishing that v_j depends upon the length N_B of the shorter block but does not depend upon the sample morphology. First we need to examine the crossover in β observed in Figure 2.

Crossover in the β-Parameter. Equation 5, which has four fitting parameters, is in fact a *phenomenological* equation proposed for the study of direct energy transfer in restricted geometries. In the context of this expression, the parameters A_1, A_2, and P are well defined, but the meaning of the parameter β remains obscure. The magnitude of this parameter seems to be particularly sensitive to edge effects, i.e., the number and distribution of donors and acceptors at the edges of the confining space. For example, in simulations of DET kinetics for donors and acceptors distributed randomly inside a sphere, we found $\beta = 0.5$ when the sphere was large, identical to the value predicted for DET in infinite three-dimensional media. As the radius of the sphere was made smaller and approached the characteristic (Förster) radius R_0 in size, the magnitude of β decreased.

In the case of DET for dyes confined to block copolymer interfaces, the behavior of β is somewhat different.

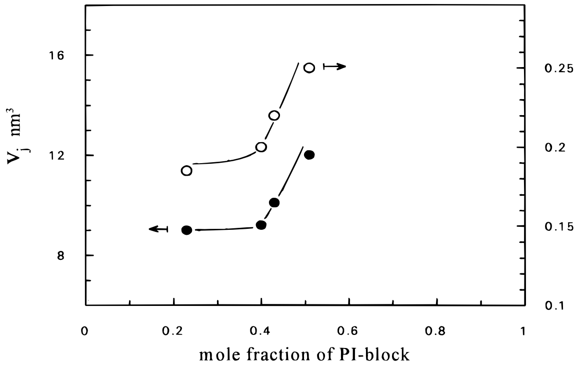

Figure 3. Variation of the volume per junction v_j and the value of β_1 at $[C_A/C_D] < 1$ for the PI–PMMA samples as a function of the fraction of PI in the block copolymer.

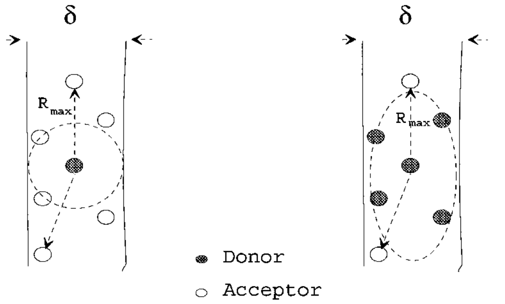

Figure 4. Representation of the acceptor (○) distribution around a donor (●) located at the center of the interface for the case (left) of a high acceptor-to-donor ratio and (right) of a low acceptor-to-donor ratio. Note that for the choice of Phe as the donor, the probability of donor–donor energy transfer is very small. The drawing indicates that the confining space is defined by the interface thickness.

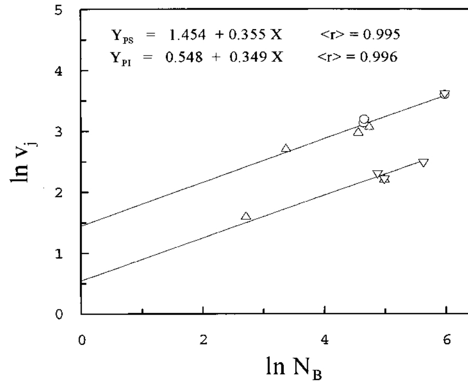

Figure 5. Dependence of the volume per junction v_j at the PS–PMMA (upper line) and PI–PMMA (lower line) interfaces upon the degree of polymerization N_B of the shorter (PS or PI) block for microdomains of spherical (△), cylindrical (○), and lamellar (▽) geometry.

For values of $[C_A/C_D] > 1$, all samples of PI–PMMA yield the same value of β, independent of the acceptor-to-donor ratio. Similar behavior was observed for the PS–PMMA samples. At lower acceptor concentrations, i.e., at $[C_A/C_D] < 1$, a crossover in β , as seen in Figure 2, was observed for all samples. They exhibit values of β_1 for $[C_A/C_D] < 1$ that vary from sample to sample (Figure 3). Since β is predicted to be concentration independent, the origin of the crossover and the variation of the low β_1 values among samples is a fascinating problem which needs a deeper understanding. In Figure 3 we show that there is a strong correlation of the magnitude of β_1 with the size v_j of the interface volume per junction. We did not anticipate this result, but having made the observation, we can now clarify in part some of the features that contribute to the magnitude of β_1.

DET experiments operate over relatively short length scales, and the maximum distance sampled in an experiment, R_{max}, can be defined in terms of R_o for the donor–acceptor pair.[9d] Here R_o has the value 2.3 nm, and R_{max} is on the order of 3.5 nm. In block copolymer interfaces, the distribution of the joints is peaked in the center of the interface. At high values of $[C_A/C_D]$, the mean separation between donor and acceptor dyes is smaller than δ and also much smaller than R_{max}. Since most donors are located near the center of the interface, they on average see a spherical distribution of acceptors, biased, of course, by the detailed shape of the acceptor distribution function (Figure 4). At low acceptor concentrations, the mean donor–acceptor separation becomes comparable to or larger than the interface thickness δ. This means that most donors see acceptors which are far removed ($\sim R_{max}$) and are confined to a space resembling an oblate ellipsoid. This situation is depicted in Figure 4.

In infinite media, β is connected with the dimensionality Δ of the medium, $\Delta = 6\beta$. Yang et al.[15] simulated DET kinetics in thin cylindrical pores. They found that β values decreased as the width-to-length ratio decreased, from a value of $^1/_2$, corresponding to $\Delta = 3$, to the value $^1/_6$ predicted for one-dimensional DET in the limit of infinitely thin cylinders. In our experiments, the analog of the "width" of the confining space is the interface thickness δ, which is constant for all of the samples, irrespective of the sample morphology. By analogy, the "length" must be related to the mean donor–acceptor (junction) separation. It is in this way that β_1, in the range of small values of $[C_A/C_D]$, becomes sensitive to the interface volume or the area occupied by a chain.

More specifically, the relationship between β_1 and v_j can be explained in the following way: Expansion of the interfacial volume per junction leads to relaxation of chain stretching in the block copolymer interface. Accompanying this relaxation, the dye–junction distribution becomes more random. The randomization of the junction distribution is reflected by an increased value of β_1, whose absolute magnitude depends upon the details of the donor–acceptor (junction) distribution in the interface.

Interface Volume per Junction. To understand how the microdomain geometry is related to the interface volume per junction v_j, we analyze its variation with block copolymer composition, which can be considered as the main feature determining block copolymer morphology. One can see from the data presented in Table 1 that v_j values do not depend upon either the sample morphology or the overall diblock copolymer length, but only on the length, N_B, of the shorter block. We find a linear increase of ln v_j with ln N_B for both PI–PMMA and PI–PMMA, as shown in Figure 5, with a slope whose magnitude is close to $^1/_3$ for both polymers.

Theoretical Considerations. The power-law behavior seen in Figure 5 can be derived from eq 3. One begins by recognizing that the molecular volume per B-chain is related to the volume per link a_B

$$v_B = a_B N_B \tag{8}$$

For strongly segregated systems, it has been established[6,8a] that the microdomain size R_B of the B-rich domain follows an expression of the form

$$R_B \approx N_B^{2/3}\chi^{1/6} \tag{9}$$

where χ is the Flory–Huggins interaction parameter. Combining eqs 3, 8, and 9, we obtain the result that the interface volume per junction v_j depends $N_B^{1/3}$. Thus, our main result is consistent with theoretical predictions for strongly segregated block copolymer systems.

$$v_j \approx \alpha \frac{a_B N_B}{N_B^{2/3}\chi^{1/6}}\delta \approx N_B^{1/3} \tag{10}$$

A curious feature of eqs 3 and 10 is that the parameter α changes its value abruptly with a change in sample morphology as, for example, when the length of the A-chain is increased. On the other hand, we see from the data in Figure 5 that the magnitude of v_j depends upon the magnitude of N_B, but does not alter with a change in sample morphology. Thus for a series of block copolymers with constant N_B but with different microdomain geometry, we obtain

$$(v_j)_{\alpha+1} = (v_j)_\alpha \tag{11}$$

where α and (α + 1) are indexes which refer to the geometry of the minor phase: α takes the value of 1 for lamellae, 2 for cylinders, and 3 for spheres. When α = 1, (α + 1) = 2, and here (α + 1) refers to cylinders. Clearly, (α + 1) can take a maximum value of 3.

If the interface volume per junction is constant for different morphologies, eqs 3 and 10 imply that a change in morphology corresponds to a discontinuous increase in the value of the microdomain size R_B. Thus if there are offsetting changes in the values of α and R_B with a change in sample morphology, eq 3 will accommodate v_j remaining constant if the radius of curvature at the interface is relatively large, since the interface thickness δ is not sensitive to the global morphology. Under these circumstances, for block copolymers with N_B constant and with increasing N_A, the jump in R_B/δ should follow the rule

$$\left(\frac{R_B}{\delta}\right)_{\alpha+1} = \frac{\alpha+1}{\alpha}\left(\frac{R_B}{\delta}\right)_\alpha \tag{12}$$

Results of this type are observed experimentally for both PI–PMMA and PS–PMMA (see Table 1). One can see from the data obtained for two PI–PMMA samples with $N_{PI} = 147$ with spherical (α = 3) and lamellar (α = 1) morphologies that the R_B/δ values increase by a factor of 3: $(R_B/\delta)_3 = 3(R_B/\delta)_1$. For the two PS–PMMA samples with $N_{PS} = 394$, one sees that the change of morphology from cylindrical (α = 2) to lamellar (α = 1) leads to a doubling of the R_B term: $(R_B/\delta)_2 = 2(R_B/\delta)_1$, in accordance with eq 12. Finally, for the PS–PMMA samples with N_{PS} = 96, 106, and 115, close enough for comparison, which have spherical (α = 3) and cylindrical (α = 2) PS microdomains, we find that $(R_B/\delta)_3 \cong 1.5(R_B/\delta)_2$, again in accord with eq 12.

Birshtein and Zhulina have examined the behavior of domain size with a change in sample morphology and predict theoretically this kind of discontinuous transition.[6,7] From an experimental point of view,[16] a jump in domain length accompanied by a smooth continuous change in interface area per chain has been observed for a concentration-induced cylinder-to-lamella transition in a block copolymer sample.

It would be useful to find an analytical expression which can describe the entire set of data presented in Figure 5. To proceed, we have to clarify the meaning of the intercept at ln N_B = 0 for the two lines corresponding to the data obtained for PI–PMMA and PS–PMMA. We have found that the intercept can be expressed as the product of χ and a_B. The χ-parameter dependence enters through the R_B/δ term in eq 3,

$$\frac{R_B}{\delta} \approx N_B^{2/3}\chi^{2/3} \tag{13}$$

This expression is obtained by combining eq 9 with the Helfand approximation for the interface thickness[17]

$$\delta = \frac{2b}{(6\chi)^{1/2}} \tag{14}$$

where b is the statistical segment length. Finally, from eqs 3, 8, and 13, we find

$$v_j \approx a_B\chi^{2/3}N_B^{1/3} \tag{15}$$

To calculate the interfacial volume per junction, we use a value of 0.124 nm^3 for a_B(PI) and 0.163 nm^3 for a_B(PS). These values can be calculated as

$$a_B = \frac{M_{\text{B-link}}}{\rho N_{\text{Av}}} \tag{16}$$

where $M_{\text{B-link}}$ is the molar mass of the polymer repeat unit ($M_{\text{PI-link}} = 68.12$ and $M_{\text{PS-link}} = 104.15$). We use a value $\chi = 0.079$ for PI–PMMA obtained by us from DET measurements,[2] and $\chi = 0.028$ for PS–PMMA obtained by small-angle X-ray scattering.[18]

We find that eq 15 can describe all of our experimental data for PI–PMMA and PS–PMMA if we introduce a coefficient of $(\pi^2/4)$ as the proportionality constant. The difference between experimental and theoretical values is in most of cases less than 10%. Thus, we believe that a proper *phenomenological* expression for the interfacial volume per junction as a function of the shorter B-block length is given by the equation

$$v_j = \frac{\pi^2}{4}a_B\chi^{-2/3}N_B^{1/3} \tag{17}$$

An analogy exists between eq 17 and current theoretical descriptions of the surface area σ per chain at the interface. We can express equations for the area per chain in terms of the effective volume per junction, $v_j = \delta\sigma$. We combine Helfand's approximation for the interface thickness (eq 14) with the equation reported by Zhulina and Semenov[19] for interface area per chain originally derived for lamellar geometry. This leads to the expression

$$v_j = \delta\sigma = Ca\chi^{-2/3}N^{1/3} \tag{18}$$

where C is the proportionality constant and a is the mean volume per link. Here we find the same power-law dependence as in eq 17.

To check the validity of eq 17, we calculate v_j and σ values for PS–PI, a widely investigated block copolymer.[5] For a PS–PI with overall chain length $N = 582$ and composition $N_{PS}/N_{PI} = 259/323$, we obtain $v_j = 12$ nm^3, identical to the value (12 nm^3) obtained for PI–PMMA with a similar overall chain length and composition (see Table 1). For this calculation, we use $\chi = 0.09$, as reported by Hashimoto[20] for PS−PI with the microstructure of a PI block rich in 1,4 additions. To obtain the value of the interface area per chain for PS−PI, we use the value $\delta = (2.0 \pm 0.5)$ nm cited by Bates,[5] to obtain $\sigma = 6$ nm^2. This result is in relatively good agreement with the value reported by Thomas [21] ($\sigma \cong 4.5$ nm^2), particularly since we need to take into account the range of experimental values reported for the interface thickness of PS−PI. It should be emphasized that the σ value for PS−PI was obtained by Thomas through the magnitude of the lattice constant, i.e., through the interdomain spacing, which is dominated by the major component of the matrix. The present results are based on analysis of the minor domain characteristics.

Summary

Direct nonradiative energy transfer experiments on labeled block copolymers yield the ratio of the microdomain size R_B to the thickness of the domain-boundary interface δ. We show that R_B/δ is related to the effective volume per junction at the interface through a dependence of v_j on $N_B^{1/3}$. The fact that the volume per junction is determined by the length of the shortest block, and not by the composition or overall length of the block copolymer, suggests that the major driving force determining the density of chain packing in the interface is the competition between the surface energy and entropy loss of the shortest block. The size of the minor domain depends, of course, on the length of the minor component, but the details of the size, particularly in terms of the number of chains per microdomain, depend in principle on the length of both the long and the short components. In other words, one expects some mutual influence between the blocks.

The dependence of the microdomain size upon the block copolymer length for the case of spherical and cylindrical micelles was considered in detail by Birshtein and Zhulina.[22] Analysis of block copolymer state diagrams shows that the microdomain size and the number of polymer chains per microdomains should be a strong function only of the shorter block length when the longer chains are nonoverlapping or weakly overlapping in the external matrix. Whether this situation exists or not was shown to depend on the length of the A-component. This type of weak interaction within the A-polymer phase should occur when the radius of the B-sphere or cylinder is larger than the unperturbed radius of gyration of the A-chain, $R_B > R_G(A)$. This situation seems to apply to the PI−PMMA and PS−PMMA samples for the range of the molecular weights we examine. We estimate for both block copolymers (with the PMMA as the major component) that R_G of the PMMA blocks is always less than the radius R_B found for our samples with spherical or cylindrical domains. For these calculations, we estimate R_G(PMMA) from $R_G = b(N_{PMMA}/6)^{0.5}$, where b is the statistical segment length with 0.67 and 0.63 nm as the mean segment length value for PS−PMMA and PI−PMMA, respectively.

The weak influence of the A-block length on the volume per junction (or on the interface area per chain) can be seen in the data for two PS−PMMA samples with a similar length of the PS-block ($N_{PS} = 106$) and different lengths of the PMMA blocks ($N_{PMMA} = 260$ and 430). Both block copolymers have a cylindrical morphology. Increasing the PMMA length by almost a factor of 2 leads to negligible (ca. 5%) decrease in the magnitude of v_j. Thus, in the range of composition and molecular weights examined here, mutual influence of the blocks on domain structure does not change the interface volume per junction. The recent theory of Birshtein and Zhulina cites limits where this simple behavior may no longer operate. Analysis of the mutual influence of the blocks on the structure of the block copolymer interfaces will be an interesting topic for future investigation.

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References and Notes

(1) Ni, S.; Zhang, P.; Wang, Y.; Winnik, M. A. *Macromolecules* **1994**, *27*, 5742.
(2) Tcherkasskaya, O.; Ni, S.; Winnik, M. A. *Macromolecules* **1996**, *29*, 610.
(3) Tcherkasskaya, O.; Spiro, J. G.; Ni, S.; Winnik, M. A. *J. Phys. Chem.*, in press.
(4) *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberg, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley: New York, 1985; Vol. 2.
(5) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(6) Birshtein, T. M.; Zhulina, E. B. *Polymer* **1984**, *25*, 1453; **1989**, *30*, 170; **1990**, *31*, 1312.
(7) Zhulina, E. B.; Birshtein, T. M. *Vysokomol. Soedin., Ser. A* **1986**, *28*, 2589; **1987**, *29*, 1524.
(8) Semenov, A. N. (a) *Sov. Phys.—JETP (Engl. Trans.)* **1985**, *61*, 733. (b) *Macromolecules* **1989**, *22*, 2849. (c) *Macromolecules* **1993**, 26, 2273.
(9) (a) Klafter, J.; Blumen, A. *J. Phys. Chem.* **1984**, *80*, 875. (b) Klafter, J.; Blumen, A. *J. Lumin.* **1985**, *34*, 77. (c) Blumen, A.; Klafter, J.; Zumofen, G. *J. Chem. Phys.* **1986,** *84* (3), 1397. (d) Levitz, P.; Drake, J. M.; Klafter, J. *J. Chem. Phys.* **1988**, *89* (8), 5224.
(10) (a) Levitz, P.; Drake, J. M. *Phys. Rev. Lett.* **1987**, *58*, 686. (b) Levitz, P.; Drake, J. M.; Klafter, J. *J. Chem. Phys.* **1988**, *89*, 5224. (c) Levitz, P.; Drake, J. M.; Klafter, J. *Chem. Phys. Lett.* **1988**, *148*, 557. (d) Drake, J. M.; Klafter, J.; Levitz, P. *Science* **1991**, *251*, 1574.
(11) (a) Pekcan, O.; Winnik, M. A.; Croucher, M. D. *Phys. Rev. Lett.* **1988**, *61*, 641. (b) Pekcan, O.; Croucher, M. D.; Winnik, M. A. *Macromolecules* **1990**, *23*, 2673. (c) Pekcan, O.; Egan, L. S.; Winnik, M. A.; Croucher, M. D. *Macromolecules* **1990**, *23*, 2210. (d) Yekta, A.; Duhamel, J.; Winnik, M. A. *Chem. Phys. Lett.* **1995**, 235, 119.
(12) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.
(13) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: London, 1984.
(14) (a) Russell, T. P.; Menelle, A.; Hamilton, W. A.; Smith, G. S.; Satija, S. K.; Majkrzak, C. F. *Macromolecules* **1991**, *24*, 5721. (b) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *J. Chem. Phys.* **1990**, *92*, 5677.
(15) Yang, C. L.; Evesque, P.; El-Sayed, M. A. *J. Phys. Chem.* **1985**, *89*, 3442.
(16) Volkova, L. A.; Andreeva, N. A.; Podolsky, A. F.; Bitsenko, M. I.; Eskin, V. A. *Vysokomol. Soedin., Ser. A* **1982**, *24*, 1180.
(17) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1972**, *56* (7), 3592.
(18) (a) Russell, T. P. *Macromolecules* **1993**, 26, 5819. (b) Shull, K. R.; Mayes, A. M.; Russell, T. P. *Macromolecules* **1993**, 26, 3929.
(19) Zhulina, E. B.; Semenov, A. N. *Vysokomol. Soedin., Ser. A* **1989**, *31*, 177.
(20) Hashimoto, T.; Ijichi, Y. *J. Chem. Phys.* **1988**, *89* (4), 2463.
(21) Winey, K. I.; Thomas, E. L.; Fetters, L. J. *J .Chem. Phys.* **1991**, *95* (12), 9367.
(22) (a) Birshtein, T. M.; Zhulina, E. B. *Conformations of Macromolecules Grafted to a Surface* (in Russian); Poustchino: 1983, 16 pp (Preprint/The Science Centrum of Biological Investigations of the Academy of Sciences of the USSR). (b) Zhulina, E. B.; Birshtein, T. M. *Vysokomol. Soedin., Ser. A* **1985**, *27*, 511.
(23) Here we use the area of the microdomain surface separating the phases rich in A- and B-polymers.

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