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Communications to the Editor

Distribution of the Chain Ends in Diblock Copolymers

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Introduction. Block copolymers composed of two immiscible components self-assemble into periodic structures. When the two chains are similar in length, lamellar structures are formed.[1] A representative drawing is presented in Figure 1, where the two components are referred to as A and B. In the strong segregation limit, the junction points become concentrated in a narrow interfacial region of thickness δ as the system adjusts to minimize the surface area per chain. As a consequence, chain segments near the interface become stretched, and the equilibrium structure represents a balance between the entropic costs of chain stretching and localization of the joints and the interfacial energy of the system. According to current theory, the structure of the system, including the lamellar brush heights h_A and h_B, depend upon the chain length ($N = N_A + N_B$), the fraction of A segments ($f_A = N_A/(N_A + N_B)$), and the interaction energy χ between segments of A and B.[2] In order to achieve significant stretching of the chains, χN must be rather large.

Because of their fundamental importance in block copolymer systems, the interface and its thickness δ have been the subject of numerous investigations, both theoretical[3−5] and experimental.[6−9] A more subtle issue concerns the locus of the chain ends.[8,10] Chain stretching is not uniform across the domains and occurs to the greatest extent near the interface. In order to maintain uniform density, the chain ends must reach back to fill space. Thus the chain ends are distributed throughout the domains. Nevertheless, there is a tendency for the chain ends to congregate near the middle of the domains.

The width of the interpenetration zone ϵ_i (where i = A or B) is determined by the mean length of a subsection of a chain from the opposite brush which traverses the midpoint of the domain. The underlying potential is fairly weak, and these subsections have close to unperturbed dimensions.[2,10] In the strong stretching limit, the interpenetration zone occupies a fraction of the lamella[2]

$$\frac{\epsilon_i}{2h_i} = \left(\frac{\pi^2}{3}\right)^{1/9} (\chi N)^{-2/9} f_i^{-2/3} \qquad (1)$$

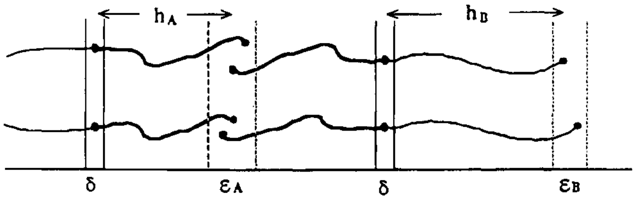

Figure 1. Block copolymers in a lamellar mesophase. The thicknesses of the A and B lamellae are $2h_A$ and $2h_B$, respectively. The width of the interface between the A and B regions is δ, and the width of the interpenetration zone for polymer A is ϵ_A.

and the fraction of chain ends[2] within the interpenetration zone e_i decreases slowly with increasing χN

$$e_i = 2^{1/2}\left(\frac{\pi^2}{3}\right)^{1/18} (\chi N)^{-1/9} f_i^{-1/3} \qquad (2)$$

Matsushita et al.[13] used SANS to examine a polystyrene−poly(vinylpyridine) (PS−PVP) diblock copolymer with deuterated PS end segments. More recently, Russell and co-workers[14] examined by specular neutron reflectivity (SNR) thin films of PS−PMMA (poly(methyl methacrylate)) block copolymers with deuterated monomer units at the ends of the PS or the PMMA block. The labeled end segments were shown to be distributed throughout the domain, even extending into the interfacial region. Numerical modeling of the system in terms of mean field theory gave good agreement with the experimental results.[15]

Here we report experiments which examine the localization of the chain ends by direct nonradiative energy transfer (DET) experiments. These experiments involve matched pairs of PS−PMMA labeled at the PMMA end with either a donor or acceptor dye. Small-angle X-ray scattering experiments provide the lamellar spacing and show that upon annealing, the lamellar spacing increases by about 10% and with a rate somewhat faster than the equilibration of the chain ends.

Experimental Section. Five PS−PMMA block copolymer samples were prepared by standard anionic polymerization methods. The two samples labeled at the junction point with phenanthrene (Phe, the donor) and anthracene (An, the acceptor) have previously been described.[9] Corresponding samples labeled at the PMMA chain end were obtained by quenching the living PMMA anion with 9-(bromomethyl)phenanthrene and 9-(bromomethyl)anthracene, respectively. The characteristics of these polymers are described in Table 1. Using similar methods, two model polymers were prepared containing either Phe or An at the end of an oligomeric PS chain ($M_n = 600$, $M_w/M_n = 1.08$).

A series of films (ca. 30 μm) containing various mixtures of donor- and acceptor-labeled polymer were prepared by solvent casting from a common good solvent (toluene) onto quartz substrates.[9] In this way, we vary the acceptor concentration while maintaining sample morphology. Fluorescence decay experiments were carried out at 23 °C using the single-photon-timing technique, both on the "as-prepared" films and on these

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Table 1. Polymer Characteristics

sample	structure	$10^{-3}M_n$	M_w/M_n	f_m[a]	ϕ_m[b]	dye content (μmol/g)	χN[c] (164 °C)
C-103	PS–Phe–PMMA	81	1.18	0.52	0.48	12.2	29
C-102	PS–An–PMMA	81	1.17	0.51	0.46	12.5	29
C-106	PS–PMMA	77	1.19	0.50	0.46		29
C-125	PS–PMMA–Phe	92	1.15	0.50	0.46	5.5	33
C-124	PS–PMMA–An	90	1.15	0.50	0.46	9.8	33

[a] Mole fraction of PMMA. [b] Volume fraction of PMMA. [c] Calculated from $\chi = 0.28 + 3.9/T$ (Russell, T. P. *Macromolecules* **1993**, *26*, 5819).

same films after annealing them at ca. 164 °C under vacuum for various periods of time.

Films for SAXS measurements (ca. 100 μm) were prepared similarly using a Petri dish and very slow drying (ca. 1 week). Films were separated from the substrate, and a portion of each film was examined directly. These experiments are referred to as scattering "through" the film. Another portion of the film was cut into thin slices which were then stacked to give a multilayer structure with the edges of the original film oriented toward the X-ray source. These are referred to as "edge" experiments. SAXS data acquisition and analysis (including corrections for absorption, background scattering, slit-height and slit-width smearing, etc.) were described elsewhere.[16]

Results and Discussion. The phenanthrene fluorescence decay profiles $I_D(t')$ from films containing no anthracene were well described by a simple exponential function. In mixtures containing increasing amounts of An-labeled polymer, $I_D(t')$ exhibited increasingly rapid decay at early times due to energy transfer. These profiles, which by eye resemble those reported in ref 9, were fitted to the expression

$$I_D(t') = A_1\left[\exp\left(-\frac{t'}{\tau_D} - P\left(\frac{t'}{\tau_D}\right)^{\beta}\right)\right] \qquad (3)$$

suggested by Klafter and Blumen[17-19] for analysis of energy transfer in restricted geometries. A restricted geometry is one characterized by at least one length on the order of the energy transfer distance R_0, and P is proportional to the probability of an acceptor being within a distance R_0 of a donor. Due to localization in the lamellar structure, the dyes experience a higher local concentration (e.g., C_A for the acceptor) than the bulk concentration $C_{A,0}$ calculated from the dye content and polymer composition. P can be written as $P = P_0(C_A/C_{A,0})C_{A,0}$, where P_0 is comprised of constants that have to be determined independently, $P_0 = (4\pi/3)R_0^3(g^I)^{\beta}\Gamma(1-\beta)$. Here the orientation parameter $g^I = 0.71$ for random immobile pairs,[20] $R_0 = 24$ Å,[9] and $\Gamma(x)$ is the gamma function. From the slope of the plot of P vs $C_{A,0}$, the ratio $C_{A,0}/C_A$ can be determined. In a lamellar system, this ratio is equal to the volume fraction of the system in which the dyes are confined. For lamellar structures with junction-labeled polymers, this ratio corresponds to the volume fraction of interphase, and δ can be deduced if the period spacing is known.

DET Experiments. $I_D(t)$ profiles for the as-cast films of end-labeled polymer yield $\beta = 0.50 \pm 0.03$ for all samples and values of P proportional to $C_{A,0}$. These data are shown as the lower two lines in Figure 2 and indicate that P values obtained for the PMMA-end-labeled samples lie very close in magnitude to those obtained for the model labeled PS homopolymer in which the donors and acceptors are randomly distributed. From this result we conclude that in the as-cast sample, the chain ends of the PMMA block are distributed essentially uniformly throughout the PMMA domains. The uppermost line in Figure 2 is that obtained for the junction-labeled polymers. The higher P values indicate that the dyes confined to the interface are present at a much higher local concentration than those attached to the chain ends.

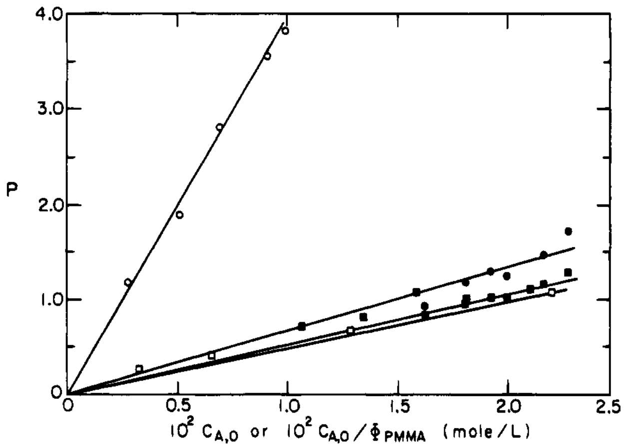

Figure 2. Plot of the parameter P vs $C_{A,0}$. Uppermost line: junction-labeled polymers C-102 + C-103 (○). Lowermost line: model system comprised of Phe- and An-labeled PS (□). From as-prepared samples of the end-labeled polymers C-124 + C-125 (■). Data from the end-labeled polymers after annealing for 15 h at 164 °C (●). The middle two lines are plots of P vs $C_{A,0}/\Phi_{PMMA}$.

When the end-labeled samples are annealed at 164 °C, cooled to room temperature, and remeasured, β remains constant but the P values increase, leveling off after 200 min of annealing. The increase in P (cf. Figure 2) indicates that upon annealing, the system rearranges in such a way that the chain ends become more concentrated in the middle of the domain. Based upon the C_A values obtained from the data, we calculate that the system undergoes the same extent of energy transfer as if the chain ends were confined to the middle 57% of the PMMA domains. Note that this analysis does not take into account the distribution of the chain ends, which Shull et al.[15] have shown to be broad. Kawasaki and Kawakatsu[12] have simulated the chain end distribution for diblock copolymer lamellar phases. For values of χN similar to that of our sample, they calculate that ϵ represents 40% of the domain thickness, with 75% of the chain ends contained within ϵ. This is also consistent with our results.

SAXS Experiments. In the SAXS experiments on as-cast samples of C-106, a broad shoulder but no peak is observed in the plot of log I vs q ($q = (4\pi/\lambda)\sin(\theta/2)$), corresponding to a 370 Å spacing in the "through" sample and 260 Å in the "edge" sample. After minimal annealing (10 min at 150 °C), a sharp peak is observed. The peak maximum (q^*) corresponds to a period of 390 Å and is accompanied by a much weaker peak at $3q^*$. Continued annealing at 150 °C leads to sharpening of both peaks and a very small shift of q^*. After ca. 130 min, the period spacing stabilizes at 400 Å. This structure can also be seen in TEM images of the annealed samples. A similar result was reported recently by Russell and Chin.[21] We conclude that the as-cast sample is in an ordered state, having a globally distorted microdomain structure with local periodicity, which becomes more ordered upon annealing.

Many isothermal growth and relaxation kinetics in block copolymer systems follow the Avrami function,[22,23] where $X(t)$ is the fractional growth at time t and k is the rate constant. For the chain ends in our system, we set $X(t)$ equal to the fractional growth of the P parameter in eq 3.

$$x(t) = \frac{P_t - P_0}{P_\infty - P_0} = 1 - \exp(-k\, t^n) \tag{4}$$

Here P_t refers to the value of P determined in a sample annealed at 164 °C for time t. Data for the first 200 min of sample annealing fit this expression rather well with $n = 0.67$. Thus the chain-end localization follows power law kinetics.[2] At 164 °C, it takes slightly more than 200 min for the chain end distribution to equilibrate. This is somewhat slower than the 130 min (at 150 °C) needed for the lamellar spacing to reach its final value.

It should be interesting in the future to compare the time scales for the approach to equilibrium for the chain ends, the A/B interface, and the period spacing for samples of different chain lengths and for samples that form spherical and cylindrical phases.

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