Macromolecules **1993,** *26,* 3147-3150

Energy-Transfer Study of Polymer Diffusion in Melt-Pressed Films of Poly(methyl methacrylate)

Yongcai Wang and Mitchell A. Winnik*

Department of Chemistry and Erindale College, University of Toronto,
80 St. George Street, Toronto, Ontario, Canada M5S 1A1

Received December 21, 1992; Revised Manuscript Received February 15, 1993

ABSTRACT: Films were prepared by melt-pressing poly(methyl methacrylate) (PMMA) powder into films at 115 °C. The PMMA was in the form of monodisperse microspheres, ca. 100 nm in diameter, labeled with either phenanthrene or anthracene (1 mol %). Energy-transfer measurements were carried out on films composed of a 1:1 mixture of these particles, as a function of annealing time and oven temperature. From fluorescence decay profiles, the extent of polymer interdiffusion was determined. Diffusion coefficients were calculated. These range from 10^{-15} cm^2 s^{-1} at 149 °C to 10^{-18} cm^2 s^{-1} at 120 °C, corresponding to an activation energy of 100 kcal/mol.

Introduction

The connection between the interdiffusion of polymer molecules across an interface and the growth in strength of the joint that is formed is a topic that has received considerable attention over the past several years. From the point of view of theory, there has been considerable progress in the description of polymer chain diffusion across an interface, especially where reptation is important.[1-5] Following a seminal paper by de Gennes,[1] major contributions have come from the laboratories of Tirrell[2] and of Wool.[3] Our theoretical understanding of the growth in strength of the joint that is formed is less complete.[4-6] It is now clear that entanglements are the major source of the strength of the joint. Thus reptative diffusion leads to the formation of entanglements on both sides of the original boundary. Once sufficient interdiffusion has occurred, the interface is completely healed, and the material recovers it virgin strength.

These theoretical developments have been accompanied by new types of experiments which allow the diffusion of polymer molecules across an interface to be measured. To follow the interdiffusion of identical polymers, some source of contrast is needed. Deuteration of one of the components serves this function for a broad spectrum of techniques that can detect the contrast between H and D. In this way various research groups have studied polymer interdiffusion using such techniques as small-angle neutron scattering (SANS),[7] specular neutron reflectivity (SNR),[8] secondary ionization mass spectrometry (SIMS),[9] forward recoil spectroscopy (FRES),[10] and ATR infrared spectroscopy (ATR-IR).[11] In the case of direct nonradiative energy-transfer (DET) experiments,[12] contrast is achieved by labeling one polymer with a dye that can act as an energy donor and the other polymer with a corresponding dye that can act as an acceptor.

Sample geometry plays an important role in the choice of technique. SANS and DET are most appropriate when one has droplets of the labeled polymer dispersed in an unlabeled matrix. The other techniques mentioned above are most appropriate for the study of layered polymer films. An early application of the SANS technique to the study of polymer interdiffusion was to films of poly(butyl methacrylate) (PBMA) prepared from PBMA latex dispersions.[7] More recently, SANS has been employed to carry out detailed investigations of interdiffusion in annealed films prepared from compression-molded polystyrene (PS) powder.[13,14] The major advantage of FRES and SIMS is that one can determine directly the concentration profile of the polymers produced through diffusion across the interface. SNR provides the highest resolution. Detailed experiments examining the evolution of the interface for polystyrene interdiffusion have recently been carried out.[8,15]

Our laboratory has devoted a substantial effort to the investigation of the DET technique for the study of interdiffusion in latex films. Most of our attention has been focused on PBMA, where we have investigated temperature effects,[12] molecular weight effects,[16] and the influence of plasticizers[17] and of polar groups at the latex surface[18] on the interdiffusion process. The two most prominent advantages of this technique are first the ease in synthesis of labeled material by emulsion polymerization, which allows a broad variety of polymer materials to be examined, and second the ready access in "beam time" for the fluorescence decay measurements that provide the necessary data. A third possible advantage of the DET technique over those requiring deuterated samples is that the cohesive energy mismatch caused by a small number of chromophores may be significantly less than that caused by extensive deuteration of one of the diffusion partners.[19] The two disadvantages of the technique for those not specifically interested in latex films are the relatively broad molecular weight distribution and the unavoidable presence of polar groups at the latex surface, both of which result from the particle preparation by emulsion polymerization. Both problems could be avoided if one could prepare the requisite particles by emulsifying preformed polymer.[20]

It is worth noting that there is a very interesting difference in the sensitivity of the SANS and DET techniques for the study of interdiffusion of polymers in films made up originally from spherical polymer particles. The DET technique is sensitive to the intermixing of two materials and thus is sensitive to the growth in volume of each individual particle. Mixing is essentially complete once polymers have diffused a distance r equal to the original particle radius, and at early times the amount of detectable signal increases as r^3. In the SANS experiment, what one follows is the change in r as the radius of gyration of the particle itself grows as a consequence of diffusion. Thus the DET technique is particularly sensitive to the early stages, whereas the SANS techniques becomes much more sensitive to later stages, of the interdiffusion process. In the experiments reported here, the distance scale over which the diffusion occurs is still much larger than the

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radius of gyration of the polymer chains undergoing this diffusion.

In this paper we report the application of the DET technique to interdiffusion in melt-pressed poly(methyl methacrylate) (PMMA) films. The films were prepared from a 1:1 mixture of phenanthrene (Phe)-labeled and anthracene (An)-labeled particles, both ca. 120 nm in diameter. In these experiments, Phe is the donor, selectively excited with light at 300 nm, and An is the acceptor.

Our ultimate goal is to correlate the extent of polymer interdiffusion with the growth in tensile strength in the PMMA films. Extensive studies of crack healing and other mechanical properties of PMMA have been described by Jud et al.[6]

Experimental Section

Materials. Poly(methyl methacrylate) particles were prepared by standard emulsion polymerization methods. The recipe employed followed exactly our previously published[12] preparation of labeled poly(butyl methacrylate) latex except for the substitution of MMA for BMA. The characterization of these materials is given below. The small amount of sodium dodecyl sulfate (SDS) used in the synthesis (2 wt % based upon monomer, ca. 10% surface coverage in the final latex) was removed from the samples by membrane filtration using a Millipore Minitan system with a membrane pore size of 10 nm. When freeze-dried, both latex samples exhibited a T_g by DSC of 107 °C.

	Phe–PMMA latex	An–PMMA latex
solid content (wt %)	30	31
particle diameter (nm)	127	120
dye content	1 mol % Phe	1 mol % An
M_w	1.4×10^5	1.5×10^5
M_n	3.6×10^4	4.2×10^4

Sample Preparation. Samples of the Phe- and An-labeled PMMA dispersions were mixed to give equal amounts of both latex particles. This mixture was then freeze-dried to yield a white powder. Sufficient powder was placed between two Teflon sheets to give a film ca. 8 mm in diameter and 0.1 mm thick. The sample was placed in a Carver Press and heat-pressed at 115 °C for 1 h at 950 psi. This treatment yielded transparent films with no tendency to become cloudy upon heating.

These nascent films were examined by fluorescence decay measurements and then placed into an oven (±0.1 °C) and annealed for various periods of time. Samples to be annealed for periods of time less than 20 min were place directly on a high mass aluminum plate, preequilibrated in the oven to ensure rapid attainment of temperature. Samples subjected to prolonged heating were first placed into a small flask fitted with a septum cap, and via syringe needles the flask was filled with an argon atmosphere to minimize film oxidation. This flask was then placed in the oven on top of the aluminum plate. These samples were withdrawn periodically from the oven and cooled to room temperature, and their fluorescence decay profiles were measured. The samples were then returned to the oven in the manner specified above.

Fluorescence Measurements. Film samples comprised of only of Phe-labeled or An-labeled polymer were examined by standard UV and fluorescence spectroscopy to ensure that neither the emulsion polymerization nor the film preparation process altered the spectra of the two chromophores. Fluorescence decay measurements of the Phe chromophore [$I_D(t)$] were carried out using the single photon timing technique. Samples were excited at 296 nm, and $I_D(t)$ was measured at ca. 350 nm. Samples containing only the Phe chromophore exhibited exponential decays (3 decades) with a lifetime τ_D of 44.5 ns. Decay profiles of films containing both Phe- and An-labeled polymer were fitted to models described below.

Results and Discussion

In Figure 1 we display three fluorescence decay profiles obtained in room temperature measurements on melt-pressed films. The top trace is of a film prepared from the Phe–PMMA sample. The decay is exponential, here over 2 decades of signal decay, with a lifetime τ_0 = 44.5 ns. Newly prepared films containing a 1:1 mixture of Phe–PMMA and An–PMMA show small deviations from exponentiallity at early times, indicating that some energy transfer is taking place. These deviations become more pronounced as the film is annealed at temperatures above T_g (here measured by DSC to be 107 °C). The middle curve in Figure 1 shows the decay for a sample annealed 4.0 min at 149 °C, and the lower curve shows that for the same sample annealed for 113 min at 149 °C. It is clear from these experiments that annealing the sample leads to a faster fluorescence decay. This indicates an increase in energy transfer, which must come about from diffusion of labeled polymer across the interparticle boundary.

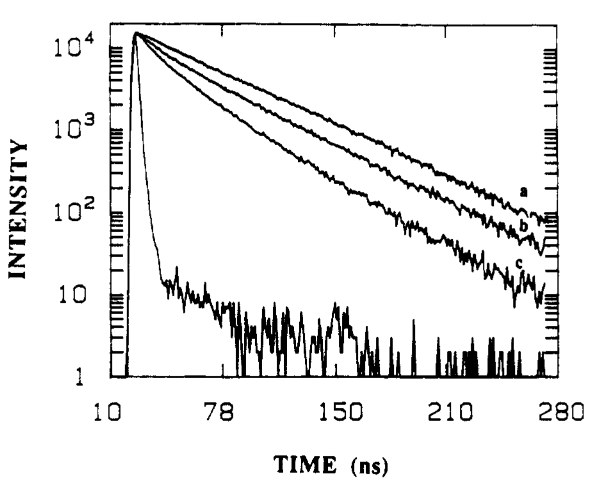

Figure 1. Fluorescence decay curves for PMMA films. The top trace (a) is of a film prepared from Phe–PMMA. The decay is exponential with τ = 44.5 ns. Traces b and c are of films prepared from 1:1 mixtures of Phe–PMMA and An–PMMA and annealed for 4 and 113 min, respectively, at 149 °C.

These fluorescence decay curves were fitted to the expression

$$I_D(t) = B_1[-t/\tau_D - P(t/\tau_D)^{1/2}] + B_2 \exp(-t/\tau_D) \quad (1)$$

where the B_1 term describes the contribution to the decay profile of those Phe which can undergo energy transfer due to diffusive mixing with an An-labeled polymer, and P is proportional to the An concentration in this domain. The B_2 term describes those Phe which remain unmixed at the time the sample is removed from the oven. In our previous experiments,[16,17] we have noted that the apparent volume fraction of mixing is given by the expression

$$f_m'(t) = B_1/(B_1 + B_2) \quad (2)$$

These apparent values must then be corrected first for the amount of interparticle energy transfer $f_m(0)$ occurring in the nascent film and for the possibility that, at long times, $f_m'(\infty)$ is not equal to unity. Thus

$$f_m = \frac{f_m'(t) - f_m'(0)}{f_m'(\infty) - f_m'(0)} \quad (3)$$

More recently we have noted that this analysis can introduce errors into the calculation of f_m if the P parameter in the fluorescence decay analysis (eq 1) does not rapidly evolve to a constant value. An alternative approach avoids this problem by integrating $I_D(t)$ to obtain the area under the normalized decay curve.[18] In this way one obtains the efficiency of energy transfer without making specific assumptions about the shape of the $I_D(t)$ profile.

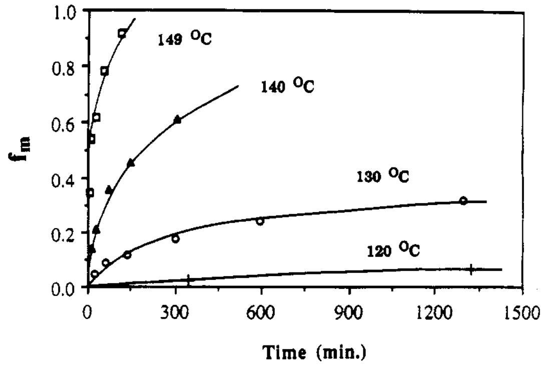

Figure 2. Values of f_m calculated from the fluorescence decay profiles for films annealed for various periods of time at the temperatures indicated.

Here we calculate f_m from the expression

$$f_m = \frac{\text{Area}(t) - \text{Area}(0)}{\text{Area}(\infty) - \text{Area}(0)} \tag{4}$$

and $f_m'(0)$ values can be calculated by comparing the integrated area in the nascent film with that of a film composed exclusively of Phe–PMMA. In our experiments, $f_m'(0)$ values were commonly on the order of 0.15, whereas $f_m'(\infty)$ values were very close to unity.

Values of f_m calculated from eq 4 are presented in Figure 2 for PMMA film samples annealed at four different temperatures. It is clear from these data that the extent of interdiffusion in these samples is extremely sensitive to temperature. It is because of this temperature sensitivity that we have confidence that polymer diffusion ceases once the film samples are removed from the annealing oven.

To proceed with the analysis, we need to calculate diffusion coefficients from the mixing data. Following arguments discussed previously,[12–14] we fit the data to a spherical diffusion model which satisfies Fick's laws of diffusion

$$\frac{\partial C(r,t)}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial C(r,t)}{\partial r}\right) \tag{5}$$

so that at time t

$$C(r,t) = \frac{C_0}{2}\left\{\operatorname{erf}\left(\frac{R+r}{2(Dt)^{1/2}}\right) + \operatorname{erf}\left(\frac{R-r}{2(Dt)^{1/2}}\right)\right\} - \frac{C_0}{r}\left(\frac{Dt}{\pi}\right)^{1/2}\left\{\exp\left(\frac{(R-r)^2}{4Dt}\right) - \exp\left(-\frac{(R+r)^2}{4Dt}\right)\right\} \tag{6}$$

A schematic drawing representing the concentration profile at $t = 0$ and at a later time is shown in Figure 3. D values are calculated by equating f_m with the fractional mass which has diffused across the interface (M_t/M_∞), where $M_\infty = (4/3)\pi R^3 C_0$, and carrying out a numerical integration to find the best D value which satisfies the equation

$$M_t = M_\infty - \int_0^R C(r)\, 4\pi r^2\, dr \tag{7}$$

D values obtained in this way are shown in Figure 4. These range from 10^{-14} cm^2 s^{-1} at 149 °C to 10^{-18} cm^2 s^{-1} at 120 °C. There is a slight tendency for the D values to decrease at later times, which we attribute to the molecular weight polydispersity of our latex samples. This tendency is significantly smaller than we observed in our study of PBMA latex films. Similar observations about the variation of D with the extent of interdiffusion have been made in polystyrene samples prepared by compression-molding mixtures of deuterated and ordinary polystyrene latex, where interdiffusion was studied by small-angle neutron scattering.[13,14] In recent experiments by the Lehigh group using polymer droplets prepared by emulsification of narrow molecular weight distribution polymer samples, values of D remained constant throughout the experiment.[20]

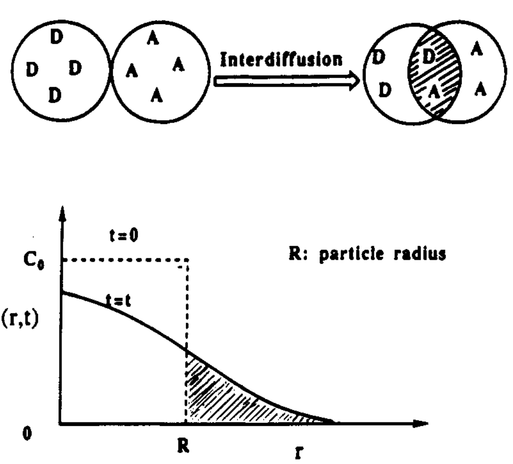

Figure 3. Schematic drawing depicting the concentration profile $C(r,t)$ of donor- or acceptor-labeled polymer at $t = 0$ and at some later time t.

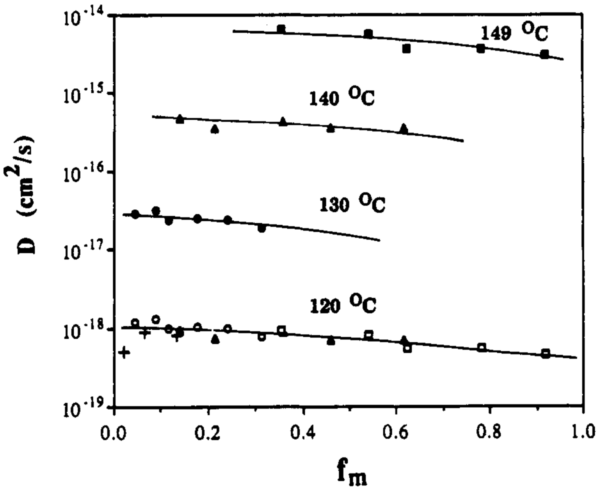

Figure 4. D values calculated from the data in Figure 2 for film samples annealed at the temperatures indicated, plotted as a function of the degree of mixing, f_m. The open symbols on the line marked 120 °C are obtained by shifting data obtained from experiments at higher temperatures using an activation energy of 100 kcal/mol. The points (+) are obtained from experimental data at 120 °C.

When the D values obtained at different temperatures are plotted in an Arrhenius fashion, a linear plot is obtained. In constructing this plot, we were careful to compare D values obtained at comparable f_m values. For the data in Figure 5, data at $f_m \approx 0.3$ were selected except for that at 120 °C, where the longest time value ($f_m = 0.12$) was used. From the slope of the plot, an activation energy of 100 kcal/mol was obtained. To emphasize the fact this this value in fact pertains to all the data, we use this value to compute D values for 120 °C. As is apparent in Figure 4, all the data superpose upon a common line. It is noteworthy that this master curve also contains the few data points we were able to obtain at that temperature.

These experiments were carried out over a rather narrow range of temperatures, from ca. T_g + 10 °C to T_g + 40 °C. In the case of poly(butyl methacrylate) latex films, we have established[11] that interdiffusion follows a classical Williams–Landel–Ferry (WLF) temperature dependence that can be described with the same WLF parameters obtained independently by Ferry's group[21] from viscoelastic measurements on bulk PBMA. Thus the linear fit to

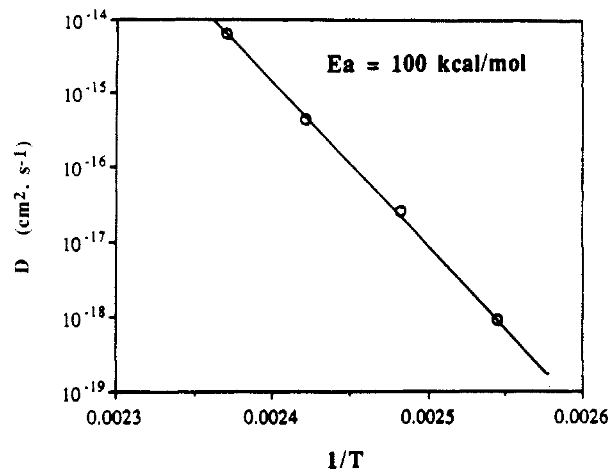

Figure 5. Arrhenius plot of the D values for $f_m \approx 0.3$.

Table I. Parameters for PMMA in the Melt

$G_N° = 5 \times 10^6$ dyn cm^{-2} [a]	Time for polymer of $M = M_w$ to diffuse R_G [$t = \langle R_G^2 \rangle / 6D$]
$M_c = 3 \times 10^4$	120 °C, 56 h
$R^2/M = 4.56 \times 10^{-17}$ cm^2 mol g^{-1}	130 °C, 2 h
$\eta_0(M_c) = 1.01 \times 10^5$ P [b]	140 °C, 6.8 min
$D = 3.24 \times 10^{-5}/M^2$ cm^2 s^{-1} [b]	149 °C, 30 s

[a] Reference 5. [b] Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1990; Chapter 15, p 468.

the data plotted in the Arrhenius form is a consequence of the narrow range of temperatures over which the data were obtained, and the large magnitude of the apparent activation energy is a reflection of how close the measurement temperatures were to T_g.

As a final exercise, we compare the D values we obtain in the above analysis with those predicted by Graessley's parametrization of the reptation model.[22] Graessley relates the magnitude of the polymer diffusion coefficient to its molecular mass M, its mean dimensions as described by the mean-squared radius of gyration R_G^2 and end-to-end distance R_F^2, and the plateau modulus $G_N°$ at the temperature of interest.

$$D = \frac{G_N°}{135}\left(\frac{\rho R_G T}{G_N°}\right)^2\left(\frac{R_F^2}{M}\right)\frac{M_c}{\eta_0(M_c)M^2} \tag{8}$$

In this expression, ρ is the polymer density and $\eta_0(M_C)$ is the melt viscosity of a polymer sample of $M = M_c$, the critical entanglement molecular mass. Using the values listed in Table I, we calculate, for 149 °C, $D = 1.6 \times 10^{-15}$ cm^2 s^{-1} for a PMMA with $M = M_w$ for our sample and $D = 2.1 \times 10^{-15}$ cm^2 s^{-1} for a PMMA with $M = M_n$ for our sample. By comparison, at 149 °C, we obtain $D = 7 \times 10^{-15}$ cm^2 s^{-1} for the initial stage of polymer interdiffusion and $D = 3 \times 10^{-15}$ cm^2 s^{-1} at longer times.

These values are remarkably close, which suggests that the approximate magnitude of D may not be very sensitive to the details of the diffusion model used. Rather this magnitude reflects the time necessary to diffuse a distance comparable to the radius of the latex.

A reviewer commented that the good agreement between our data and eq 8 may be fortuitous and may not apply at different temperatures. D values calculated from eq 8 are sensitively dependent upon how the melt viscosity of the polymer varies with temperature. This issue could be settled if appropriate melt viscosity data were available. We are unaware of such data, but there is one indication in the literature that another property of PMMA that should satisfy WLF behavior, the α-relaxation, exhibits a similar temperature dependence over our range of temperatures.[23]

Summary

Direct nonradiative energy-transfer experiments were carried out on melt-pressed PMMA films comprised of a 1:1 mixture of donor- and acceptor-labeled PMMA microspheres. When these films were annealed in an oven at temperatures between 120 and 150 °C and subsequently cooled to room temperature, the extent of energy transfer was found to increase, indicating that polymer diffusion was taking place. From the increase in the extent of energy transfer, the degree of intermixing and the cumulative mean diffusion coefficients for the polymer were calculated. D values were on the order of 10^{-18} cm^2 s^{-1} at 120 °C and 10^{-15} cm^2 s^{-1} at 149 °C, corresponding to an activation energy of 100 kcal/mol.

Acknowledgment. The authors thank the Ontario Centre for Materials Research and NSERC Canada for their support of this research.

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