Macromolecules 1988, *21*, 2091-2094

Photon Correlation Spectroscopy from Dilute Polymer–Polymer Mixtures

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Received October 13, 1987

ABSTRACT: We examine the molecular weight, concentration, and temperature dependences of the initial decay of the light-scattering photon correlation from dilute mixtures of low molecular weight polystyrenes in poly(methylphenylsiloxane). We observe the q^2 dependence previously reported from these mixtures. For polystyrene molecular weights substantially larger than that of the poly(methylphenylsiloxane) macromolecules, the infinite dilution limit of the diffusion coefficient extracted from the initial decay follows a molecular weight dependence close to $M^{-0.5}$. For the very dilute mixtures studied, the variation of the diffusion coefficient with concentration appears to be independent of temperature. The temperature dependence of the initial decay rate of the correlation deviates from an Arrhenius behavior as the coexistence curve of the mixture is approached.

Introduction

It has recently been reported that the photon correlation mode of dynamic light scattering is able to provide information on the mutual diffusion coefficient of compatible polymer mixtures.[1,2] In this paper we report results on very dilute solutions of the system polystyrene (PS)–poly(methylphenylsiloxane) (PMPS) previously studied.[1,2] We shall be concerned here with the possibility of extracting concentration and molecular weight dependence of the observed diffusion mode from homogeneous one-phase dilute compatible mixtures at temperatures below the critical temperature. The phase diagram of PMPS ($M_w \simeq 2800$) and PS ($M_w \simeq 9000$) has been investigated by Nose and Nojima,[3] whose results indicate an upper critical point of approximately 100 °C for this system. Our experiments performed at temperatures of 50 and 65 °C are by necessity limited to very low concentration of PS since additional PS will lead to phase separation. In this concentration regime, the initial slope of the photon correlation exhibits an unambiguous wavevector-squared-dependence behavior of a diffusion character over a scattering angle range from 45° to 120°. However, because of the non-single-exponential decay of the correlation function, one can only tentatively assign the q^2 dependence of the initial slope to the binary diffusion coefficient of the system. As proposed by Murschall et al., the nonexponential character of the correlation arises from the density fluctuations, which for a polymeric liquid melt are q independent in the photon correlation regime. Since one would expect that a strong coupling between concentrations fluctuations and density fluctuations would lead to a deviation from the q^2 dependence of the concentration relaxation,[4] one may assume that the observed q^2 dependence is related to the mutual diffusion coefficient of the system. Such an assumption needs further verification; in what follows we have associated the initial decay rate Γ of the correlation function to a diffusion coefficient D by taking Γ equal to $2Dq^2$. The variation of D with molecular weight and concentration of polystyrene examined here reveals some of the characteristics of this diffusion mode at the two temperatures investigated. We also report the temperature dependence of D over a wide range of temperatures for one sample; deviations from Arrhenius behavior occur as one approaches the coexistence curve.

Experimental Section

The polystyrene samples $M_w = 2000$ with $M_w/M_n = 1.3$, $M_w = 10\,200$ with $M_w/M_n = 1.07$, and $M_w = 17\,500$ with $M_w/M_n = 1.04$ were obtained from Polysciences, Inc. A sample of $M_w = 12\,200$ with $M_w/M_n = 1.02$ was obtained from Scientific Polymer Products, Inc. The poly(methylphenylsiloxane), $M_w = 2600$ with $M_w/M_n = 1.5$, was obtained from Petrarch Systems, Inc. The polystyrene samples were used as purchased without further purification. From GPC measurements and fractionation, the poly(methylphenylsiloxane) appeared to contain a significant amount of short-chain oligomers; it was dried for 6 days under vacuum to remove volatile impurities before use.

All light-scattering samples were prepared by weighing the two components. The two homopolymers were directly mixed at 120 °C except for the samples of polystyrene with $M_w = 17\,500$. For homogeneous mixtures to be obtained, the samples were kept in an oven at 120 °C for 3 h, taken out and carefully shaken by hand, and then allowed to cool slowly to room temperature. This procedure was repeated four times. The samples were then slowly filtered twice through 0.2-μm Teflon filters (Millipore Co.) into dust-free scattering cells and sealed with parafilm. The filtration procedure was carried out in a dust-free environment. The higher molecular weight polystyrene samples ($M_w = 17\,500$) were prepared by dissolving both polymers in toluene and filtering the solution as described above. The toluene was removed under vacuum at 60 °C for 6 days by fitting the scattering cells with filters that prohibited the entry of dust particles but allowed toluene to evaporate.

The samples were allowed to stand for at least 1 week after filtration before light-scattering measurements were performed. We could not work with samples of polystyrene concentration below $\sim 0.1 \times 10^{-2}$ g/mL as the correlation signal-to-noise ratio became too small and the error involved in determining a diffusion coefficient became too large. For polystyrene of $M_w = 17\,500$, the highest composition for which we performed the measurements was 0.469×10^{-2} g/cm^3. For higher attempted compositions, the samples became turbid at 50 °C, indicating that a phase separation had occurred. The scattering cells were centrifuge tubes (Pyrex, 5 mL, o.d. = 13 mm) that were cleaned with Chromerge and distilled water. They were then repeatedly rinsed with filtered water to avoid dust particles. The sample-containing cells were immersed into the refractive index matching glycerine contained in a C-105 Brice–Phoenix cylindrical light-scattering cell.

The photon correlation spectrometer consisted of a Lexel 85 argon ion laser (λ = 4880 Å) in conjunction with an EMI 9789B photomultiplier tube and a Birnboim correlator. A temperature-controlling bath and jacket for the Brice–Phoenix cell allowed the temperature constant to be held to better than ±0.1 °C. The experiments were performed in the homodyne mode, and the scattering angle was varied from 45° to 120° in 15° increments.

Results and Discussion

The initial slope of the correlation function was analyzed by fitting the logarithm of the normalized experimental autocorrelation function to a polynomial of second order in time.[4] A minimum of seven initial data points of the correlation decay were used with a typical interval time of $\Delta\tau = 25.6$ μs. The initial slope thus extracted always showed a very good q^2 dependence. In Figure 1 we plotted the initial decay constant Γ versus q^2 for a sample of

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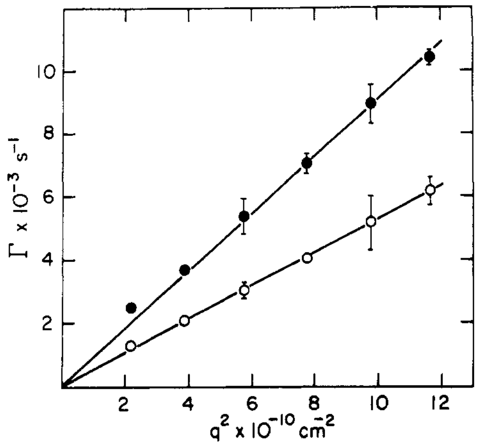

Figure 1. Initial decay constants Γ of the photon correlation versus q^2, the square of the scattering vector for a 4.34 × 10^{-3} g/cm^3 solution of PS (M_w = 10 200) in PMPS at 50 (○) and at 65 °C (●).

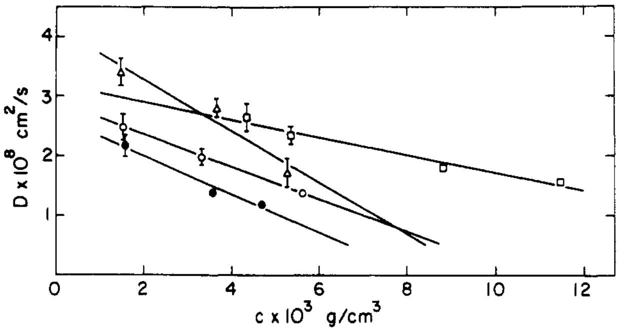

Figure 2. Dependence of the diffusion coefficient D, extracted from the initial decay, versus concentration at 50 °C for M_w = 2 000 (⧋), M_w = 10 200 (⊡), M_w = 12 200 (⊙), and M_w = 17 500 (●).

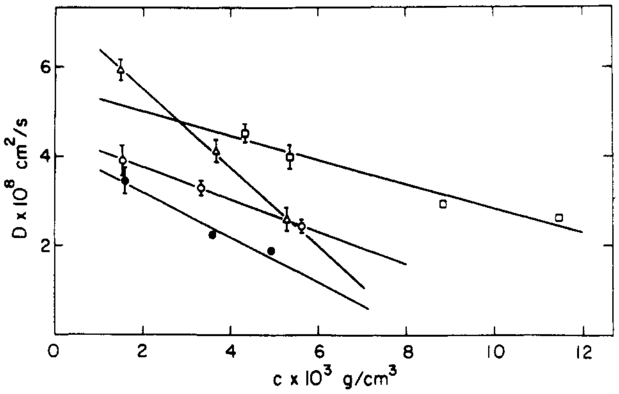

Figure 3. Dependence of the diffusion coefficient D, extracted from the initial decay, versus concentration at 65 °C for M_w = 2 000 (⧋), M_w = 10 200 (⊡), M_w = 12 200 (⊙), and M_w = 17 500 (●).

polystyrene of molecular weight 10 200 at a composition of 4.34 × 10^{-3} g/cm^3 in poly(methylphenylsiloxane). The slope of the best-fit straight line is taken to be twice the diffusion coefficient D.

The effect of polystyrene concentration on the diffusion coefficients as measured above is shown in Figure 2 for 50 °C and in Figure 3 for 65 °C. Within our experimental errors, the diffusion coefficient decreases linearly with concentration in the limited concentration range examined. For the three larger molecular weight polystyrene samples the trend is a steeper decrease in D with concentration as molecular weight increases. This trend is, however, violated by the results of the M_w = 2000 samples, for which we could not find an entirely satisfactory explanation. This PS sample has an appreciably higher degree of polydispersity (M_w/M_n = 1.3) as opposed to the other samples ($M_w/M_n \leq 1.1$), which has not been taken into account and which could have affected the light scattering data. Another possibility is that aggregates may have been present at the higher concentrations of the M_w = 2000 samples, causing the steeper decrease of D with concentration. However, the results could also be due to the fact that at M_w = 2000, the PS molecules are smaller or comparable in size to the PMPS molecules, whereas the higher molecular weight PS molecules are 4–7 times larger, leading to different mechanisms.

Table I
Values of $D°$ and k from Least-Squares Fits of D versus c

	t = 50 °C		t = 65 °C	
M_w(PS)	$10^8D°$, cm^2/s	$10^{-2}k$, cm^3/g	$10^8D°$, cm^2/s	$10^{-2}k$, cm^3/g
2 000	4.15 ± 0.41	1.05 ± 0.19	7.28 ± 0.41	1.21 ± 0.17
10 200	3.21 ± 0.28	0.46 ± 0.05	5.54 ± 0.33	0.49 ± 0.04
12 200	2.89 ± 0.26	0.94 ± 0.13	4.48 ± 0.59	0.80 ± 0.17
17 500	2.65 ± 0.32	1.22 ± 0.19	4.19 ± 0.45	1.21 ± 0.14

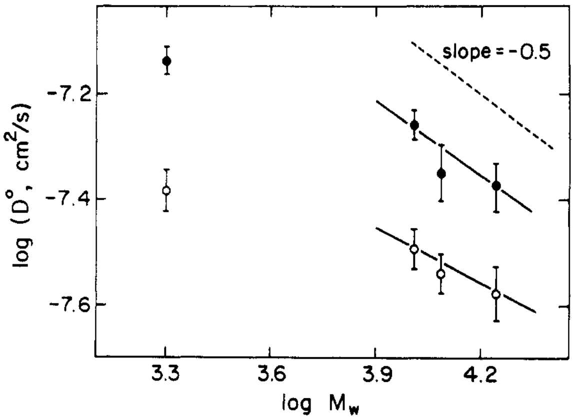

Figure 4. Infinite dilution limit of the tracer diffusion of polystyrene $D°$, obtained by extrapolation of the previous results, plotted as log $D°$ versus log M_w. The full lines represent best fits to the three higher molecular weights, and the dashed line represents a slope of $-^1/_2$. Data are at 50 (○) and at 65 °C (●).

The results of the extrapolated infinite dilution limit of the diffusion coefficients, $D°$, and the slopes, k, of the best-fit straight lines to the results of Figures 2 and 3 are summarized in Table I. Figure 4 shows a plot of log $D°$ versus log M_w. Leaving aside the lowest molecular weight ($M_w \simeq 2000$) results, our limited data seem to indicate a molecular weight dependence of $D°$ close to $M_w^{0.5}$. At 50 °C, a linear regression analysis of the slope of log $D°$ versus log M_w gives −0.34 ± 0.04 for the three highest molecular weights; at 60 °C, the slope is 0.47 ± 0.03 for the same samples. The dashed curve in Figure 4 represents a slope of −0.5. If these diffusion coefficients represent indeed the tracer diffusion $D°$ of polystyrene of M_w = 10 200, 12 200, 17 500 in poly(methylphenylsiloxane) of $M_w \simeq 2600$, the polytyrene molecules are diffusing in a fashion akin to a Stokes–Einstein diffusion of a random coil (similar to their behavior in an organic Θ solvent) than in the "Rouse" fashion ($D° \sim M_w^{-1.0}$) that has been expected and observed for polymeric liquids.[5] The results for $D°$ of M_w(PS) = 2000 can then be interpreted as having more of a "Rouse" character, where the friction on the chain is the sum of the frictions on all the subunits along the chain and leads to lower value of $D°$ than would have been extrapolated from the higher molecular weight results in Figure 4.

Two equations have been proposed that relate the mutual diffusion coefficient of a binary polymer mixture to the tracer diffusion coefficients of the two species.[1] In the

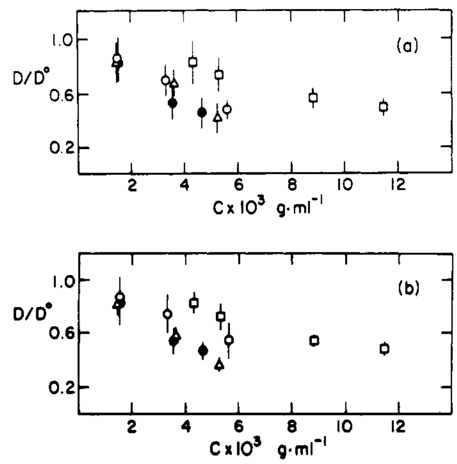

Figure 5. Normalized diffusion coefficients $D/D°$ versus concentration at 50 (a) and at 65 °C (b); symbols are as in Figure 2.

Table II
Summary of Results for D and $D/D°$

PS (M_w)	10^3c, g/cm^3	10^8D, cm^2/s 50 °C	10^8D, cm^2/s 65 °C	$D/D°$ 50 °C	$D/D°$ 65 °C
2 000		4.15	7.28	1.00	1.00
	1.49	3.40	5.93	0.82 ± 0.15	0.81 ± 0.09
	3.665	2.80	4.13	0.67 ± 0.10	0.57 ± 0.07
	5.281	1.72	2.58	0.41 ± 0.11	0.35 ± 0.06
10 200		3.21	5.54	1.00	1.00
	4.339	2.64	4.54	0.82 ± 0.16	0.82 ± 0.09
	5.539	2.35	4.00	0.73 ± 0.12	0.72 ± 0.10
	8.830	1.80	2.93	0.56 ± 0.07	0.53 ± 0.04
	11.469	1.56	2.61	0.49 ± 0.06	0.47 ± 0.05
12 200		2.89	4.48	1.00	1.00
	1.536	2.47	3.91	0.85 ± 0.17	0.87 ± 0.22
	3.325	1.99	3.30	0.69 ± 0.11	0.74 ± 0.15
	5.622	1.36	2.44	0.47 ± 0.07	0.54 ± 0.13
17 500		2.65	4.19	1.00	1.00
	1.568	2.18	3.45	0.82 ± 0.19	0.82 ± 0.18
	3.589	1.38	2.23	0.52 ± 0.12	0.53 ± 0.10
	4.692	1.20	1.91	0.45 ± 0.11	0.46 ± 0.07

very dilute solutions considered here, where the volume fraction of polystyrene is orders of magnitude smaller than that of poly(methylphenylsiloxane), $\Phi_A(\mathrm{PS}) \ll \Phi_B(\mathrm{PMPS})$, both equations reduce to the simple form

$$D = D_A(1 - 2\chi\phi_A N_A) \qquad (1)$$

where D_A is the concentration dependent tracer diffusion of PS, χ is the temperature-dependent Flory interaction parameter, and N_A is the degree of polymerization of polystyrene. Equation 1 is obtained by assuming that the Φ_B terms are dominant in both the thermodynamic component and the frictional component of D. The concentration dependence of D observed in our experiments could come from two sources: $D_A(\phi_A)$ or $\chi\phi_A$. The values of $D/D°$ listed in Table II are independent of temperature within experimental errors although the values of the unnormalized D change appreciably between 50 and 65 °C. We may conclude that the contribution of the temperature-dependent component of the χ parameter in eq 1 is negligible and we can write

$$D \simeq D°(1 - kc) \qquad (2)$$

where $-k$ is the slope of the best-fit straight lines through the data $D/D°$ versus concentration c presented in Figure 5. The values of k are also independent of temperature within our experimental error (Table I). For polymer–solvent systems, k in eq 2 represents typically a hydrodynamic interaction parameter, which for polymer–Θ solvent system[6,7] follows the scaling law $M_w^{0.5}$. Ignoring the results of the lowest molecular weight samples, the dependence of k on M_w in the polymer–polymer system considered here appears to be much stronger even though the limited data and the large uncertainties do not allow an unambiguous analysis. This strong dependence may be due to the temperature-independent component of the χ parameter term in eq 1.

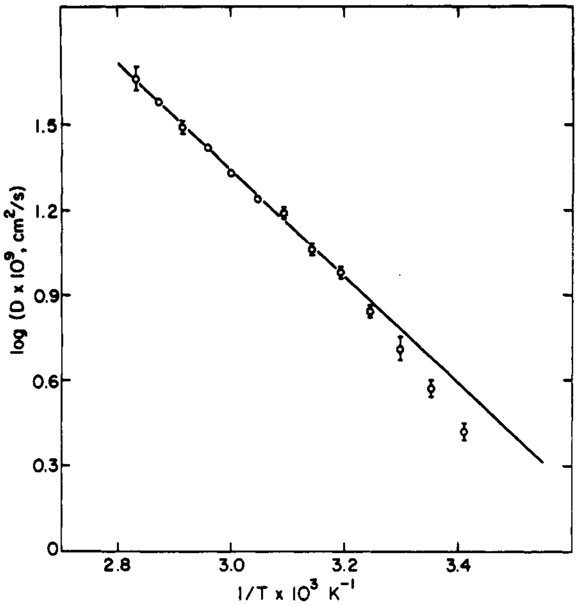

Figure 6. Arrhenius plot of the temperature dependence of D for polystyrene M_w = 10 200 at 1.147 × 10^{-2} g/cm^3. Deviations occur at $1/T$ = 3.2 × 10^3 K^{-1} or approximately 40 °C.

The temperature dependence of the initial decay of the light-scattering correlation from 20 to 80 °C was studied for a solution of PS with M_w = 10 200 at the concentration of 1.147 × 10^{-2} g/cm^3 in PMPS. The measurements were made at a scattering angle of 90° except for the two temperatures of 50 and 65 °C, which were studied over a wide range of scattering angles to establish the q^2 dependence reported above. Away from the coexistence curve,[3] above 40 °C (or below $1/T \simeq 3.2 \times 10^{-3}$ K^{-1}), the diffusion coefficient extracted from the initial decay obeys an Arrhenius law with an activation energy of 35.7 kJ/mol. As the coexistence curve is approached, deviations occur as shown in Figure 6 and the diffusion coefficient is "slowing down". The glass transition of this sample can be estimated from an empirical relation[1] to be practically unchanged from the glass transition of PMPS due to the very small concentration of PS in the sample. Since the deviations from Arrhenius behavior occurs at a temperature less than a 100 K from the glass transition temperature T_g = 228.6 K, it is natural to attempt to describe the temperature dependence of the initial decay of the correlation in terms of a Vogel-type equation[1]

$$\Gamma^{-1} = \Gamma_\infty^{-1} \exp\frac{B}{T - T_\infty} \qquad (3)$$

where the activation parameter $B = 2.303\, C_1C_2$, and $T_\infty = T_g - C_2$, with C_1 and C_2 being the Williams–Landel–Ferry coefficients.[8] In Figure 7, we show however that the experimental data cannot uniquely determine the values of B and C_2. The same set of data has been fit with T_∞ = 168.6 K (i.e., C_2 = 60) and T_∞ = 208.6 K (i.e., C_2 = 20) to yield equally satisfactory correlations with slopes B = 1080 K and B = 576 K, respectively. Since the first set of B and C_2 values is closer to the corresponding values in pure polystyrene whereas the other set of values is closer to the corresponding values of pure poly(methylphenylsiloxane),[1] it is unlikely that an approach based on just a

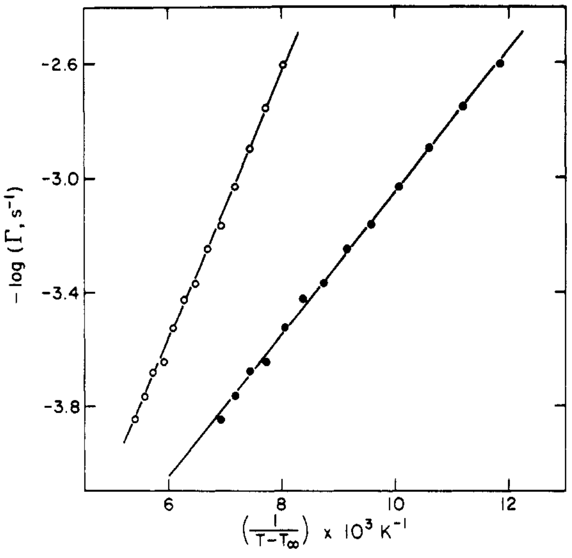

Figure 7. Experimental decay rates correlated with eq 3 for T_∞ = 168.6 K with slope B = 1080 K (○) and for T_∞ = 208.6 K with slope B = 576 K (●). The slopes are obtained by a least-squares fit.

temperature study can be used to distinguish which of the two species has the dominating effect on the mutual diffusion coefficient.

Conclusion

We have observed by photon correlation the q^2-dependent diffusion mode previously reported on mixtures of polystyrene and poly(methylphenylsiloxane) mixtures. For polystyrene molecular weights of 10 200, 12 200 and 17 500, which are substantially larger than the PMPS solvent molecular weight 2 600, the infinite dilution limit $D°$ of the diffusion coefficient extracted from the initial decay of the correlation appears to follow a Stokes–Einstein diffusion mechanism with a molecular weight dependence close to $M^{-0.5}$. In the very small concentration regime of polystyrene studied here, the estimated contribution from the temperature-dependent component of the thermodynamic interaction term is very small and the values of $D/D°$ remain unchanged within experimental error from their values at 50 °C to their values at 65 °C. Since both D and $D°$ vary substantially with temperature but their ratio does not, we have monitored primarily the decrease of the tracer diffusion of polystyrene with concentration. The "hydrodynamic interaction" parameter k describing this decrease appears to have a stronger dependence on molecular weight in this polymeric solvent than the one expected in a small-molecule Θ solvent, possibly due to the entropic component of χ. The temperature dependence of the initial decay rate of the correlation obeys an Arrhenius law at temperature far away from the coexistence curve of the mixture; deviations occur as the coexistence curve and the glass transition temperature are approached. A Vogel-type equation can correlate the temperature dependence of the relaxation time related to the diffusion (Γ^{-1} s) over the entire temperature range studied rather well, but very different sets of parameters appear to give an equally good fit to the experimental data.

Acknowledgment. We acknowledge the financial support of the Polymers Program of the National Science Foundation under Grant DMR-8411850. C.C. thanks E. Kramer for a useful discussion.

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Photophysical Studies of Molecular Mobility in Polymer Films. 1. Oxygen Mobility in Polymer Films Monitored by Quenching of the Triplet–Triplet Absorption of Bromopyrene

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ABSTRACT: Oxygen mobility in several polymer films has been monitored by measuring oxygen quenching of the excited triplet state of film-incorporated bromopyrene observed via its triplet–triplet (T_1–T_n) absorption. Cross-linking did not impose any restriction on oxygen movement in the SU8 epoxy film below the glass transition temperature, and the oxygen quenching rate increases markedly with temperature in an uncured epoxy film; the effect is relatively small in a completely cross-linked film. A significant effect of polymer chain structure on the oxygen quenching rate was observed and a possible mechanism discussed. The quenching rate constants in these polymers increase in the order poly(dimethylsiloxane) ≫ polystyrene > poly(ethyl methacrylate) ≳ cellulose acetate ~ poly(vinyl acetate) > epoxy SU8 film ≳ poly(ethylene terephthalate) (Mylar). The quenching rate constants are much higher than that expected from the bulk macroviscosity of the film and are of the order 10^6–10^9 M^{-1} s^{-1}. Both nitrogen and oxygen plasticize the glassy SU8 film and increase the effectiveness of oxygen quenching; the observed pressure effect is in agreement with the "dual-mode" theory.

Introduction

The molecular motion of low molecular weight solutes in polymer films is of fundamental importance for both kinetic theory and technology. In the technological field an understanding of movement in polymer films has been vital in recent years with the development of a wide variety of packaging films, surface protective coatings, and drug delivering membrane systems. The mobility of oxygen in

0024-9297/88/2221-2094$01.50/0