Tracer Diffusion Measurement in Polymer Solutions Near the Glass Transition by Forced Rayleigh Scattering

Forced Rayleigh scattering, a relatively recently developed optical technique, is used to measure tracer diffusion coefficients in polymer-solvent mixtures near the system glass transition temperature, T_g. The technique has a wider range of potential application than has yet been realized, and so is presented in some detail. The objectives were to obtain data necessary to scrutinize free volume theory, and to understand so-called anomalous, non-Fickian diffusion effects observed by others in polymer-solvent mixtures near T_g. Data on dye tracer diffusion coefficients in the systems polyvinyl acetate-toluene, polystyrene-toluene, and polystyrene-tri-m-tolyl phosphate were obtained over a polymer concentration range from infinite dilution to 96 wt. %. Small molecule diffusion coefficients are seen to vary by as much as nine orders of magnitude (10^{-14} to 10^{-5} cm^2/s) over this concentration range. The data are in reasonable accord with expectations based on the Duda-Vrentas version of free-volume theory.

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Introduction

A basic understanding of molecular diffusion in polymer-solvent systems is important in the design and analysis of many industrial processes. The very high viscosities that are characteristic of polymer systems make it difficult to enhance mass transfer by mechanical means, thus making diffusion the rate-controlling factor in many processes. An example is found in polymer production. In a polymerization reactor, the rates of several steps of a free radical chain reaction may be determined by the diffusion of the species in the highly viscous polymer-monomer mixture, especially when conversion to polymer is high. The phenomenon of limiting conversion, premature cessation of polymerization due to vitrification, reflects sharp decreases in diffusivity as the polymer content in the reaction mixtures rises. A second example is the devolatilization process, where small amounts of residual species such as monomers and other chemicals added during polymerization are removed from the polymer product in order to meet health and environmental standards. Many technological applications of polymers also require knowledge of diffusion data. Examples include barrier properties of polymers in packaging applications, controlled release of drugs, doped electrically-conducting polymers, and polymer-modified electrodes.

Since measurements of diffusivity are frequently time-consuming and difficult, several attempts have been made to provide correlative or predictive theories for reliable estimates of diffusion coefficients in solutions where one of the species is a macromolecule. In this sense, "correlative" refers to the use of all available diffusion data to extract necessary parameters in the theory, while "predictive" theories require minimal or no diffusion data to obtain parameters for the prediction of diffusion coefficients over a wide range of temperature and concentration. At temperatures far above the system glass transition temperature, free-volume-based theories have been applied successfully to many polymer-solvent systems. The Fujita (1961) version of the free-volume theory is one of the earliest and most straightforward. It has been useful in describing the temperature and concentration dependence of diffusion coefficients in polymer-solvent systems (Fujita, 1968). However, it involves parameters that do not have clearly established molecular significance. Vrentas and Duda (1977a,b, 1979) proposed a modified version of the free-volume theory that redressed possible

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shortcomings in the Fujita theory, and has predictive as well as correlative capabilities. Their version of the free-volume theory is to some extent supported by experimental data (Vrentas et al., 1985) obtained through the traditional sorption experiment, in which a polymer sample is exposed to a macroscopic concentration gradient of penetrant and the rate of sorption is monitored by periodic sample weighing. Sorption experiments give the binary mutual diffusion coefficient.

For single-molecule, or "self-," diffusion in polymer-solvent systems in the vicinity of or below the system glass transition temperature, T_g, apparently no molecular-level theories exist. The lack of experimental data for single-molecule diffusion at temperatures near T_g undoubtedly hinders the development of such theories. Experimental measurements of binary mutual diffusion coefficients in this region are usually complicated by the coupling of diffusion and relaxation processes, which leads to a variety of apparently anomalous phenomena and makes molecular interpretation of experimental data ambiguous (Park, 1968; Hopfenburg and Stannett, 1973; Frisch, 1980). The presence of anomalous phenomena reflects primarily the nonequilibrium nature of the sorption process. As diluent molecules diffuse through the polymer sample, the concentration of diluent varies with time and position in the sample. Thus the system glass transition temperature also varies with time and position, since part of the sample is plasticized by absorbed diluent while the rest remains glassy. Since sorption occurs through the surfaces of polymer films, the surface concentration of diluent is an important boundary condition that must be established and controlled (Long and Richman, 1960; Crank and Park, 1951).

In this work a relatively new optical technique, forced Rayleigh scattering (FRS), has been adopted to study the tracer diffusion coefficient, D_t, of small molecules in polymer solutions above, near, and below the system glass transition temperature. This transient optical grating technique creates a spatially periodic concentration profile of photochromic dyes, and subsequently follows its dispersion by diffusion. This technique circumvents the nonequilibrium effects of the sorption experiment, and also permits measurement of diffusion coefficients as small as 10^{-14} cm^2/s. The traditional sorption technique permits measurements of diffusion coefficients as small as 10^{-12} cm^2/s, although this limit has been extended to 10^{-17} cm^2/s using specially prepared polymer powder samples (Berens and Hopfenberg, 1982). In addition, FRS measures tracer diffusion coefficients, instead of the mutual diffusion coefficients measured by the sorption technique. The tracer diffusion coefficient is that of a single molecule in a multicomponent system, and therefore may be more accessible theoretically than the mutual diffusion coefficient. Its measurement is of particular interest in building a molecular level picture of transport. It is important to emphasize that FRS and sorption measurements are complementary; the former offers a unique opportunity to probe single-molecule behavior, while the latter is more generally applicable and is closer to most situations of technological importance. Furthermore, FRS applies primarily to the diffusion of molecules of monomer size or greater, while sorption techniques are readily used for smaller diluents such as O_2, CO_2, and H_2O as well.

Currently, this experiment is being used to acquire diffusion data in order to provide a broader basis for a critical evaluation of current theory and for the development of the next generation of theory. Questions that can ultimately be addressed by this technique include:

1. How does D_t vary with T both above and below T_g?
2. Is there a distinctive change in $D_t(T)$ at or near T_g?
3. Is there evidence of the anomalous diffusion regimes observed in sorption experiments?
4. Over what range of composition and temperature can free-volume theory adequately describe the important features of the data?
5. Under what conditions of diluent concentration, temperature, diffusant size and shape, etc., is the complexity of the more elaborate and powerful Vrentas-Duda model justified or required in preference to the simpler Fujita theory?

To date, diffusion coefficients have been measured ranging over nine orders of magnitude, in solutions ranging from 0 to 96% polymer, and do *not conflict* with free volume ideas at this preliminary stage. The purpose of this paper is to describe the experimental approach, and to illustrate its power in this particular application.

The FRS Experiment

The forced Rayleigh scattering (FRS) technique, also known as holographic relaxation spectroscopy (HRS), was first developed to study thermal diffusion in solids (Pohl et al., 1973; Pohl, 1979), liquids (Eichler et al., 1973), and liquid crystals (Urbach et al., 1978; Rondelez et al., 1978a). Diffusion of dye-labeled polymers in melts (Antonietti et al., 1984; Nemoto et al., 1984, 1985) and solutions (Hervet et al., 1979; Leger et al., 1981; Wesson et al., 1984), and diffusion of photochromic dyes themselves in liquid crystal solutions (Hervet et al., 1978), gelatins (Chang and Yu, 1983; Wesson et al., 1982), polymer melts (Sillescu et al., 1985), and solutions (Landry, 1985) have also been examined using this technique. Diffusion in some biological systems has also been investigated by Rhee et al. (1984) and Stewart et al. (1986), using the same technique. A similar transient grating approach has also been applied to the study of the dynamics of energy transport in molecular solids (Phillion et al., 1975; Rondelez et al., 1978b; Salcedo et al., 1978; Fayer, 1982; Lutz et al., 1981; Nelson and Fayer, 1980; Nelson et al., 1982).

FRS may be viewed as a three-step process. In step one, two intense, mutually coherent laser beams of wavelength λ intersect at an angle θ in the sample, producing an interference pattern sinusoidal in intensity with period $d = \lambda/2\sin(\theta/2)$. In step two, this pattern is recorded in the sample by the presence of a small quantity of photochromic dye moieties, as those dye molecules A in the constructive interference fringes undergo isomerization to a spectrally distinct form B. The resulting sinusoidal concentration profile of A and B acts as an optical grating, generally with both refractive index and absorption coefficient contributions. Step three consists of directing a third laser beam through the grating, and monitoring the diffracted intensity at an angle determined by the Bragg condition. The diffracted intensity decays exponentially in time as the grating is erased by the interdiffusion of the two dye isomers A and B. Thus the decay time constant depends directly on the dye diffusion coefficient, assuming that the thermal reconversion $B \rightarrow A$ is slower than the diffusion process, a condition satisfied by a suitable choice of dye. This decay frequently (but not always, see below) follows the functional form

$$V(t) = [A\exp(-t/\tau) + B]^2 + C^2 \qquad (1)$$

where $V(t)$ is the measured photovoltage, τ is the time constant of the decay ($=d^2/4\pi^2 D$), and A, B, and C are proportional to the diffracted, coherently scattered, and incoherently scattered electric fields, respectively. Since the quantity $B^2 + C^2$ is determined from the measured signal baseline, Eq. 1 is a three-floating-parameter fit. A plot of τ vs. d^2 yields D from the slope. The presence of nondiffusive contributions to the grating decay will be revealed by deviations from the d^2 dependence.

There are a number of advantageous features of the FRS experiment that make it extremely useful in a wide range of molecular transport studies. These features include:

1. FRS can be used to measure diffusion coefficients from 10^{-5} to 10^{-14} cm^2/s, with typical uncertainties in the range 1 to 10%, and thus covers a very wide range of interest.

2. Samples may be either solids or liquids, and may vary over the complete range of polymer molecular weight, and polymer or diluent concentration. The main requirement is that the sample be optically transparent for a thickness on the order of 1 mm.

3. The motion of the dye or dye-labeled molecules is measured directly as a function of relevant variables; no elaborate mathematical analysis is required to extract a diffusion coefficient.

4. No imposed macroscopic concentration gradient is required; diffusion can be measured in samples at equilibrium, or under controlled nonequilibrium conditions.

5. Spatial and temporal resolution is inherent; i.e., diffusion coefficients may be determined as a function of position in the sample, and as a function of time.

6. Dyes may be derivatized or grafted to vary diffusant structure without significantly affecting their photochromic properties.

7. FRS is inherently a uniaxial experiment, in the sense that only diffusion perpendicular to the grating axis contributes to the decay. This may be used to advantage in the study of an anisotropic system, such as an oriented polymer film.

8. Only very small sample volumes (1 mm^3) and dye concentrations (<0.005 g/g) are required.

There are, of course, practical considerations that must be taken into account in FRS experiments. In addition to the necessity for clean samples to minimize background scattering, a major limitation is the necessity of dealing with ternary systems; i.e., in a polymer solution, where the solvent self-diffusion coefficient is the desired property, there are three components: polymer, solvent, and dye. However, an extension of the Vrentas-Duda theory to ternary systems by Ferguson and von Meerwall (1980) can be shown to give the following connection between the dye tracer diffusivity and the solvent self-diffusion coefficient

$$\ln\left(\frac{D}{D^o}\right)_{\text{dye}} = \frac{(\hat{V}^*M)_{\text{dye}}}{(\hat{V}^*M)_{\text{solvent}}} \cdot \ln\left(\frac{D}{D^o}\right)_{\text{solvent}} \tag{2}$$

if the weight (or volume) fraction of the dye is approaching zero. Here, $\hat{V}^*$ is the specific critical hole free volume required for a jump, M is molecular weight, and D^o is the diffusion coefficient in the limit of zero diluent concentration. A similar expression can be derived for the Fujita version of the free-volume theory. Consequently, if the dye concentration is low enough to approximate the limit of zero dye concentration, and if the proportionality of Eq. 2 can be established, solvent self-diffusion coefficients should be extractable from the dye diffusion coefficients measured by the FRS technique. Assessment of the validity of Eq. 2 is one of the aims of the present work.

For many dyes of interest, the photoisomerization is reversible. This relaxation takes place over a wide time scale range, depending on the particular dye involved and on the medium in which the dye is dispersed. The dye isomer lifetime τ_d may be defined as the reciprocal of the reconversion rate constant if the reaction follows a simple, unimolecular mechanism (Turro, 1978). If dye reconversion occurs on a time scale comparable to that for diffusion, and if the two processes are independent, then the decay time constant, the diffusion coefficient, and the dye lifetime are related by

$$\frac{1}{\tau} = \frac{4\pi^2 D}{d^2} + \frac{1}{\tau_d} \tag{3}$$

At very small diffusion rates the second term in Eq. 3 becomes much greater than the first term and the diffusion coefficient cannot be determined accurately. This problem can be avoided with the use of photobleaching dyes, i.e., dyes that undergo an irreversible photoisomerization. However, samples prepared using photobleachable dyes may have a limited utility due to the eventual depletion of probe dye molecules.

Another possible complication in the interpretation of the experiment arises if the dye and its photoisomer diffuse at different rates. In Eq. 1 it is assumed that there is only one decay time describing the diffusion process. However, the writing process actually creates two gratings, one in each dye isomer. If the two isomers have different diffusivities due to their difference in size and shape, an additional exponential term must be added to Eq. 1 (Rhee et al., 1984). At temperatures above the glass transition temperature, the two diffusion coefficients are usually quite close. However, at temperatures below the glass transition temperature, where the dependence of diffusivity on molecular shape may be much greater, the two diffusion coefficients associated with the two isomers could differ markedly. If this is the case, Eq. 2 is not expected to be valid without being modified by an additional term containing molecular shape factors. This situation is discussed further in the Appendix, and in connection with the presentation of the results.

Experimental Details

Setup

A schematic diagram of the apparatus is shown in Figure 1. All components are mounted on a 4 ft. × 10 ft. (1.2 m × 3 m) vibration isolation table (Newport Corporation, RS-410-12). All mirrors are rigidly mounted, front-surface mirrors; the positions of the mirrors are adjustable. The system shown allows easy variation of the grating spacing d from 1.5 to 40 μm using the 488 nm line of the continuous wave (CW) argon ion laser (Spectra Physics 165) as the writing laser. The reading laser is either an attenuated helium-neon laser (Uniphase 1105P, 632.8 nm) or a "GreNe" helium-neon laser (Melles Griot 05-SGR-871, 543 nm). At the sample the writing beam power is typically 150–250 mW and the reading beam power ranges from 0.1 to 3

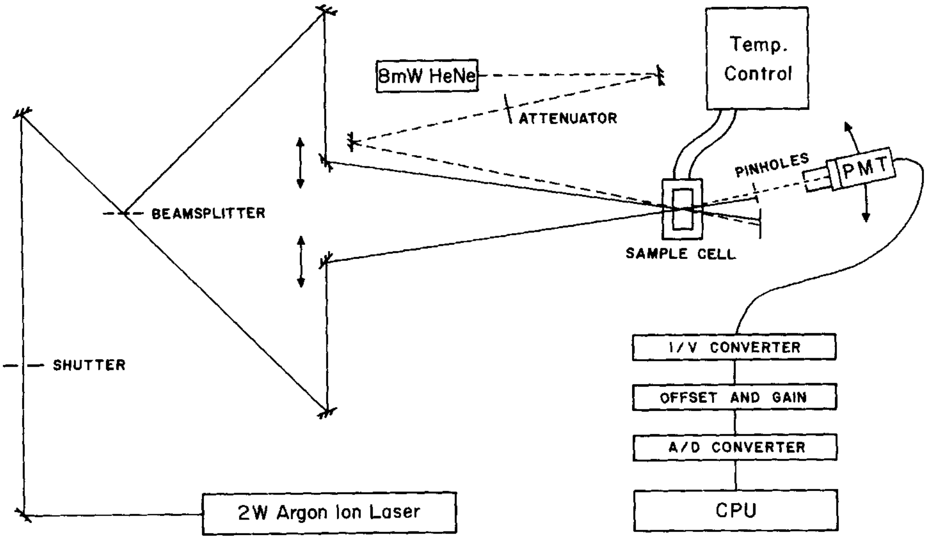

Figure 1. FRS experimental arrangement.

mW. The CW writing beam is pulsed with a shutter and driver (UniBlitz 26L, SD-1000). Typical exposure times for the writing process range from 2 to 200 ms, depending on the dye and its concentration.

The diffracted reading beam intensity is monitored by a photo-multiplier tube (Hamamatsu R928) connected through an amplifier/offset circuit to a data collection board (Data Translation DT-2801) in a Zenith Z-150 microcomputer. The data collection board allows a maximum throughput of 13.7 kHz with a 12-bit analog-to-digital converter. With the on-board clock, experimental durations from 0.073 s up to 160 s are possible, while an external clock trigger extends the time range to arbitrarily long experiments. Each experiment entails collecting 1,000 data points at a given angle over approximately five exponential decay times. The data are then transferred to a computer (Masscomp, MC500) for curve fitting using a Marquardt-based nonlinear regression routine.

Temperature control to 0.01°C is obtained using heating and flowthrough cooling baths (Neslab Instruments, EN-850, EX-300, respectively) and a copper cell-holding jacket. The temperature is measured by balancing the resistance of a calibrated thermistor across a five-place Wheatstone bridge (Leeds and Northrup 4725).

Materials

Two polymer-solvent systems, polyvinyl acetate (PVAc) (Polysciences, Inc., $M_w = 5.0 \times 10^5$) in toluene (Fischer Chemical Co. spectrograde) and polystyrene (PS) (Pressure Chemical Company, $M_w = 9.0 \times 10^4$ and $M_w = 1.0 \times 10^5$, $M_w/M_n \leq 1.06$) in toluene, were studied in this work using both methyl red (J. T. Baker Chemical Co.) and azobenzene (Eastman Kodak Co.) as the probe dye. As these two polymer-solvent systems have been studied by other techniques (Vrentas et al., 1985), comparisons of dye diffusion data with correlated solvent self-diffusion data are thus possible. Another system, polystyrene/tri-m-tolyl phosphate (TCP) (Eastman Kodak Co.), is also being investigated.

FRS samples must be dust-free, microscopically homogeneous, and have a precise, constant composition. To meet these requirements, several different schemes for sample preparation were followed. A first scheme involves dilute (i.e., less than 20 wt. % polymer) solutions, in which both the dye and the polymer were dissolved in the desired solvent. Each solution was then filtered with 0.05–0.5 μm filters (Millipore Corp.) into a 2 mm path length glass cell (NSG Precision Cells). The dye concentration in all solutions varies from 0.1 to 0.5% g/g; over this range, no dependence of the measured diffusion coefficient on dye concentration has been detected. A second scheme involves dissolving both dye and polymer in a volatile solvent, then filtering and evaporating off the solvent and rediluting with the solvent of choice. A third scheme is to pack the cells with purified polymer, then add the dye-solvent mixture in appropriate amounts. Each scheme was best suited for a particular system. Dilute PVAc-toluene solutions were prepared by the first scheme. Preparation of concentrated PVAc-toluene solutions followed the second scheme. Polystyrene was purified by dissolving and filtering in a chloroform solution, precipitating in methanol, and drying in a vacuum oven. All polystyrene-toluene solutions were then prepared by the third scheme. Preparation of homogeneous polystyrene-TCP solutions requires particular care. While dilute polystyrene-TCP-azobenzene solutions were made by direct mixing of the three components, concentrated polystyrene-TCP-azobenzene solutions were made by freeze-drying the polymer-solvent-dye mixture out of benzene solution; the product was then melted directly in the scattering cells.

Methyl red, which has an absorption maximum at 490 nm, works well in dilute toluene solutions, but its short photoisomer lifetime (<100 s in pure toluene) makes it less desirable for solutions of more than about 60% polymer. Azobenzene ($\lambda_{max} = 440$ nm) works well in all TCP solutions and in concentrated toluene solutions, but apparently yields no signal in toluene solutions containing less than about 65% polymer; the reason for this is not yet clear. The study of dye photochemistry in polymer matrices itself is a subject of great interest and is under extensive research (Horie et al., 1985a,b). The lifetime of azobenzene ranges up to at least 5 h, depending on the polymer concentration.

Results and Discussion

Figures 2 and 3 show typical experimental signals from the PMT. Figure 2 is the decay of a PS-toluene solution (71% g/g polymer) at 35°C with a grating spacing of 12.28 μm. Figure 3, which shows a decay-growth-decay type of signal, is the result of a 90% PVAc-toluene solution at 15°C with $d = 15.72$ μm. Decays that could be fitted by Eq. 1, as in Figure 2, resulted from dilute PS-TCP-azobenzene solutions, dilute PS-toluene-methyl red solutions, and methyl red diffusion in pure toluene. Decays as shown in Figure 3 were typical of all PVAc solutions, concentrated (>85% PS) solutions of PS-toluene-azobenzene, and concentrated solutions of PS-TCP-azobenzene examined so far, and must be fitted with an additional exponential term (Eq. A1).

As is shown in Figures 2 and 3, the quality of fit by either Eq. 1 or Eq. A1 is excellent except for the initial rise in signal, which represents the writing process and involves spectroscopic and thermal effects that are difficult to model. Fitting to the experimental signal can be applied to data as soon as the exponential portion of the decay begins. It is straightforward to demonstrate that starting the fit at different times after the initial rise does not affect the decay constant obtained by nonlinear regression. Decay times resulting from the fitting algorithm are plotted as $1/\tau$ against $1/d^2$, as suggested by Eq. 3. The slope of the line yields the diffusion coefficient of the dye, and the intercept gives the dye lifetime in the system. If the two decay times are very close, the average of the two decay times from the five-parameter fit are plotted to obtain the diffusion coefficient. Figure 4 is the plot of $1/\tau$ vs. $1/d^2$ for azobenzene diffusion in a 96% PVAc solution at 30°C. The five-parameter fits gave values of 1.05 ± 0.05 for τ_1/τ_2 and -1.00 ± 0.01 for A_1/A_2, a dye lifetime of 9×10^3 s, and a diffusion coefficient of 1.97×10^{-12} cm^2/s.

Since this is a tracer technique, the diffusion of the dye is expected to parallel the diffusion of the solvent. Equation 2 indicates that the logarithm of D_d and D_1 should be linearly related, with the proportionality constant increasing with dye molecular weight. Plots of log D_d vs. log D_1 testing this idea are shown in Figures 5 and 6. The self-diffusion coefficients of toluene in PVAc and PS were obtained by the correlative version of the Vrentas-Duda theory (Vrentas et al., 1985). The slope of log D (methyl red) vs. log D (toluene) is 1.96 ± 0.12 for the PVAc-toluene system and 1.70 ± 0.09 for PS-toluene solutions, while

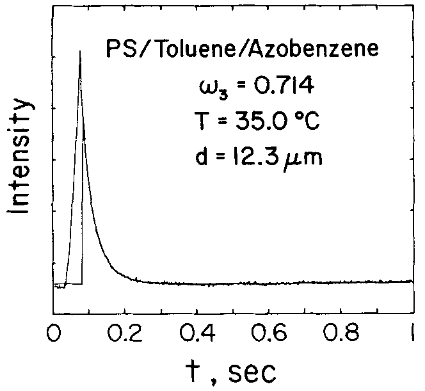

Figure 2. Typical experimental single exponential decay signal.

The smooth curve represents a fit to Eq. 1.

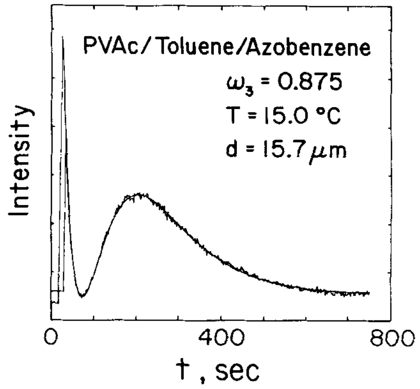

Figure 3. Typical experimental decay-growth-decay signal.

The smooth curve represents a fit to Eq. A1.

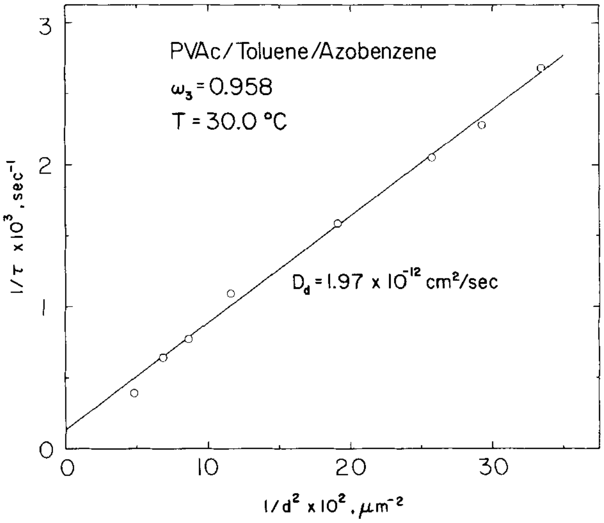

Figure 4. $1/\tau$ vs. $1/d^2$ plot, with slope $= 4\pi^2 D_d$ and intercept $= 1/\tau_d$.

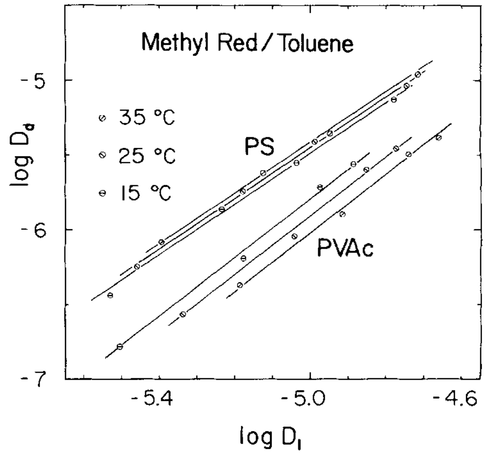

Figure 5. Measured log D_d for methyl red vs. calculated log D_1 for toluene.

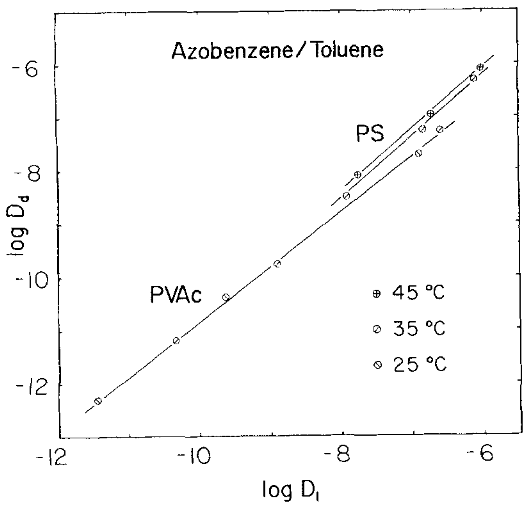

Figure 6. Measured log D_d for azobenzene vs. calculated log D_1 for toluene.

the corresponding azobenzene slope is 1.16 ± 0.06 for the PS-toluene system and 1.03 ± 0.10 for the PVAc-toluene system. The predicted slopes are 2.29 for methyl red and 1.67 for azobenzene with $\hat{V}^*$ estimated by the method detailed by Haward (1970). Considering the level of approximation inherent in the theory, this agreement is quite good. The discrepancy may arise from at least two assumptions in the theory. The predicted values *assume spherical* dye molecules moving through the fluid, and also that the dye molecules move as a single, rigid jumping unit. Since neither azobenzene nor methyl red are perfectly spherical, and may show a preference for motion along one axis, it is quite plausible that the diffusion coefficients should be larger than those predicted for a sphere of equal volume. Furthermore, some degree of flexibility in the dye may contribute to the enhanced dye diffusion.

Another interesting point concerning the data in Figures 5 and 6 is that the PVAc-toluene-dye slope differs slightly from the PS-toluene-dye slope, contrary to the prediction of Eq. 2. One possible explanation for this might involve the relative polarities of PVAc and PS, and the tendency of the dye isomer to partition between polymer-rich and solvent-rich regions.

The temperature dependence of diffusion coefficients in polymers over the range from T_g to T_g + 100 K can usually be described by a WLF-type equation derived from free-volume ideas:

$$\log \frac{D(T_s) \cdot T}{D(T) \cdot T_s} = \frac{-C_1^s(T - T_s)}{C_2^s + (T - T_s)} \equiv \log a_T \qquad (4)$$

Figure 7 shows some data plotted in the WLF format, with C_1^s = 10.4, C_2^s = 144.9 for the 96% PVAc-toluene system using 328 K as the reference temperature, T_s, and C_1^s = 3.06, C_2^s = 99 for the 79% PS-toluene system using 308 K as the reference. These parameters can be referred to the glass transition or any other temperature by

$$C_1^s = C_1^g C_2^g / (C_2^g + T_s - T_g) \qquad (5)$$

$$C_2^s = C_2^g + T_s - T_g \qquad (6)$$

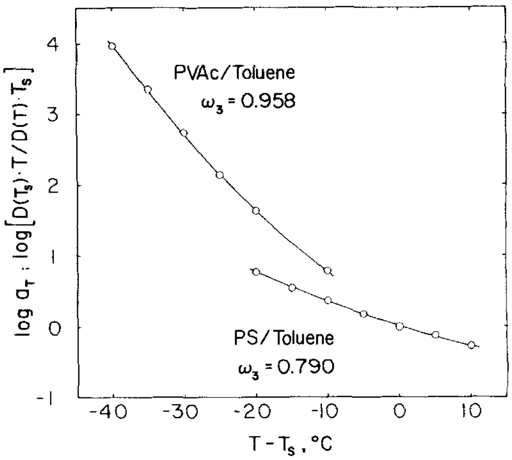

Figure 7. WLF plot for the 79% PS-toluene solution and the 96% PVAc-toluene solution.

Equations 5 and 6 give C_1^g = 1.85 and C_2^g = 164 for the 79% PS-toluene solution with T_g = 373 K; C_1^g = 9.08 and C_2^g = 165.9 for the 96% PVAc-toluene solution with a reference temperature of 349 K. Since the WLF parameters in the literature are usually for pure polymers, it is difficult to make quantitative comparisons with the parameters obtained in this experiment, which are for polymer solutions. However, Ferry (1980) has pointed out that C_1^g decreases while C_2^g increases as the polymer becomes more diluted; the experimentally obtained parameters are consistent in this respect.

Figure 8 and 9 are plots of dye diffusivity vs. polymer concentration for the two systems, PVAc-toluene and PS-toluene, respectively. For the PVAc-toluene system there is a perceptible drop in the diffusion coefficient of methyl red between 0 and 10% polymer concentration, as is shown in Figure 8. This phenomenon may also be reflected in the fact that for the diffusion of methyl red in pure toluene, the decay signal observed is single exponential, whereas as soon as PVAc was added to the solution, a decay-growth-decay type of signal was observed. There is also a discontinuity due to the change of dye, particularly noticeable in Figure 9, which occurs at 65% g/g polymer. This is consistent

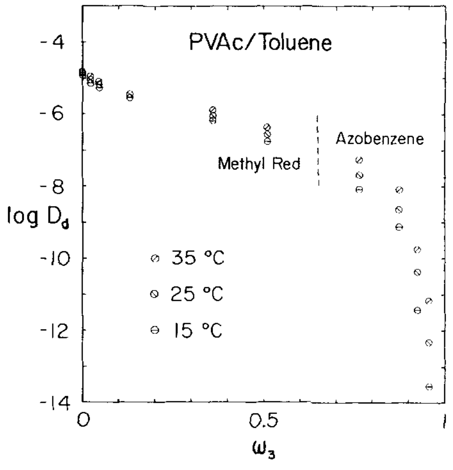

Figure 8. Log D_d vs. polymer weight fraction for PVAc-toluene solutions.

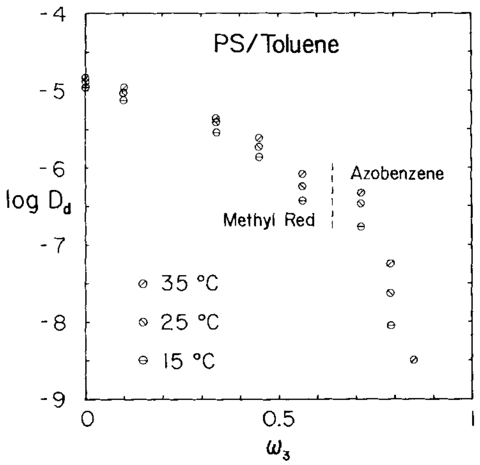

Figure 9. Log D_d vs. polymer weight fraction for PS-toluene solutions.

with the fact that the slope of log D (methyl red) vs. log D (toluene) differs from that of log D (azobenzene) vs. log D (toluene). In both systems, the diffusion coefficient drops dramatically at the high polymer concentration end, which is not unexpected due to the reduction in free volume as polymer concentration increases. Also, the sensitivity to temperature increases as polymer concentration increases. All diffusion data shown are taken above the system glass transition temperature. The azobenzene diffusivity can be converted to methyl red diffusivity by applying Eq. 2 to both dyes, which gives

$$\log D(\text{methyl red}) = (a' - ab'/b) + (b'/b) \log D\,(\text{azobenzene}) \qquad (7)$$

where a and b are the intercept and slope from the log D_d vs. log D_1 plot for the polymer-toluene-azobenzene system, while a' and b' are corresponding values for the polymer-toluene-methyl red system. Figure 10 is the methyl red diffusivity vs. polymer concentration plot for the PVAc-toluene system at three different temperatures with all azobenzene data converted to methyl red data. The order of magnitude of the diffusion coefficient is changed by as much as eight decades from this conversion. Solid curves in Figure 10 represent fits by the Duda-Vrentas version of the free volume theory (Vrentas et al., 1984), which gives

$$\log D_d = \log D_o - \frac{E}{2.303RT} - \frac{\xi_{23}/\xi_{13}}{2.303} \cdot \frac{\omega_1 \hat{V}_1^* + \omega_3 \hat{V}_3^* \xi_{13}}{\hat{V}_{FH}/\gamma} \qquad (8)$$

with the dye concentration approaching zero. The nonlinear regression gives $D_o = 3.25 \times 10^{-3}$ cm^2/s, $E = 0.569$ kcal/gmol, and $\xi_{23}/\xi_{13} = 1.983$. All other parameters were obtained from Vrentas et al. (1985). The ratio of ξ_{23} to ξ_{13} is equivalent to the proportionality constant of the log D_d vs. log D_1 plot. The agreement between the value obtained from nonlinear regression and the value obtained from Figure 5 is excellent. The fit indicates that the concentration dependence of dye tracer diffusivity in a three-component system is in reasonable agreement with the free-volume ideas embodied in the theory of Duda and Vrentas.

The use of methyl red in dilute solutions is necessitated by the observation that azobenzene provides an adequate signal only in concentrated PVAc-toluene and PS-toluene solutions, and in PS-TCP solutions over the complete concentration range. Since some PS-TCP solutions are less viscous than polymer-toluene solutions in which azobenzene will not work, this problem is not simply a viscosity effect, but rather more probably a chemical effect of the matrix. Azobenzene is generally more desirable than methyl red due to its longer lifetime. In Figure 11, the azobenzene dye lifetime is plotted vs. the measured diffusion coefficient. It can be seen that the lifetime increases significantly with increasing polymer concentration and/or decreasing temperature, and this increase correlates well with the decrease in D_d. This suggests that the reconversion kinetics are greatly slowed by the decrease in free volume, as has been shown by Sung et al. (1985) and Horie et al. (1985a). This is very important in enabling D values down to 10^{-14} cm^2/s to be measured with azobenzene. Also included in Figure 11 is a line corresponding to the value of τ_d at which mass diffusion and dye reconversion give equal contributions to the decay rate for a spacing of 2 μm. Thus, this line is a rough demarcation of the measurable D_d regime for this polymer-solvent-dye system.

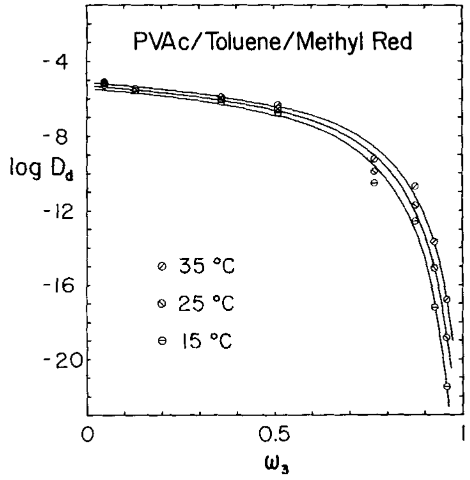

Figure 10. Methyl red diffusivity vs. PVAc weight fraction.

Solid curves represent fits by Vrentas-Duda free volume theory.

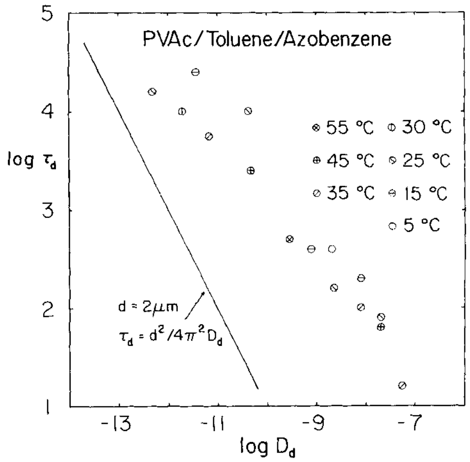

Figure 11. Log τ_d vs. log D_d for azobenzene in PVAc/toluene.

Concluding Remarks

Forced Rayleigh scattering has been used to measure diffusion coefficients ranging over nine orders of magnitude in this study. This technique is extremely useful in the study of slow diffusion processes that may be inaccessible by other experimental techniques. Based on an extension of the free-volume theory to ternary systems, solvent diffusion behavior can be extracted from the dye diffusion data if the dye is present in trace amounts. Diffusion data obtained so far do not conflict with free-volume ideas above T_g, and support the suggested simple theoretical relation between dye and solvent diffusion behavior. However, the relation between dye and solvent diffusion coefficients is not expected to be simple at temperatures below T_g, where the dependence of diffusion coefficient on molecular shape is much greater. More data are needed to provide a thorough, quantitative test of theory. Further experiments will be conducted at temperatures near and below the glass transition temperature. It is hoped that these self-diffusion measurements in glassy polymer solutions will eventually provide the basis for a thorough theoretical treatment of small-molecule diffusion in glassy solutions paralleling that already established for diffusion above the glass transition temperature.

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Notation

a = constant, Eq. 7
a' = constant, Eq. 7
a_T = shift factor, Eq. 4
A = preexponential factor, Eq. 1
A_1 = preexponential constant, Eq. A1
A_2 = preexponential constant, Eq. A1
b = constant, Eq. 7
b' = constant, Eq. 7
B = coherent scattering, Eqs. 1, A1
C = incoherent scattering, Eqs. 1, A1
C_1^s = characteristic constant, Eqs. 4, 5, 6
C_2^s = characteristic constant, Eqs. 4, 5, 6
C_1^g = characteristic constant, Eqs. 5, 6
C_2^g = characteristic constant, Eqs. 5, 6
d = grating spacing created by writing beams
D = diffusion coefficient
D^o = diffusion coefficient in the limit of zero diluent concentration
D_o = preexponential factor, Eq. 8
D_1 = solvent diffusion coefficient or diffusivity of one of the dye isomers (Appendix)
D_2 = diffusivity of the other dye isomer (Appendix)
D_d = dye diffusion coefficient
D_t = tracer diffusion coefficient
E = critical energy per mole needed to overcome attractive forces
M = molecular weight
T = temperature
T_g = glass transition temperature
T_s = reference temperature, Eq. 4
V = signal voltage
$\hat{V}^*$ = specific critical hole free volume required for a jump
$\hat{V}_1^*$ = specific critical hole free volume of solvent required for a jump
$\hat{V}_3^*$ = specific critical hole free volume of polymer required for a jump
$\hat{V}_{FH}$ = average hole free volume per gram of mixture

Greek letters

γ = overlap factor for free volume
θ = angle between two writing beams
λ = wavelength
ξ_{13} = ratio of critical molar volume of solvent jumping unit to critical molar volume of jumping unit of polymer
ξ_{23} = ratio of critical molar volume of dye jumping unit to critical molar volume of jumping unit of polymer
τ = decay time constant, Eq. 1
τ_1 = decay time constant, Eq. A1
τ_2 = decay time constant, Eq. A1
τ_d = dye lifetime
ω_1 = weight fraction of solvent
ω_3 = weight fraction of polymer

Appendix

The decay-growth-decay signal, Figure 3, has been observed by a number of authors, including Miles (1983), Wesson (1983), Antonietti et al. (1984), Wesson et al. (1984), Rhee et al. (1984), Stewart et al. (1986), and Zhang and Wang (1986). It is generally agreed that the bump is due to multiple gratings formed in the sample. The writing process inevitably creates two gratings, one in each dye isomer. Furthermore, these two gratings are spatially 180 degrees out of phase with each other, and therefore the electric fields at the detector diffracted from each grating are opposite in sign. The detector then sums and squares the two contributions. Since the two isomers have different shape and size, they may diffuse with different rates. Both isomers are dilute in the sample and so move independently. The resulting signal then has the form:

$$V(t) = [A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + B]^2 + C^2 \quad \text{(A1)}$$

where A_1/A_2 is always negative. When the two isomers have identical diffusion coefficients, Eq. A1 reduces to Eq. 1. Simulations based on Eq. A1 with B and C set to zero have been performed with different A_1/A_2 and τ_1/τ_2 ratios. Three different general signal shapes are found from the simulation, as shown in Figure A1. The first type of signal can be represented by a single exponential decay. The second type clearly shows a growth in the signal after the initial decay, followed by another decay. In the third type of signal, the initial decay period is so short that only a growth-decay signal is observed.

Figure A2 shows regions of the $-A_1/A_2$ vs. τ_1/τ_2 plane where each of the signal shapes can be expected. Numbers in Figure A2 refer to different signal shapes shown in Figure A1. τ_1/τ_2 is determined by solution composition, system temperature, and other factors affecting D, such as molecular shape and size.

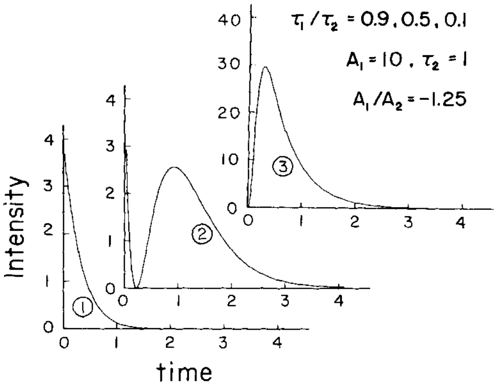

Figure A1. Different forms of decay signal from simulations of Eq. A1.

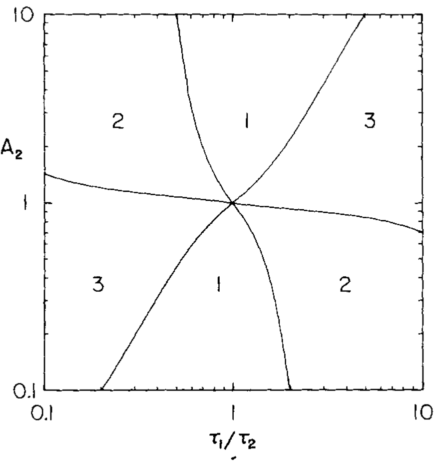

Figure A2. Regions of the A_1/A_2 vs. τ_1/τ_2 plane where each of the signal shapes in Figure A1 can be expected.

A_1/A_2 is largely determined by the contrast in refractive index and/or extinction coefficient between each dye isomer and the bulk solution, which in turn depends on the wavelength of the reading beam. Since both τ_1 and τ_2 reflect mass diffusion processes, they should obey the d^2 dependence, regardless of system temperature and concentration, with τ_1/τ_2 being equal to D_2/D_1. The fact that the ratios τ_1/τ_2 and A_1/A_2 are independent of d is strong support for this interpretation of the observed signal shape. Figure A3 shows results from a PS-toluene-azobenzene (93% polymer) solution at 45°C. The temperature is lower than the system glass transition temperature, and consequently the two isomers have significantly different diffusion coefficients. The signal shape observed is that of the second type. In contrast, all PVAc-toluene data shown in this report were taken at temperatures above the system glass transition temperature, and the ratios τ_1/τ_2 and $-A_1/A_2$ were very close to unity.

Literature cited

Antonietti, M., J. Coutandin, R. Grutter, and H. Sillescu, "Diffusion of Labeled Macromolecules in Molten Polystyrene Studied by a Holographic Grating Technique," *Macromolecules*, **17**, 798 (1984).

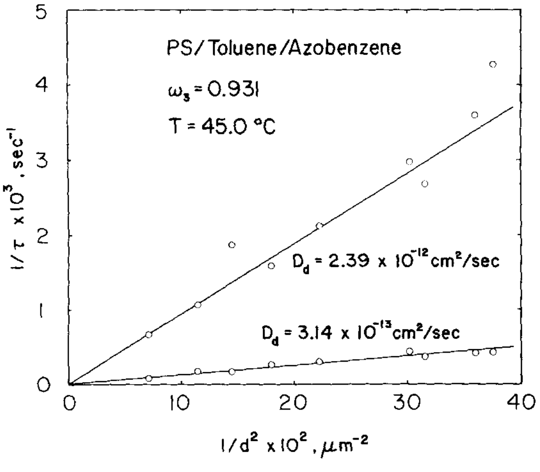

Figure A3. $1/\tau_1$ and $1/\tau_2$ vs. $1/d^2$ for a PS-toluene solution with 93% polymer at 45°C.

Berens, A. R., and H. G. Hopfenberg, "Diffusion of Organic Vapors at Low Concentrations in Glassy PVC, Polystyrene, and PMMA," *J. Membrane Sci.*, **10**, 283 (1982).

Chang, T., and H. Yu, "Self-Diffusion of Gelatin by Forced Rayleigh Scattering," *Macromolecules*, **17**, 115 (1983).

Crank, J., and G. S. Park, "Diffusion in High Polymers: Some Anomalies and Their Significance," *Trans. Faraday Soc.*, **47**, 1072 (1951).

Eichler, H., G. Salje, and H. Stahl, "Thermal Diffusion Measurements Using Spatially Periodic Temperature Distribution Induced by Laser Light," *J. Appl. Phys.*, **44**, 5383 (1973).

Fayer, M. D., "Dynamics of Molecules in Condensed Phases: Picosecond Holographic Grating Experiments," *Ann. Rev. Phys. Chem.*, **33**, 63 (1982).

Ferguson, R. D., and E. von Meerwall, "Free-Volume Interpretation of Self-Diffusion in Ternary Systems: n-Paraffin-Hexafluorobenzene-cis-4-Polybutadiene," *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1285 (1980).

Ferry, J. D., *Viscoelastic Properties of Polymer*, 3rd ed., Wiley, New York (1980).

Frisch, H. L., "Sorption and Transport in Glassy Polymers—A Review," *Polymer Eng. Sci.*, **20**, 2 (1980).

Fujita, H., "Diffusion in Polymer-Diluent Systems," *Fortschr. Hochpolym. Forsch.*, **3**, 1 (1961).

———, "Organic Vapors above the Glass Transition Temperature," *Diffusion in Polymers*, J. Crank and G. S. Park, eds., Academic Press, New York (1968).

Haward, R. N., "Occupied Volume of Liquids and Polymers," *J. Macromol. Sci.-Revs. Macromol. Chem.*, **C4**(2), 191 (1970).

Hervet, H., L. Leger, and F. Rondelez, "Self-Diffusion in Polymer Solutions: A Test for Scaling and Reptation," *Phys. Rev. Lett.*, **42**, 1681 (1979).

Hervet, H., W. Urbach, and F. Rondelez, "Mass Diffusion Measurements in Liquid Crystals by a Novel Optical Method," *J. Chem. Phys.*, **68**, 2725 (1978).

Hopfenberg, H. B., and V. Stannett, "The Diffusion and Sorption of Gases and Vapors in Glassy Polymers," *The Physics of Glassy Polymers*, R. N. Haward, ed., Wiley, New York (1973).

Horie, K., K. Hirao, I. Mita, Y. Takubo, T. Okamoto, M. Washio, S. Tagawa, and Y. Tabata, "Red Fluorescence from the Merocyanine Form of Spirobenzopyran," *Chem. Phys. Lett.* **119**, 499 (1985a).

Horie, K., M. Tsukamoto, and I. Mita, "Photochemistry in Polymer Solids. 7: Photochromic Reaction of Spiropyran in Polycarbonate Film," *Eur. Polym. J.*, **21**, 805 (1985b).

Landry, M. R., "Polymer and Small Molecule Diffusion in Polymer Solutions and Bulk Systems," Ph.D. Thesis, Univ. Wisconsin, Madison (1985).

Leger, L., H. Hervet, and F. Rondelez, "Reptation in Entangled Solutions by Forced Rayleigh Light Scattering," *Macromolecules*, **14**, 1732 (1981).

Long, F. A., and D. Richman, "Concentration Gradients for Diffusion of Vapors in Glassy Polymers and Their Relation to Time-Dependent Diffusion Phenomena," *J. Am. Chem. Soc.*, **82**, 513 (1960).

Lutz, D. R., K. A. Nelson, C. R. Gochanour, and M. D. Fayer, "Electronic Excited State Energy Transfer, Trapping by Dimers and Fluorescence Quenching in Concentrated Dye Solutions: Picosecond Transient Grating Experiments," *Chem. Phys.*, **58**, 325 (1981).

Miles, D. G., "Application of Forced Rayleigh Scattering to the Diffusion of Proteins and a Protein Photochromic Label," Ph.D. Thesis, Univ. North Carolina, Chapel Hill (1983).

Nelson, K. A., R. Casalegno, R. J. D. Miller, and M. D. Fayer, "Laser-Induced Excited State and Ultrasonic Wave Gratings: Amplitude and Phase Grating Contributions to Diffraction," *J. Chem. Phys.*, **77**, 1144 (1982).

Nelson, K. A., and M. D. Fayer, "Laser-Induced Phonons: A Probe of Intermolecular Interactions in Molecular Solids," *J. Chem. Phys.*, **72**, 5204 (1980).

Nemoto, N., M. R. Landry, I. Noh, T. Kitano, J. A. Wesson, and H. Yu, "Concentration Dependence of Self-Diffusion Coefficient by Forced Rayleigh Scattering: Polystyrene in Tetrahydrofuran," *Macromolecules*, **18**, 308 (1985).

Nemoto, N., M. R. Landry, I. Noh, and H. Yu, "Temperature Dependence of the Self-Diffusion Coefficients of Polyisoprene in the Bulk State," *Polym. Comm.*, **25**, 141 (1984).

Park, G. S., "The Glassy State and Slow Process Anomalies," *Diffusion* *in Polymers*, J. Crank and G. S. Park, eds., Academic Press, New York (1968).

Phillion, D. W., D. J. Kuizenga, and A. E. Siegman, "Subnanosecond Relaxation Time Measurements Using a Transient Induced Grating Method," *Appl. Phys. Lett.*, **27,** 85 (1975).

Pohl, D. W., "Forced Rayleigh Scattering," *IBM J. Res. Develop.*, **23,** 604 (1979).

Pohl, D. W., S. E. Schwarz, and V. Irniger, "Forced Rayleigh Scattering," *Phys. Rev. Lett.*, **31,** 32 (1973).

Rhee, K. W., D. A. Gabriel, and C. S. Johnson, Jr., "Diffraction from Multiple Gratings in Holographic Relaxation Spectroscopy: Application to Bovine Serum Albumin Labeled with Benzospiropyran," *J. Phys. Chem.*, **88,** 4010 (1984).

Rondelez, F., H. Hervet, and W. Urbach, "A Sensitive Optical Grating Method for Flash Photolysis: Application to the cis-trans Photochemical Isomerization of Azo Dyes," *Chem. Phys. Lett.*, **53,** 138 (1978a).

———, "Origin of Thermal Conductivity Anisotropy in Liquid Crystalline Phases," *Phys. Rev. Lett.*, **41,** 1058 (1978b).

Salcedo, J. R., A. E. Siegman, D. D. Dlott, and M. D. Fayer, "Dynamics of Energy Transport in Molecular Crystals: The Picosecond Transient Grating Method," *Phys. Rev. Lett.*, **41,** 131 (1978).

Sillescu, H., C. H. Wang, and J. Coutandin, "Diffusion of Dye Molecules in Polymers Above and Below the Glass Transition Temperature Studied by the Holographic Grating Technique," *Macromolecules*, **18,** 587 (1985).

Stewart, U. A., C. S. Johnson, Jr., and D. A. Gabriel, "Holographic Relaxation Spectroscopy of Human IgG: Photoinduced Aggregation," *Macromolecules*, **19,** 964 (1986).

Sung, C. S. P., I.-J. Chin, and W.-C. Yu, "A Novel Fluorescence Technique for Monitoring Cure Reactions in Epoxy Resins," *Macromolecules*, **18,** 1510 (1985).

Turro, N. J., *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA (1978).

Urbach, W., H. Hervet, and F. Rondelez, "Thermal Diffusivity Measurements in Nematic and Smectic Phases by Forced Rayleigh Light Scattering," *Mol. Cryst. Liq. Cryst.*, **46,** 209 (1978).

Vrentas, J. S., and J. L. Duda, "Diffusion in Polymer-Solvent Systems. I: Reexamination of the Free-Volume Theory," *J. Polymer Sci., Polymer Phys. Ed.*, **15,** 403 (1977a).

———, "Diffusion in Polymer-Solvent Systems. II: A Predictive Theory for the Dependence of Diffusion Coefficients on Temperature, Concentration, and Molecualar Weight," ibid., 417 (1977b).

———, "Molecular Diffusion in Polymer Solutions," *AIChE J.*, **25,** 1 (1979).

Vrentas, J. S., J. L. Duda, and H.-C. Ling, "Self-Diffusion in Polymer-Solvent-Solvent Systems," *J. Polymer Sci., Polymer Phys. Ed.*, **22,** 459, (1984).

Vrentas, J. S., J. L. Duda, H.-C. Ling, and A.-C. Hou, "Free-Volume Theories for Self-Diffusion in Polymer-Solvent Systems. II: Predictive Capabilities," *J. Polymer Sci., Polymer Phys. Ed.*, **23,** 289 (1985).

Wesson, J. A., "Mass Diffusion in Polymeric Systems by Forced Rayleigh Scattering," Ph.D. Thesis, Univ. Wisconsin, Madison (1983).

Wesson, J. A., I. Noh, T. Kitano, and H. Yu, "Self-Diffusion of Polystyrene by Forced Rayleigh Scattering," *Macromolecules*, **17,** 782 (1984).

Wesson, J., H. Takezoe, H. Yu, and S. P. Chen, "Dye Diffusion in Swollen Gels by Forced Rayleigh Scattering," *J. Appl. Phys.*, **53,** 6513 (1982).

Zhang, J., and C. H. Wang, "Simultaneous Measurements of the Diffusion Coefficients of the Dye Molecule and its Photoproducts by the Holographic Grating Technique," *J. Phys. Chem.*, **90**(2), 296 (1986).

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