

Penetrant diffusion in poly(methyl methacrylate) near T_g : dependence on temperature and polymer weight fraction

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Abstract

Forced Rayleigh scattering was employed to measure diffusion coefficients for a ternary system comprising camphorquinone or diacetyl in poly(methyl methacrylate) with methyl isobutyrate as the diluent. Measurements were made at polymer weight fractions, w_p , over the range 0.78–0.90 and temperature 25–50°C for camphorquinone (which spans the glass transition regime), and at $w_p = 0.9$ and 0.95 and at room temperature for diacetyl. Results for camphorquinone show a strong temperature dependence, with diffusion coefficients changing as much as two orders of magnitude between 25 and 50°C, and showing high activation energies for diffusion ≈ 125 kJ mol⁻¹. No sharp change in the activation energy for diffusion was observed as the glass transition is crossed. The pre-exponential factor for the diffusion coefficient decreased dramatically through the glass transition. The diffusion coefficients of small penetrants in glassy polymers appear strongly dependent on the molecular size. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The diffusion of small molecules and oligomers in polymers plays an important role in many areas of polymer processing and applications of polymers. To give some examples: the kinetics and molecular weight distribution of free radical polymerizations [1–3], the development of composite particle morphology in seeded semibatch emulsion polymerization [4], membrane separation [5], and controlled-release technologies [6]. Free radical polymerization kinetics may also be diffusion-controlled, especially at intermediate to high conversion [1], while in systems which become glassy at high conversion, propagation reactions, and thus chain transfer to monomer [7], can also become diffusion-controlled, and hence dependent on the mobility of the monomer molecules.

In order to understand these various processes it is important to have values for the diffusion coefficients of both monomeric and oligomeric species as a function of polymer weight fraction. The system required for obtaining diffusion data of relevance to polymerization is ternary: polymer, small amounts of tracer (to represent monomeric or oligomeric radicals), and a solvent (which is monomer in an

actual polymerizing system). While data for rubbery systems can be obtained from pulsed-field gradient NMR [8,9], there is a paucity of results for glassy systems or for systems near T_g .

The goal of this study was to acquire such data by studying the diffusion of a tracer dye in a polymer–solvent solution at various temperatures and at polymer weight fractions spanning the glass transition regions. The range around the glass transition is particularly interesting because this is where the diffusion changes from being very slow in the glassy system to relatively rapid in the rubbery system. The amount of data for tracer molecules of size comparable to monomers and oligomers in the literature [10–13] is insufficient to see trends or provide discriminating tests of theory.

2. Forced Rayleigh scattering

Part of the reason for the scarcity of experimental data for diffusion of species comparable to monomers in glassy polymers is because many techniques for measuring diffusion coefficients are either unable to measure very slow diffusion, require excessively long time scales, or produce unreliable results: e.g. techniques are based on macroscopic perturbations of the system such as in permeation experiments

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or swelling rates of a polymer latex. Such macroscopic perturbations may move the system far from an equilibrium state, thus potentially inducing spatial inhomogeneities in concentration, stress, and material properties, and leading to time-dependent diffusion coefficients. Such cases may result in uncertainty in precise chemical composition, non-Fickian diffusion, and difficulties in experimental interpretation, therefore giving misleading results. While pulsed field gradient (PFG) NMR is a method commonly used to measure diffusion coefficients of small molecules in polymers [8], and avoids macroscopic perturbations to the system, it is only capable of obtaining values of diffusion coefficients down to about $10^{-10} \text{ cm}^2 \text{ s}^{-1}$. Diffusion coefficients for small molecules in glassy polymers are typically much lower than this, rendering PFG NMR ineffective for the study of diffusion in glassy polymers.

Forced Rayleigh scattering (FRS), also known as the ‘Laser-Induced Holographic Grating’ technique, was employed for this study because of its ability to directly measure diffusion of a photoactive tracer molecule over length scales on the order of 10^2 nm . This reduces the time scales required for the measurements to experimentally reasonable limits, ranging from seconds to days. The combination of the possible length scales and reasonable time scales for the FRS experiment provide a wide range of accessible diffusion coefficients for measurement, ranging from 10^{-5} to $10^{-16} \text{ cm}^2 \text{ s}^{-1}$ [14]. This covers many different systems including polymer glasses, melts and polymer solutions, and is particularly suitable for spanning the glass transition.

It should be noted that it is possible that for very short distance scales (or corresponding timescales) the apparent (measured) diffusion coefficients may not correspond to the ‘true’ long-time limit in very glassy systems. This may limit the applicability of the FRS technique in some systems. Observed diffusion coefficients in very glassy systems should perhaps be regarded as upper limits to the ‘true’ long-time values. This will be discussed later.

The FRS experiment involves two basic steps: writing and reading. During the writing step two mutually coherent laser beams are crossed within the sample, establishing an interference pattern in which the light intensity varies sinusoidally. The duration of the writing step is usually a fraction of a second, which is much shorter than the duration of the reading step. The crossing angle of the beams, θ , and the wavelength of the lasers, λ , determine the period of the interference pattern, $d = (\lambda/(2 \sin \theta/2))$. Dye molecules in the volume exposed to the crossed laser beams undergo a photoreaction. The interference pattern of the crossing laser beams creates a sinusoidal concentration profile in the exposed volume for both dye and photoproduct. These concentration gradients (gratings) of the dye and the photoproduct are 180° out-of-phase and relax at different rates when the dye and photoproduct have different diffusion coefficients. For Fickian diffusion, each concentration grating remains sinusoidal, while the amplitude, ΔC_i , decays

exponentially with time [15]:

$$\Delta C_i = \Delta C_0 e^{-q^2 D_i t} \quad (1)$$

where $q = 2\pi/d$ and D_i is the tracer-diffusion coefficient of species i . If the lifetime for the photoproduct is comparable to the time scale of the experiment then reconversion of the photoproduct back to the dye contributes to the relaxation of the grating and the expression becomes more complicated [14]. Fortunately, this is not the case for the penetrants used in this study [13].

The second step in an FRS experiment, the reading step, monitors the relaxation of the concentration gratings, wherein the amplitude is probed using a non-exciting laser beam. In this work the reading beam was the same as the writing beam but the beam power was attenuated for the reading step to minimize the further conversion of dye into photoproduct during the reading step. This beam was directed at the first-order Bragg angle and the intensity of the diffracted light, related to the amplitude of the grating, was monitored over time. The intensity of this diffracted light decays as the grating decays which in turn depends on the diffusion coefficients of the dye and the photoproduct. The time dependence of the diffracted intensity is given by [15]:

$$I_d = \left[A_1 e^{-t/\tau_1} - A_2 e^{-t/\tau_2} + B_{\text{coh}} \right]^2 + B_{\text{incoh}} \quad (2)$$

where B_{coh} and B_{incoh} are terms related to the small amount of coherently and incoherently scattered light, and the pre-exponential factors, A_1 and A_2 , depend on the Bragg diffraction process, physical properties of the dye and photoproduct, and the concentration difference, ΔC_0 . The negative sign for A_2 reflects the 180° phase difference between the diffracted optical fields of the dye and the photoproduct. The terms τ_1 and τ_2 are the characteristic times for relaxation of the concentration gratings for the dye and photoproduct, respectively, which in turn give the diffusion coefficients through the equation $1/\tau_i = q^2 D_i$. Data from Veniamonov and Sillescu for phenanthrenequinone as penetrant in PMMA suggest that improvements using stretched exponentials in the fit are relatively unimportant for penetrants of the size used in the present study [16].

3. Materials and methods

Methyl methacrylate monomer (Aldrich) was distilled before use; the methyl isobutyrate (Aldrich), diacetyl (Aldrich, 99%), and the camphorquinone (Aldrich, 99%) were used as supplied.

The samples were prepared by the method described below (apparently not used hitherto in the preparation of samples for FRS), in order to meet the following requirements. The sample must be homogeneous, pure, and of a precisely known composition, due to the strong sensitivity of the material properties and diffusive behavior to the

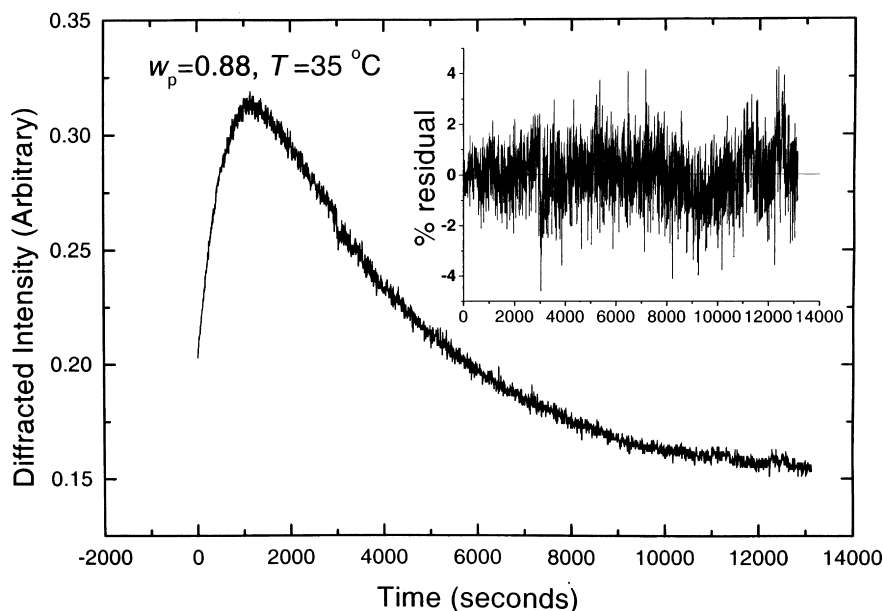


Fig. 1. Typical experimental FRS decay profile. The data are for a PMMA/methyl isobutyrate sample, $w_p = 0.875$, $T = 35^\circ\text{C}$. The percentage residuals for the best fit to Eq. (2) are shown in the inset.

weight fraction polymer. The samples were prepared by mixing monomer, inert diluent, and tracer dye, to form an initially homogeneous mixture, and added to flexible metal sample cells, which were then sealed. The cells that were used in this study were made from a flexible copper frame (metal thickness < 1 mm, sample cell thickness ≈ 3 mm), with large open windows in the front and rear, and a seal at one end. Microscope slides were attached to the windows with an Araldite® K-138 (Ciba-Geigy) adhesive kit. After several days of drying, the sample cell could be filled with the reaction mixture, and sealed with a Teflon® ring and screw. The spacing between the glass windows was approximately 2 mm, which was much greater than the grating spacing in the FRS experiments. Thus, the transient holograms formed during the experiment were “thick” holograms.

The samples were polymerized via γ -radiolysis (^{60}Co source, with a strength of about $0.1\text{--}0.4$ kGy h^{-1}) of the cell, for a period varying between 6 h and several days. The γ -rays initiated polymerization inside the sample cells (it is also possible that side reactions may have occurred during this step). The samples were left in the γ source for sufficient time for complete conversion of monomer to polymer. Some samples were prepared by this method in spectroscopic cells, and residual monomer content was examined by near-IR spectroscopy. No detectable residual monomer was found, indicating complete conversion of monomer to polymer had occurred, within the detection limit of less than 0.5%. The final composition of the samples could be precisely controlled by careful weighing of the components in the reaction mixture, before addition to the cell. Sample preparation by such a method should result in a final mixture that is homogeneous, and contains no initiator

by-products. The amount of tracer dye in the present experiments was kept between 0.2 and 1% by weight, as recommended in the literature [13].

An upper limit exists for the time that the samples may be left in the γ source, due to potential scission or cross-linking of the polymer. PMMA tends to undergo scission [17–19] in the source, whereas other polymers may undergo cross-linking. A significant amount of either of these processes is undesirable: polymer matrix molecular weights that are too low may yield diffusion coefficients with a dependence on the molecular weight of the matrix, and cross-linking will reduce the apparent diffusion coefficients. The molecular weights of two samples were checked by GPC, and high molar masses (of the order of 10^5 g mol^{-1}) were observed; this is sufficiently high that, for penetrants of the size used here, any effects of matrix molecular weight can be ignored [16].

The basic experimental setup was similar to that described in the literature [20]. The reading and writing beams were generated by a Spectra-Physics Stabilite 2017 CW Ar^+ laser, operating at 514.5 nm. The blocking of the beams during the reading or writing steps was performed using mechanical shutters (Newport 846HP shutters), controlled by computer software. The laser spot size was of the order of a few square millimeters, allowing a thick grating (both depth and width), including several thousand diffraction fringes. The diffracted beam in the writing step was directed onto a photomultiplier tube connected to a current amplifier (Keithley 427 current amplifier), which was connected to a National Instruments PC-plus A/D board on a computer. The resulting voltage corresponding to the intensity of the diffracted beam was recorded as a function of time by software.

4. Results and discussion

For each sample, measurements were taken at several different points (physical locations within the sample) to ensure spatial homogeneity. In every case the values at different points within the sample agreed with each other within experimental error. This suggests that the samples were homogeneous. Also, in cases where the times required were experimentally reasonable, the crossing angle of the writing beams was varied to see if the diffusion coefficients obtained over different length scales agreed with each other. The periods of the gratings were varied from 370 to 1100 nm. Again, the diffusion coefficients obtained all agreed with each other within experimental error.

The dye and photoproduct for camphorquinone have slightly different sizes and geometries and therefore have different diffusion coefficients. In the case of camphorquinone the dye diffuses faster than the photoproduct, due to the photoproduct's slightly greater molecular volume [13]. Also since the pre-exponentials in Eq. (2) have opposite signs, the curve may show an initial increase due to the relaxation of the dye grating followed by a decreasing portion due to the relaxation of the photoproduct grating. The decay curve may not always have this type of shape; in fact there are actually several different characteristic curve shapes in an FRS experiment [21], depending on the relative values of the decay constants, pre-exponential factors, and the coherent scattering term in Eq. (2). However, the shape of the curve encountered almost exclusively in this work was one with an initial rise followed by a decreasing portion which approached a baseline intensity. A typical decay curve is shown in Fig. 1, along with the residuals for the best fit to Eq. (2) (inset). As the decay curves from the FRS experiments contain information about the diffusion of each of these molecules, it is theoretically possible to obtain two distinct diffusion coefficients for the dye and photoproduct from each FRS experiment. Most of the discussion here is about the diffusion coefficients for camphorquinone, those for its photoproduct and for diacetyl having poor reproducibility. The decay constants were extracted from the decay curves by fitting to Eq. (2), using a non-linear least-squares minimization routine (Tablecurve for Windows[®]). Checks for false minima were made by variation of starting parameters, and by examination of the residuals for the best fit to the curves. The faster decay constant, which corresponds to a faster diffusion coefficient, is for the camphorquinone dye, which has a smaller molecular volume.

There are two main reasons for the difficulty in reproducing the experimental diffusion coefficients for the photoproduct. The first occurs for the experiments with high weight fractions of polymer. Since the diffusion is very slow in these samples, it was necessary to collect data for long periods ranging from several hours to one or two days. Often these experiments would be stopped early before the decay had a chance to reach a baseline intensity. In these

cases the fitted parameters for the decay of the photoproduct have large uncertainties and result in poor reproducibility for the photoproduct diffusion coefficients. The other difficulty is related to scatter in the experimental data points resulting from contributions to the measured intensity due to any other light sources (attempts were made to minimize this effect by shutting off all other lights while performing experiments), fluctuations in laser power, and scattered reflections of the beam off walls and other surfaces. The effect of the scatter in the data points is to make the true shape of the decay curve less clear. This can become a problem for the very fast decays because the number of data points collected during the experiment was greatly reduced. The problem is magnified for the photoproduct because this portion of the curve tends to have a less defined curvature than the fast portion of the decay associated with the relaxation of the dye grating. Therefore, the scatter in the data points tends to mask any shape that may be present in the portion of the decay curve associated with the photoproduct. This is less of a problem for the very long experiments because the scatter in the data tends to be averaged over the large number of experimental points and the shape of the curve becomes more evident.

In general, the more pronounced shape of the initial portion of the decay curve associated with the dye facilitated fitting of the results and produced more reproducible values for the diffusion coefficients for the dye than were obtainable for the photoproduct.

The large scatter of the experimental data at any composition was a recurring problem to which no simple solution could be found. Similar studies have generally shown smaller scatter [16,22–24]. The scatter here may be due to a combination of sources: for example, uncertainty in fitting parameters (since there are a large number of free variables here, due to the complex interaction between dye and photoproduct diffusion coefficients), drifts in temperature (in combination with a large activation energy), and possible changes in sample composition. There is also the possibility that the dyes used here (both diketones) may cause problems due to their photochemistry. If there is a significant effect of the dye on the matrix, or significant changes in concentrations throughout the grating region (such as microscopic heterogeneity), the grating may not be completely preserved during the reading step. Certainly, large deviations from the expected decay profile were observed in some cases. However, most of the data included in this study showed good agreement between the expected and the experimental (fitted) decay profiles. The choice of dyes was based primarily on their small molecular size (of the order of common monomers), and availability. It is assumed that dye selection had little effect on the quality of the experimental data; however, this cannot be guaranteed.

4.1. Anomalous diffusion?

Anomalous diffusion can occur when the random walk of

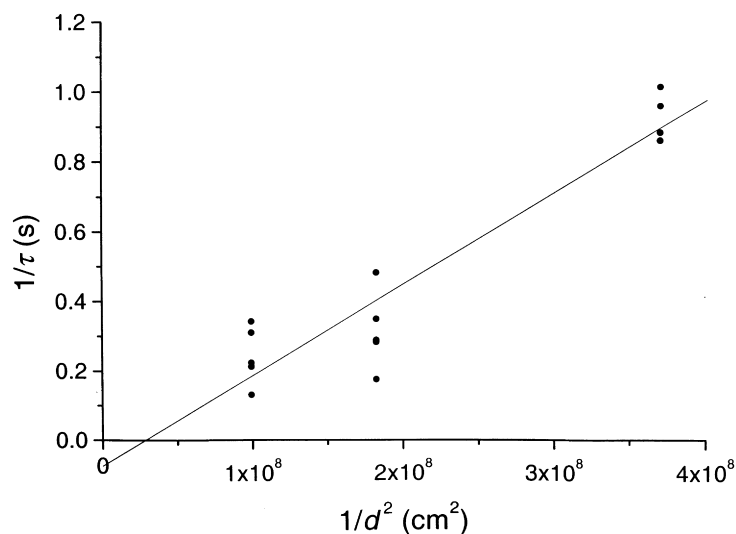


Fig. 2. Plot of inverse decay constant for camphorquinone versus reciprocal squared grating spacing. The data are for PMMA/methyl isobutyrate, $w_p = 0.85$, $T = 25^\circ\text{C}$.

the molecule has not been given sufficient time for the expression $\langle r^2 \rangle = 6Dt$ to become valid. This can arise from the nature of the distribution of jump properties (lengths and times); it takes a finite time for a diffusing molecule to sample this distribution fully. Under these circumstances, for very short distance scales (or corresponding timescales) the apparent (measured) diffusion coefficients may not correspond to the “true” long-time limit in very glassy systems [25–27]. Thus short-time behavior may show an apparent diffusion coefficient greater than the long-term limit. Such an example can be observed from simulations of small-molecule diffusion in glassy polymers [28–30]. It is difficult to predict such a distance scale for a particular system. True long-term behavior could be experimentally verified by examination of the time-dependence of the apparent diffusion coefficient (which should be time-independent), although this may often be difficult, due to experimental limitations.

If diffusion is anomalous in the FRS experiments, plots of the reciprocal time constant (the apparent value of $q^2 D_i$) versus $1/d^2$ (see Eq. (1)) may be curved. The apparent diffusion coefficients in such a case will be faster for the shorter timescales than for longer. This results in a negative intercept from an apparent linear fit. Such a test may expose anomalous diffusion, given a sufficiently broad range of decay constants, due to the predicted curvature and negative intercept. However, in most experimental cases, curvature is unlikely to be distinguishable, due to physical limitations for changing of the crossing angle resulting in a relatively small range of possible grating spacings, and the errors in estimating the intercept may be too large for the sign to be clearly determined. It should also be noted, however, that non-diffusive contributions to the observed decays alone would give a positive intercept. If the magnitude of the non-diffusive contributions is large, these may hide an

otherwise possibly negative intercept. This supposition was tested for the sample of $w_p = 0.85$, at several temperatures. Since anomalous effects are most likely to be observed at lower temperatures, the results are shown for 25°C in Fig. 2. This represents the combination of lowest temperature/highest w_p that was systematically studied here, and thus the most likely candidate for anomalous effects. The data presented in Fig. 2 show no obvious upwards curvature. The intercept is negative, but has an uncertainty larger than this nominal negative value. It is clear that the scatter of the data is large, and the results are inconclusive. The same problem was observed for all other sample/temperature combinations studied.

Thus, although anomalous diffusion may have a significant effect for some glassy systems, there is not clear evidence that anomalous diffusion was significant for the current system. However, it may be best to regard the observed diffusion coefficients as upper limits to the true values.

4.2. Matrix relaxation: annealing effects?

It is quite possible that in the glassy regime, the polymer/penetrant system is not in an equilibrium state and may undergo changes over periods of days or even months. This complicates the study of diffusion as the T_g is traversed by introducing this time dependence. Sillescu and co-workers [16,23] observed diffusion coefficients decreasing over time due to physical aging in the glassy region. In many cases the time required for the diffusion coefficient to reach its lower limit in the glassy region can be very long. Zhang and Wang [22] observed physical aging in PMMA below the T_g . They found that when the system was 10°C below the T_g the diffusion coefficients were still decreasing after 4 days. At 1°C below the T_g , the diffusion coefficient leveled

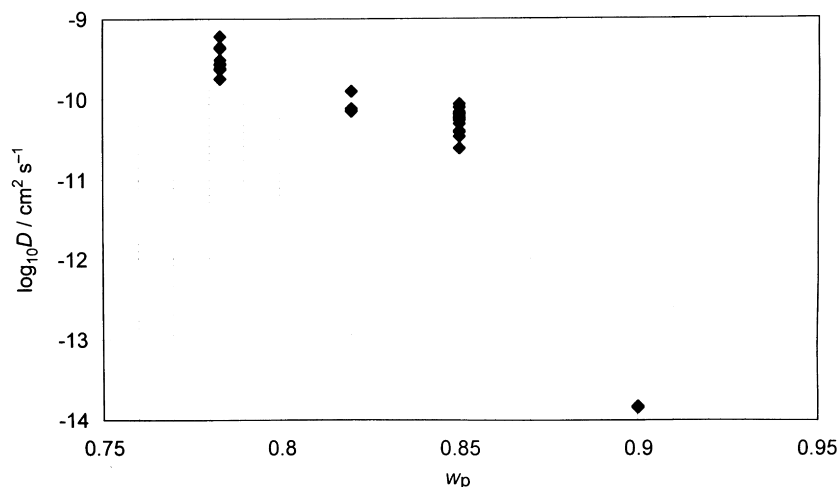


Fig. 3. Measured diffusion coefficients of camphorquinone in a PMMA/methyl isobutyrate matrix at different weight fractions of polymer at 40°C.

off in less than 24 h. To the best of our knowledge, no studies of aging have been reported for polymer/solvent systems in the glassy region, such as the systems used in the work presented here. However, the effect of aging would be expected to be less for systems with solvent, since the presence of solvent tends to reduce the extra free volume present in the glassy system. In this work, the diffusion coefficients for the samples at w_p of 0.88 and 0.90 were about three orders of magnitude less than for the other samples studied, which is probably due to the onset of the glass transition. In an attempt to alleviate the problem of time dependent diffusion coefficients, all measurements made for these samples were taken after allowing the sample to remain at the desired temperature for at least 12–24 h prior to the measurement. This study was not aimed specifically at determining the time dependence in the present system, so it is quite possible that the diffusion

coefficients have not reached their long-time limit. However, since the measurements seem to be reproducible for different experiments without ensuring that the aging time was constant in each case, we believe that within experimental error the diffusion coefficients are equal to the long time limit. However, it is also possible that the relaxation processes for these samples is so slow that changes in the diffusion coefficients due to physical aging of the polymer was simply not detectable on the time scale for which the samples were allowed to age in these experiments.

4.3. Glass transition temperature

Fig. 3 shows individual measured diffusion coefficients of camphorquinone in PMMA/methyl isobutyrate matrices at different values of w_p ; it can be seen that the scatter in duplicate measurements is relatively small. Fig. 4 shows

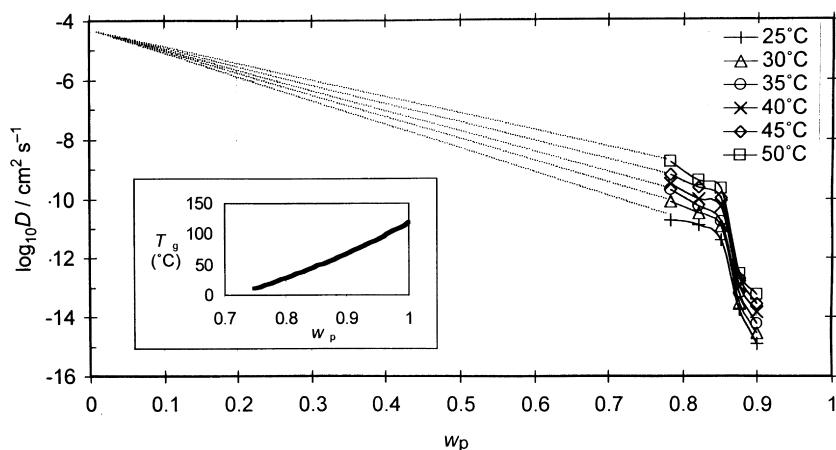


Fig. 4. Dependence of diffusion coefficients of camphorquinone in a PMMA/methyl isobutyrate matrix as functions of temperature and of weight fraction polymer; each point is the average of a number of individual measurements of the type shown in Fig. 3. The points at $w_p = 0$ are estimated by the Wilke–Chang equation [31], and the connecting lines are for visual purposes only. The inset shows T_g as a function of w_p as predicted using the Kelley–Bueche equation and the free-volume parameters of Faldi et al. [12].

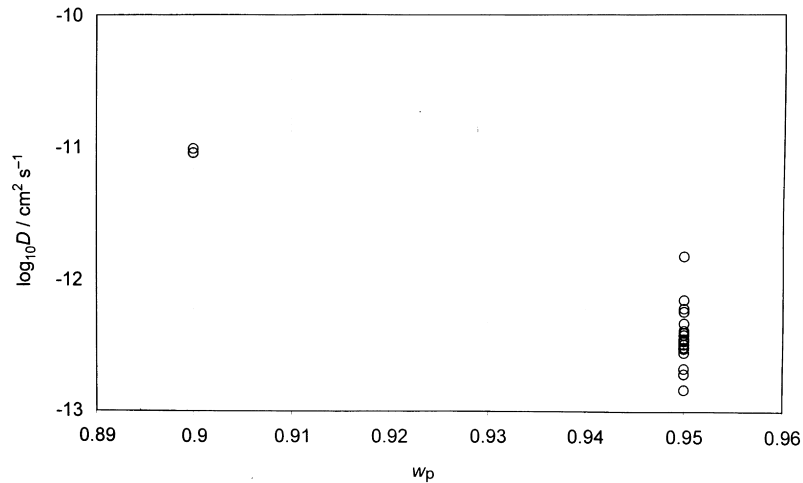


Fig. 5. Measured diffusion coefficients for diacetyl in a PMMA/methyl isobutyrate matrix as function of weight fraction polymer.

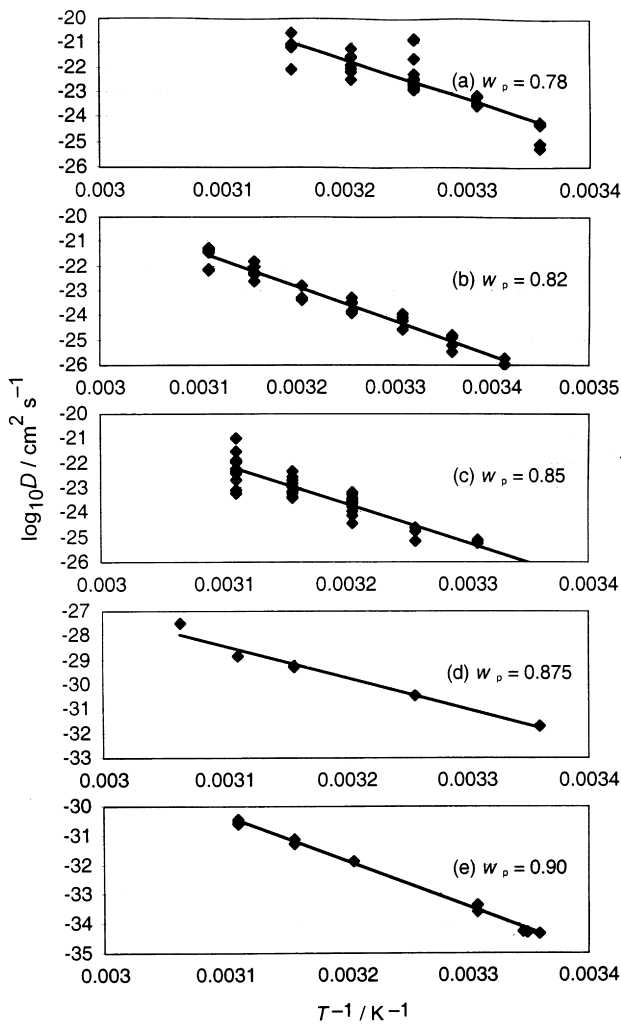


Fig. 6. Arrhenius plots of the diffusion coefficient of camphorquinone in various PMMA/methyl isobutyrate matrices: w_p values (a) 0.78; (b) 0.82; (c) 0.85; (d) 0.875, and (e) 0.90. Comparison with the results in Fig. 4 shows that the activation energy does not appear to change with w_p through the glass transition.

the collected data over the entire range of temperature and w_p ; each point is the average of a number of different measurements at each w_p of the type shown in Fig. 3. The diffusion coefficients at $w_p = 0$ in methyl isobutyrate, as estimated using the Wilke–Chang equation for diffusion in liquids [31], are also shown for comparison. For this estimate, the molar volume for camphorquinone was estimated from data for camphor, since no such information is available for camphorquinone. Nevertheless, these points should represent an acceptable estimate, and are shown solely to give some perspective of the overall trend that the diffusion coefficients will follow as the polymer weight fraction is decreased. Corresponding data for diacetyl at 25°C are shown in Fig. 5; these data are subject to much greater scatter than those for camphorquinone.

It is important to note that the temperature dependence of D is much lower in the pure solvent. The rapid variation at $w_p \sim 0.87$ arises near the glass transition. Two points must be borne in mind in this context.

- The value of the glass transition temperature depends on which physical property is being measured, since different physical properties can depend differently on the microstructure and penetrant dynamics and microstructure. Thus temperature at which the diffusion coefficient (which is a dynamic property) shows a rapid change, for a given w_p , might have a value which is smaller but significantly different value from the T_g measured, say, by DSC (which is governed by near-equilibrium microstructure).
- The glass transition temperature T_g is a function of the amount of monomer present (i.e. of w_p): the monomer acts as a plasticizer. This can be expressed as the Kelley–Bueche relationship [32,33] in terms of free-volume theory for rubbery polymers. The predicted dependence of T_g on w_p using the free-volume parameters of Faldi et al. [12] (which are fitted to T_g data obtained by DSC for PMMA with diluent MMA

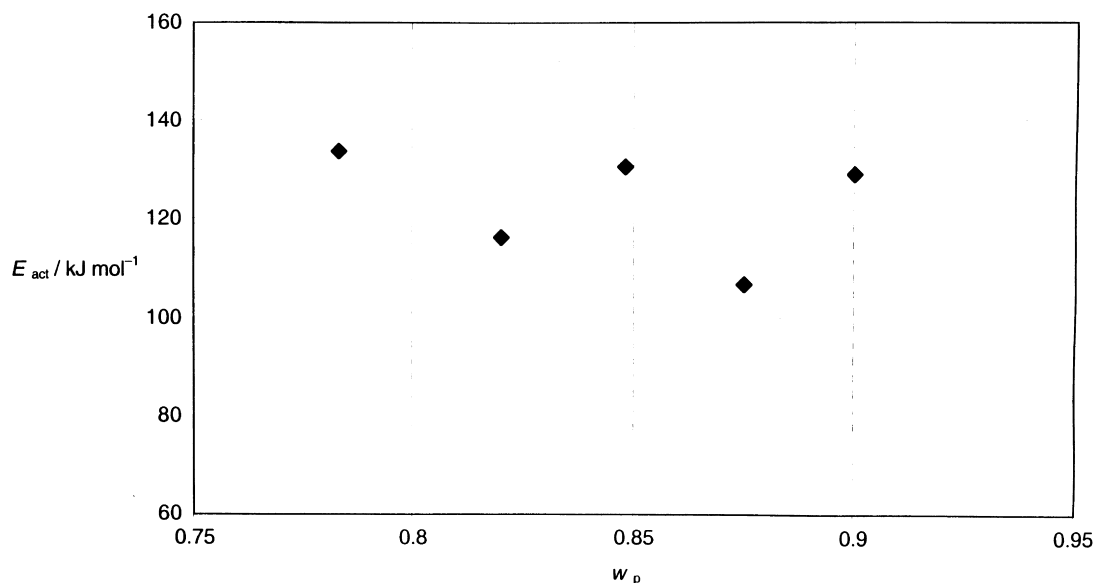


Fig. 7. Activation energy for camphorquinone diffusion coefficients as a function of weight fraction polymer.

monomer, rather than the methyl isobutyrate as in the present system) is shown as an inset in Fig. 4.

The data of Fig. 4 show that, at a given temperature, the diffusion coefficients show a rapid change with w_p over the range $w_p \approx 0.84 - 0.87$. It is apparent from Fig. 4 that the temperature dependence of this rapid-change range of w_p is weak, and moreover that the temperature at which this occurs for a given w_p is close, but not identical, to the T_g values from the parameters of Faldi et al.; the difference may or may not be significant because of the small difference in diluent.

4.4. Temperature dependence

The experimental diffusion coefficients as a function of temperature for camphorquinone for various polymer weight fractions are shown as Arrhenius plots in Fig. 6a–e. The samples with lower polymer weight fractions show more scatter in the data points, especially at higher temperatures. This may be simply because of the short time scales, sometimes a matter of seconds, required for the relaxation of the gratings in these cases. As discussed above, the fact that these runs contain fewer experimental points causes the effect of the scatter in the data points to be greatly increased, resulting in more uncertainty in the fitted parameters and more variability in the diffusion coefficients. Since these experiments take such a short amount of time, it was possible to repeat them several times and thus obtain an adequate average for the diffusion coefficients based on several experiments.

An extension of free volume theory to a ternary system such as the present has been developed [34]; however, many of the parameters required for such a calculation for the current systems are not available, and thus its application to the most of the present data would be not more than a

curve-fitting exercise (although useful comparisons can be made at $w_p = 1$, and are implemented in a companion paper [35]). Free volume theory predicts that the activation energy is small in systems far above T_g , and it should decrease as solvent concentration is increased for systems above the T_g . This inference is supported by the results of Zhang and Wang [36] for diffusion of camphorquinone in polystyrene/dioctyl phthalate (DOP) solutions above the T_g , where E_{act} was found to decrease as the DOP concentration was increased. From Fig. 4 it is clear that the temperature dependence of the diffusion coefficient must decrease as the polymer concentration is decreased from 0.78 to 0 (pure solvent).

The data in Fig. 6a–e are fitted acceptably by an Arrhenius temperature dependence. The activation energies from these Arrhenius plots are shown in Fig. 7: the diffusion coefficients depend strongly on temperature for this system, with activation energies for diffusion ranging from 106 to 133 kJ mol^{-1} .

It is especially noticeable that the activation energies of Fig. 7 do not depend strongly on polymer fraction, even though the system passes through the glass transition over this range of w_p (see Fig. 4). Activation energies of this order of magnitude have been reported previously for relatively large molecules such as camphorquinone in glassy polymers. For instance, Wang et al. report a value of 178 kJ mol^{-1} for camphorquinone diffusing in pure polystyrene at temperatures between 69 and 77°C [21], although this value should be regarded with some discretion due to the narrow temperature range over which the experiments were conducted. Activation energies for diffusion in polymers in excess of 150 kJ mol^{-1} are common [37]. It should also be noted that E_{act} will increase with increasing penetrant size. For smaller molecules, values ranging around 10–30 kJ mol^{-1} would be more typical: for example, Bazhin et

al. report a value of 30 kJ mol^{-1} for oxygen diffusion in PMMA between 77 and 300 K [38].

Is this observed insensitivity of E_{act} to w_p through the glass transition in accord with what is expected from theory? Extension of the free volume theory of Vrentas and Duda for diffusion in glassy solutions [39,40] predicts a decrease in the apparent activation energy for diffusion below the T_g for quenched samples; this decrease is predicted to be greater for large penetrants and may not be seen at all for smaller ones [34]. A quenched sample is one in which the temperature is brought below the T_g and the diffusion measurement taken shortly thereafter. The extension of free volume theory to glassy solutions includes a time dependence related to volume contraction below the T_g . This is described by including a term of the extra “frozen free volume” which is present in the glassy state as a result of the chains being constricted and not being able to relax at a sufficiently fast rate. This extra frozen free volume will decrease over time as the volume of the sample slowly contracts to its equilibrium value. This will result in a diffusion coefficient that also decreases over time, due to the decreasing free volume. This theory implies therefore that if diffusion coefficients measured above the T_g were used to extrapolate below the T_g , then measurements of the diffusion coefficients below the T_g for quenched samples would be greater than these extrapolated predictions [24]. As the temperature is decreased below the T_g , the difference between the extrapolated values and the measurements will increase. Below the T_g , the diffusion coefficient is predicted to be greater, and hence probably the E_{act} is predicted to be less; on the contrary, if the dominant mechanism for diffusion does not change as T_g is traversed, then the activation energy would approach that extrapolated from above the T_g . As discussed in an earlier section, it cannot be stated with confidence that the present system is truly in a condition of (moderate) stasis. Given this caveat, the observation of an E_{act} which is independent of w_p is therefore in contradiction to standard free-volume theory. Moreover, as will be discussed in a subsequent paper [35], the fundamental concepts of free-volume theory are thought to be inapplicable to penetrant diffusion in glassy polymers, since quite a different mechanism is operative: simulations [29,41–44] suggest instead penetrant diffusion in glassy polymers occurs by occasional jumps between cavities through the opening of a “neck”. Indeed, molecular dynamics simulations and experiment suggest that a hopping mechanism for penetrant diffusion sets in well before the glass transition temperature [45]. Moreover, it is found [35] that the free-volume model underestimates experimental diffusion coefficients by many orders of magnitude, with predicted activation energies a factor of about two larger than those found experimentally in the present paper.

Is the observed insensitivity of E_{act} to w_p in accord with other data? Several papers have reported changes in the temperature dependence of the diffusion coefficient as T_g

is crossed. Zhang and Wang saw no change in E_{act} for camphorquinone in poly(*t*-BMA) [13] as T_g was crossed but for diacetyl in PMMA [22] they observed a drop in D by three orders of magnitude immediately after the T_g was crossed. The measurements for diacetyl in PMMA were taken 1 h after changing the temperature, so the effect of aging is most likely a factor in these measurements. Sillescu and coworkers [16,23] saw a decrease in E_{act} below the T_g for polystyrene, polyethylstyrene and polycarbonate for quenched samples. Frick et al. [24] studied the temperature dependence of azobenzene in polystyrene/toluene solutions of 81, 83 and 84% polystyrene. They found that E_{act} was less below the T_g but the change in E_{act} was 30% less for the 81% solution than for the 83 and 84% solutions, which were essentially equal. Again however, these measurements were for samples that were not given much time to age.

There are several possible reasons why no change in E_{act} was observed across T_g . There seemed to be no systematic change in observed diffusion coefficient with time (typical annealing times being 12 h to many days), and it is therefore likely that the diffusion coefficients measured here are close to their long time limits. However, the time required for the polymer matrix to relax to its equilibrium state may be very long and thus it is also possible that the system is essentially “frozen” near T_g , and the apparent activation energies have not had sufficient time to change, thus giving an apparent activation energy that is independent of temperature, and equal to a value in the rubbery regime. This possibility is considered unlikely; however, as we did not conduct specific studies to determine these time frames for the present system, there is no guarantee that the diffusion coefficients have reached their long time limits. However, another factor that may be important here is that there was a substantial amount of solvent present in samples used in this study, which in itself decreases the extra free volume present in a glassy system and may increase the rate at which the matrix relaxes below T_g . Frick et al. [24] found a decrease in E_{act} across T_g for polystyrene/toluene solutions, but these were for quenched samples and used aberchrome as the dye. Aberchrome is larger, and diffuses more slowly, than camphorquinone; increasing the penetrant size tends to increase the likelihood that E_{act} will change as T_g is traversed [34]. Ehlich and Sillescu [23] noted that changes in E_{act} at T_g are often only observed for the slowest diffusants.

Several researchers have observed a change in E_{act} with temperature and conversion immediately before T_g [13,22–24]. However, these studies have used samples which were not given time to relax to their true equilibrium state. The results of the current study suggest that there is only a weak, if any, dependence of the activation energy for diffusion on the weight fraction polymer across the glass transition. A possible implication of this is that there may be no significant change in the mechanism for diffusion of camphorquinone in PMMA/methyl isobutyrate solutions throughout this region; however the large change in pre-exponential factor (as distinct from activation energy) as the system

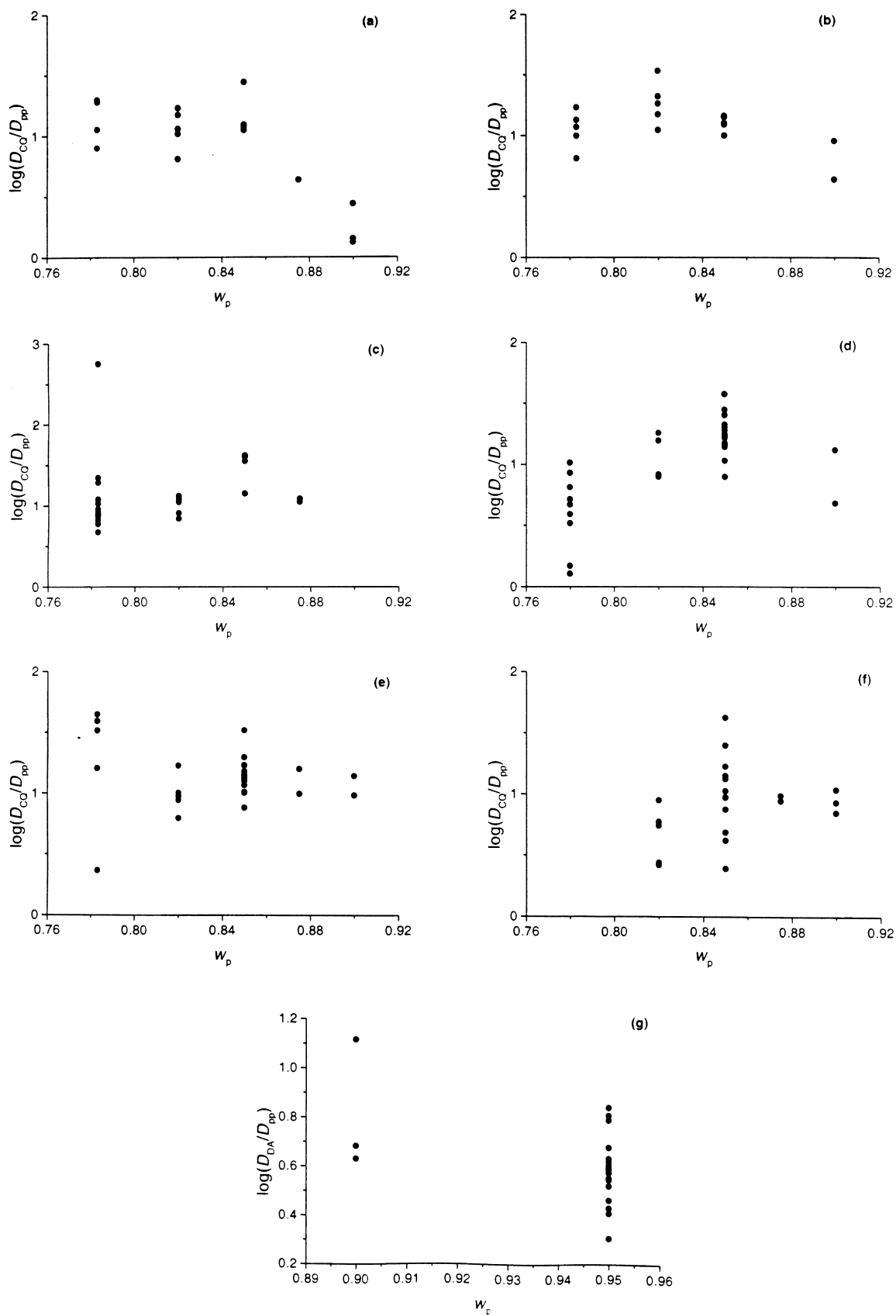


Fig. 8. Ratios of diffusion coefficients for the tracer dye versus its photoproduct as a function of sample composition for camphorquinone at: (a) 25°C; (b) 30°C; (c) 35°C; (d) 40°C; (e) 45°C; (f) 50°C; and (g) for diacetyl at 25°C.

goes through the glass transition presented in the following section suggests otherwise.

4.5. Dependence on solvent concentration

Fig. 4 shows the experimental diffusion coefficients for camphorquinone as a function of the weight fraction of polymer (the lines drawn between the points in this figure are purely for visual purposes and do not represent any type of fitting). At each temperature, it is apparent that as the glass transition is crossed, the diffusion coefficients decrease by over three orders of magnitude. This behavior is expected because the stiffness of the polymer chains in the glassy regime will restrict the redistribution of free volume and hinder the diffusion of the penetrant. As discussed in the previous section, E_{act} does not change significantly as the glass transition is crossed, and the temperature dependence of the observed rapid change in D through the glass transition is thus a decrease in the pre-exponential factor for diffusion. This pre-exponential factor in such systems may describe a large number of phenomena. For example, if the diffusion process is considered a random walk in three dimensions ($D = \frac{1}{6} k_{\text{jump}} L^2$, where k_{jump} is the jumping frequency, and L is the typical jump length), the effective frequency factor contains information regarding both the jump length and frequency.

Diffusion is expected to proceed via two different mechanisms either side of the glass transition. For the rubbery regime, free volume appears a good model. At the extreme end of the glassy regime (with essentially no added diluent, and only a trace amount of penetrant), simulations [28–30,46] imply that diffusion over significant distance scales is dependent on relatively rare “hopping” events between neighboring cavities. On the current experimental evidence, it is not possible to convincingly argue either for or against a change in mechanism through the glass transition, since there are factors which may argue for either case.

4.6. Dependence on penetrant species

Fig. 8a–f show the ratios of the diffusion coefficients for the tracer dye and photoproduct as a function of composition, at each temperature where measurements with camphorquinone were taken, and Fig. 8g shows the limited data for diacetyl at 25°C. Although dye and photoproduct are of similar sizes, there seems to be relatively large differences in their diffusion coefficients; however, these differences are subject to significant experimental uncertainty. In most cases, very little dependence of the ratios on w_p were distinguishable within the experimental scatter. However, there appears that there may be a very small maximum in the ratio at most temperatures near $w_p = 0.85$, which is approximately the point immediately before the large decrease in diffusion coefficients (see Fig. 4). At 25°C, the ratio appears to decrease beyond this point, but there are insufficient data to be certain that this effect is real. Overall,

the ratios of diffusion coefficients appear to be approximately independent of w_p in this region.

It can be seen from Figs. 4 and 5 that, for the limited amount of diffusion data for diacetyl, the diffusion coefficients for the smaller diacetyl dye are much larger than for the camphorquinone at an equivalent value of w_p , as may be expected. This size dependence is very strong (with the smaller diacetyl diffusing much more rapidly than the camphorquinone), and is also implied by the large difference in diffusion coefficients between tracer dyes and their photoproducts, although the differences in molecular sizes are rather small. Unfortunately, only limited data are available for comparison, and no systematic study of size dependence is possible.

5. Conclusions

- The diffusion coefficients in polymer/solvent solutions are most sensitive to the solvent concentration near the glass transition where only a few percent change in the polymer concentration can change the diffusion coefficient by several orders of magnitude.
- Polymer solutions at high weight fraction of polymer exhibit very high apparent activation energies, in excess of 100 kJ mol^{-1} , for diffusion of large molecules such as camphorquinone.
- No sharp change in the apparent activation energy for diffusion is observed as the glass transition is crossed for systems containing small amounts of solvent and allowed to age after the temperature of the system is changed.
- The activation energy for diffusion of camphorquinone in PMMA was apparently independent of w_p as the system goes through the glass transition, but the pre-exponential factor decreases dramatically through the glass transition. The first observation is in contradiction to the predictions of free-volume theory.
- The diffusion coefficients of small penetrants in glassy polymers appear to be very strongly dependent on molecular size, as indicated by the large difference between diffusion coefficients for camphorquinone and diacetyl in similar glassy PMMA matrices.

In a subsequent paper [35], these results are compared with the predictions of two models for these diffusion processes.

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