Dye Diffusion in Polycarbonate in the Presence of Additives

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ABSTRACT: The tracer diffusion coefficient of the photoproduct of camphorquinone (CQ) in polycarbonate (PC) is measured as a function of temperature and additive concentration. The additivies are dioctyl phthalate and 1,3- and 1,4-dichlorobenzene. The effects of polymer molecule weight distribution and the presence of plasticizer molecules on the tracer diffusion coefficient are investigated. In the nearly monodisperse PC or PC containing no plasticizer, the diffusion coefficient precipitously decreases as the sample temperature is lowered toward T_g. The rapid decrease of the diffusion coefficient in the vicinity of T_g is, however, not observed in the plasticized PC. Empirical equations based on free volume theory are developed to describe the temperature and concentration dependence of the tracer diffusion coefficient.

Introduction

There exists extensive literature on the investigation of the polymer solution in which the polymer is the minor component. Many fewer studies are carried out in the polymer solution in which the polymer is the major component. The polymer solution of the latter type is often referred to as the plasticized polymer, because of the well-known plasticizer effect whereby the elastic modules and the glass transition temperature of the polymer are reduced by the small molecular species.

The plasticizer effect accelerates the cooperative α-relaxation process, and it significantly influences the viscoelastic properties of the polymer.[1] The effect results in a sharp reduction in all relaxation times and is satisfactorily explained in terms of free volume theory.[1] The α-relaxation involves the main-chain motion, and the change of the average free volume is considered the controlling parameter for the relaxation time.

In recent investigations of the translational diffusion processes of photochromous dye molecules in amorphous polymers using the holographic grating relaxation (HGR) technique, we have shown that the dye diffusion coefficients strongly depend on the dye concentration.[2] When the concentration of the dye molecules is negligibly small (less than 0.5%), the translational diffusion coefficient is found to be determined predominantly by the size of the dye molecule and by the viscoelastic property of the polymer host.[2,3] In the very low dye concentration limit, the dye molecules serve as tracers. The tracer diffusion coefficient (or the self-diffusion coefficient of the dye molecules in the environment of the polymer) is closely associated with the monomer diffusion coefficient of the polymer host.[1] The connection of the tracer diffusion coefficient with the monomer friction coefficient of the host polymer chain has been discussed by Ferry.[1] The result of temperature dependence studies of the tracer diffusion coefficient above T_g displays a non-Arrhenius behavior; the tracer diffusion coefficient is found to follow the form of the Williams–Landel–Ferry (WLF) equation, with the WLF coefficient C_2^D identical with that of the C_2 coefficient associated with the viscoelastic property of the pure polymer. The C_1^D coefficient is found to scale in accordance with the size of the diffusant and that of the polymer segment causing free volume fluctuations.[3-5]

The introduction of plasticizer into the dye/polymer system will alter the dye tracer diffusion coefficient, because the addition of plasticizer adds free volume to the system. On the other hand, the addition of plasticizer might also cause a structural change in the glassy polymer. NMR studies show that adding the plasticizer in PC will affect the behavior of the PC chain motion.[6] The behavior change in the chain motion has been related to the β-suppression effect[7,8] and to the decrease in the amplitude of the density fluctuation of the PC below T_g.[6] If the decrease in the amplitude of the density fluctuation is significant, it might result in the retardation of the trace diffusion coefficient.

Another effect associated with the addition of plasticizer is the introduction of the diffusional coupling, if the dye concentration is sufficiently large so that a dye molecule will interact with plasticizer as well as with other dye molecules. The intermolecular interactions introduce the thermodynamic and kinetic couplings in the diffusion equation. In kinetic coupling, the velocity correlation between a dye molecule and a plasticizer molecule or between two dye molecules will become important. The thermodynamic coupling and the velocity correlation give rise to an off-diagonal diffusion tensor component in the diffusion equation; the diffusional behavior of dye molecules and that of plasticizer are then coupled. In this case, analysis of the HGR result must utilize the mutual diffusion theory of a ternary system.[9] However, by keeping the concentration of dye molecules vanishingly small (less than 0.5 wt %), the pair velocity correlations cannot be important and one can interpret the HGR experimental result in terms of tracer diffusion of the dye molecules in the plasticized polymer environment.

Ferguson and Meerwall[10] have compared the free volume model in the form of the Fujita equation[11] with that of the Vrentas–Duda[12] (V–D) theory to interpret the self-diffusion data in ternary systems. The V–D theory reduces to the Fujita equation provided that $\zeta_{12} = 1$, where ζ_{12} represents, in the polymer host, the ratio of the critical volume of a jumping unit of component 1 (the probe molecule) to the critical volume of the jumping unit of component 2 (the plasticizer). Both the Fujita and V–D free volume equations provide a scaled relationship between the self-diffusion coefficient of the probe and that of the plasticizer. In the present system, the jumping units for the probe and for the plasticizer involve the entire molecule; we expect that $\zeta_{12} = 1$. Thus, in accordance with the free volume theory, $D_1/D_{1o} = D_2/D_{2o}$, where D_{1o} and D_{2o} are, respectively, the self-diffusion coefficients of the probe and plasticizer before any significant amounts of probe and plasticizer are added to the polymer. Thus, in the framework of free volume theory, the effect of adding plasticizer to the probe/polymer system is to provide additional contribution to the free volume of the system, and one can extend the Fujita theory[11] to describe the

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present ternary systems.

We consider in this paper the tracer diffusion coefficient of camphorquinone (CQ, the dye molecules) in polycarbonate (PC) plasticized by dichlorobenzenes (DCB). The tracer diffusion coefficient of CQ is measured as a function of DCB concentration and temperature.

The temperature dependence of tracer diffusion coefficients of CQ in PC without added plasticizer was previously published by Wang and Xia.[13] The CQ diffusion data reported in ref 13 are, however, more than 2 orders of magnitude smaller than the diffusion data of tetrahydrothiophene-indigo (TTI) in PC reported by Ehlich and Sillescu.[14] Furthermore, the diffusion data of ref 14 show a smooth change in the vicinity of the glass transition temperature, T_g, whereas, the data of Wang and Xia show a more rapid decrease as the temperature is decreased toward T_g. One of the objectives of this work is to examine the cause of the discrepancy and then to provide an explanation for the different results that have been reported.

Experimental Section

Several types of poly(bisphenol-A carbonate) (PC) samples are used in the holographic grating relaxation (HGR) experiment. One type is purchased from the General Electric Co. with the trade name Lexan 4, and it is used without further fractionation. The molecular weight of Lexan 4 is characterized by using GPC; it gives $M_w = 2.27 \times 10^4$ and $M_w/M_n = 2.15$. This PC sample is referred to as PC-w, where w is to indicate a wide molecular weight distribution. The second type of PC used in the experiment is obtained by washing the PC-w sample to remove any trace of plasticizer that was added in the process of producing Lexan 4. The washing procedure consists of dissolving the PC pellets in dichloromethane. The solution is then filtered to remove dust. PC is precipitated from the solution by adding methanol (a nonsolvent). The precipitated PC powder is removed and dried under vacuum at 150 °C for 2 days. The washed PC-w sample is designated PC-w′. The third type is obtained by fractionating Lexan 4 and then selecting narrow fractions with a nearly monodisperse molecular weight distribution: $M_w = 3.6 \times 10^4$ and $M_w/M_n = 1.03$; $M_w = 1.12 \times 10^4$ and $M_w/M_n = 1.12$. These PC samples were referred to as PC-n. The letter n indicates narrow distribution. The narrow distribution sample was obtained by first dissolving the PC-w sample in chloroform and then gradually precipitating fractions of PC with methanol. The molecular weight and molecular weight distribution of precipitated fractions of PC were determined with GPC, using THF as a solvent and polystyrene as a standard.

To prepare the set of samples containing dichlorobenzene for the HGR experiment, about 0.5% (by weight) of camphorquinone (CQ) and a desirable amount of dichlorobenzene (DCB) were added to each type of the PC sample, initially placed in a test tube. The test tube was shaken to yield a homogeneous mixture and was then quickly heated (under N_2 atmosphere) to 250 (for the one containing PC-w′) or 275 °C (for that containing PC-n) to melt the sample. To prevent thermal degrading, due to high temperature, the PC melt containing CQ and DBC was kept at high temperatures under N_2 atmosphere for 4 days to obtain a homogeneous mixture. The sample with PC-n was kept at 275 °C for only 4 h, due to the high temperature. The homogeneous hot melt was then quenched to room temperature, yielding a transparent yellowish solid rod. A slice of the quenched PC was then cut from the rod and polished into a circular disk having a thickness of about 1 mm. The polished disk was mounted in a specially designed copper holder for the HGR measurement. The technique used for the temperature variation was the same as that employed previously.[13]

Three different PC samples [one PC-w′, one PC-n, and one PC-w′ plasticized with 0.8% dioctyl phthalate (DOP)] were also prepared by utilizing a temperature-controlled hydraulic press. The DSC measurement of these samples all showed a T_g of 150 °C. The PC sample (PC-w′, PC-n, or plasticized PC-w′) in powder form was mixed with 0.5% (by weight) CQ powder. The mxiture was then thoroughly blended in a blender. After being mechanically mixed, the PC powder containing CQ was placed in a hydraulic press at a temperature of 280 °C and then pressed (in about 10 min) to an optically clear disk with a thickness of about 0.4 mm. The disk was mounted in the copper holder for the HGR experiment.

Table I
Values of T_g and the Measured Diffusion Data at T_g for DCB-Plasticized PC at Various Concentrations

plasticizer concn, wt %	T_g, K	$D(T_g)$, cm^2/s	plasticizer concn, wt %	T_g, K	$D(T_g)$, cm^2/s
		1,3-DCB			
0	150	4.5e-12	3.63	121.5	4.9e-12
0.66	143.6	6.0e-12	5.42	109.0	6.1e-12
1.48	134.7	5.6e-12			
		1,4-DCB			
1.08	137.7	3.2e-11	5.31	108.1	4.0e-11
3.43	124.3	3.3e-11			

A last set of two samples was prepared by placing PC-n (or PC-w′) and CQ powder in a test tube. The test tube containing the sample was again sealed under a nitrogen atmosphere and subsequently heated to 280 °C to melt the sample. The melted sample was kept at 280 °C for 3 days to assure homogeneity. Afterward, the sample was quenched to room temperature. This method of preparation was identical with that employed in the previous work.[13]

The glass transition temperatures of the DCB-plasticized PC samples were determined by using a Perkin-Elmer Delta series DSC. The results are given in Table I. The glass transition temperature of the PC sample containing less than 0.5 wt % CQ is found to be the same as that of pure PC (150 °C), indicating that the small amount of CQ introduced has a negligible effect on the T_g of pure PC.

Below 0.5% dye concentration, the mutual diffusion coefficient was found not varying with further decrease in the dye concentration. At such a low concentration, we have reached the tracer diffusion limit. The presence of DCB significantly lowers the glass transition temperature. In this work, the concentration of CQ is kept at less than 0.5 wt %. Therefore, the diffusion coefficient reported here corresponds to the tracer diffusion coefficient of CQ in PC or plasticized PC.

The holographic grating was induced by crossing two equal intensity beams derived from an argon ion laser operated at the wavelength equal to 514.5 nm. The angle between two writing beams was varied from 5.7° to 33.6°, corresponding to a grid spacing $d = \lambda/2 \sin(\theta/2)$ varying from 0.887 to 5.15 μm, respectively. The optical setup was similar to that employed in the previous work on the diffusion study of CQ in PC without the presence of additives.[13] The grating arises mainly from the phase hologram, as 514.5 nm falls on the tail of the absorption band of CQ in PC. In the vicinity of T_g, each data point in the diffusion measurement was obtained after 4 h of temperature equilibration.

Results and Discussion

The diffraction efficiency $\eta(t)$ arising from the modulation in the refractive index owing to mass diffusion of the unreacted dye molecule (u) and its nonreversible photoproduct (p) has been shown to be given by[15]

$$\eta(t) = (ae^{-t/\tau_p} - be^{-t/\tau_u})^2 \qquad (1)$$

In eq 1, we do not add constants arising from coherent and incoherent background contributions to the diffraction efficiency, as they can be minimized by a careful sample preparation procedure.[16] Parameters a and b are optical constants that can be of either the same or opposite sign. When they have the same sign, eq 1 shows a decay–rise–decay shape. On the other hand, it gives a monotonous decay shape if a and b have the opposite sign.[15]

We show in Figure 1 the experimentally observed diffraction intensity vs time curve for two temperatures

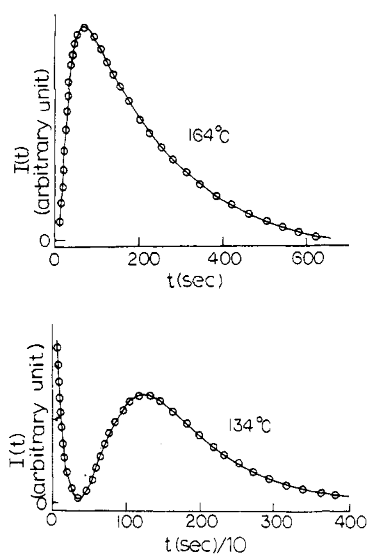

Figure 1. Comparison of observed and calculated diffraction intensity vs time curves for the PC-w sample containing only CQ dye at two temperatures. The calculated curves are obtained by using $a = 33.51$, $\tau_p = 3.25$ s, $b = 31.23$, and $\tau_u = 20$ s for the sample at 164 °C and by using $a = 30.05$, $\tau_p = 418$ s, $b = 29.31$, and $\tau_u = 2800$ s for the sample at 134 °C. The writing angle (2θ) for the 164 °C curve is 11.4° and that for the 134 °C curve is 33.6°.

for the PC-w sample containing only the CQ dye. Also shown in Figure 1 are the curves calculated by using eq 1. The parameters employed in the calculation are given in the figure caption. Clearly eq 1 adequately describes the experimental result, and it shows in the present case that a and b have the same sign, consistent with that previously observed.[13] The relaxation time extracted from the curve fitting can also be obtained by plotting ln (I) vs time (t) and then calculating the decay time constant from the slope at long times. The slope method is more convenient, but it can only provide the time constant for the photoproduct (CQP).[15] Since here we are most interested in the study of the effect of additives on the tracer diffusion coefficient, we adopt the more convenient slope method. The diffusion coefficient data reported in this work are referred to that of the photoproduct of CQ (CQP).

The diffusion coefficients of CQ and CQP are designated D_1 and D_2, respectively. They are related to the relaxation time τ_1 and time τ_2 by

$$D_i = \frac{\lambda^2}{16\pi^2\tau_i \sin^2(\theta/2)} \qquad i = 1, 2 \qquad (2)$$

The temperature dependence of the diffusion coefficient D_2 in PC containing different concentrations of 1,3-DCB is shown in Figure 2. The presence of DCB has a pronounced effect on the diffusion coefficient. It significantly increases the diffusion coefficient, due mainly to plasticization of the polymer chain which results in decreasing the polymer local friction (or relaxation time) and also results in the lowering of the glass transition temperature (Table I). Discussion of the plasticizer concentration dependence of D_2 will be given in a later section.

One notes that the temperature dependence of D_2 is non-Arrhenius, with the effective activation energy for diffusion, defined as

$$E_D = RT^2\left(\frac{\partial \ln D_2}{\partial T}\right)_p \qquad (3)$$

increasing nonlinearly with decreasing temperature. The non-Arrhenius behavior indicates that the diffusion process of CQ in plasticized PC is determined by the polymer system and is better described by free volume theory. One further notes that there is no discernible unusual change in D_2 at or in the vicinity of T_g in the PC-w or plasticized PC-w samples, in contrast to the PC-n or PC-w′ results, to be described subsequently.

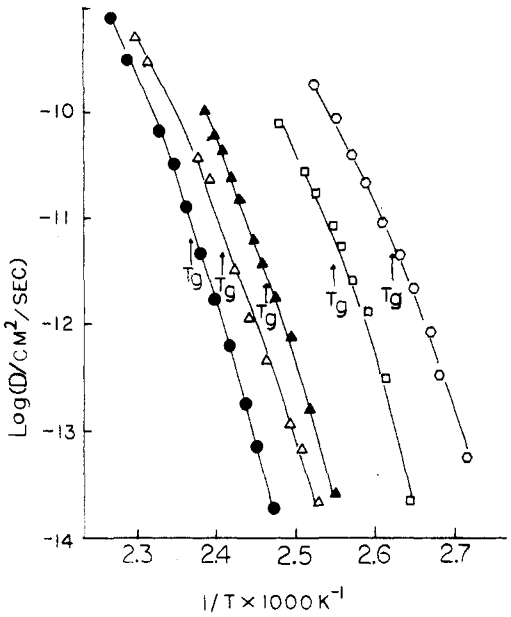

Figure 2. Temperature dependence of the diffusion coefficient D_2 in PC containing different concentrations (by weight percent) of 1,3-DCB: (●) DCB/PC-w = 0; (△) DCB/PC-w′ = 0.66; (▲) DCB/PC-w′ = 1.48; (□) DCV/PC-w′ = 3.65; (○) DCB/PC-w′ = 5.42.

In polycarbonate (PC), the plasticizer effect associated with the acceleration of the α relaxation and the "antiplasticizer" effect related to the β suppression are both present.[7,8,17,18] The effects on the dynamic mechanical and the dielectric relaxation spectra of PC owing to the addition of DCB and other molecular additives have been reported by Fischer et al.[6] They show in these studies that the additives modify the polymer motion and suppress the β peak; at the same time the additives induce a new relaxation peak, due possibly to cooperative motions involving both the polymer and the additives. The deuteron NMR study in the glassy range of PC solution suggests that the suppression of the β peak and the appearance of the new relaxation peak may be associated with the retardation of the phenyl ring flips on the chain. The phenyl ring flips are coupled to density fluctuations.

In recent tracer diffusion studies of dye molecules in polymer hosts, we show that at the vanishing dye concentration the dye tracer diffusion coefficient is closely related to local density volume fluctuations in the polymer host.[19] The density fluctuations of the polymer host provide free volume for the dye molecules to diffuse. In the PC/additive mixture below T_g, small-angle X-ray scattering (SAXS) studies show that the additives lower the amplitude of volume (in density) fluctuations. The decrease in density fluctuations is postulated to be the cause for the β suppression.[6] The fact that the tracer diffusion coefficient below T_g does not experience a decrease when a small amount of DCB is added is an indication that the β-suppression effect does not change the free volume fluctuation to the extent of affecting the CQP tracer diffusion coefficient. This then shows that the "local mode" related to small-amplitude rocking and translational motions of the PC chain proposed for interpreting the SAXS data does not influence the am-

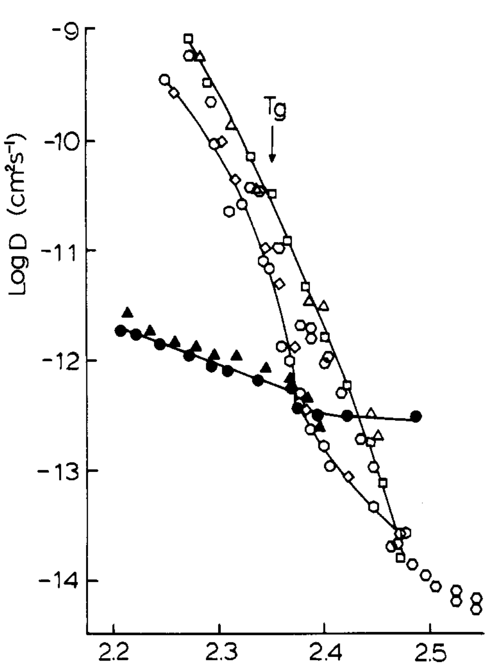

Figure 3. Temperature dependence of the diffusion coefficient of CQP in various PC samples: (○) PC-n with $M_w = 3.60 \times 10^4$, $M_w/M_n = 1.03$; (○) PC-n with $M_w = 1.12 \times 10^4$, $M_w/M_n = 1.12$; (◇) PC-w′; (△) PC-w′ with 0.8% DOP; (□) PC-w; (●) previous data by Wang and Xia; (▲) Pc-w′ (and PC-n) prepared in the N_2 atmosphere at 280 °C for 3 days; (○) data of Ehlich and Sillescu.

plitude of fluctuations sufficiently to affect the CQP diffusion process.

A model based upon the changes in the volumetric and the free volume properties of a glassy polymer upon addition of a low molecular weight diluent has also been proposed by Vrentas et al.[20] to account for the antiplasticization effect. This theory requires the concentration dependence of the free volume data, which can, in principle, be estimated from the thermal expansion coefficients of the polymer and the polymer mixture at the glass transition temperature. However, these thermodynamic data, as well as the free volume data of DCB, are not available, and we shall not attempt this type of calculation. Nevertheless, the fact that we do not detect the antiplasticization effect on the tracer diffusion coefficient below T_g in the PC/DCB system suggests, in the spirit of the Vrentas free volume model,[20] that the decrease in the free volume in the DCB-plasticized PC at the limiting zero DCB concentration is smaller than the free volume introduced by the additive itself.

Shown in Figure 3 is the temperature dependence of the diffusion coefficient of CQP in two types of polycarbonate. While both PC-n and PC-w have the same glass transition temperature, CQP diffuses faster in PC-w by about a factor of 7.

In PC-w, the diffusion coefficient decreases smoothly with decreasing temperature and there appears to be no distinguishable effect due to the onset of the glass transition of the host polymer. This is in contrast to the results in PC-n and washed PC-w (or PC-w′) samples, in which the diffusion coefficient experiences a rapid drop in the vicinity of T_g (see Figure 3). Tracer diffusion coefficient data in other amorphous polymers at the temperature in the vicinity of T_g also show a rapid drop as the temperature is decreased from above toward T_g.[16] The rapid decrease reflects the "freezing-in" of the chain motion associated with the α-relaxation process of the amorphous polymer. However, such a rapid decrease in the diffusion coefficient is suppressed if the dye concentration is large[16] or if the polymer is plasticized (see below). Thus, the difference observed in PC-w′ (or PC-n) and PC-w is likely to be due to the presence of a small amount of very low molecular weight portion of PC in PC-w. The very low molecular weight PC is removed by fractionation and is absent in the PC-n sample. The difference in the two samples may also be attributed to the inclusion of a trace amount of small molecular weight additives that plasticize Lexan 4 during the manufacturing process. The additive molecules are removed in PC-w′. As shown in Figure 3, there appears to be no discernible difference between the diffusion data in PC-n and those in PC-w′, confirming our earlier observation that for the polymer in which the molecular weight is sufficiently high that asymptotic value of the T_g is reached the tracer diffusion coefficient is independent of the polymer molecular weight and the molecular weight distribution.[5,21]

The diffusion data of TTI in PC reported by Ehlich and Sillescu[14] are also included in Figure 3 for comparison. Their data agree well with our PC-w results. Since the PC-w is the raw Lexan 4 sample, it contains low molecular weight PC and some trace amount of plasticizer introduced during manufacturing. The fact that the data of Ehlich and Sillescu show a smooth change in the diffusion coefficient on both sides of T_g, rather than a more rapid decrease as shown in our PC-n or PC-w′ results, is an indication that the PC sample used by them contains plasticizer. We show in Figure 3 the data for the sample obtained by adding 0.8% (by weight) DOP to our PC-w′ sample; these results are similar to those obtained for the PC-w, and they also do not display the rapid decrease in D as the temperature is decreased toward T_g. (Adding 0.8% DOP to PC does not result in changing T_g.) In passing, we observe that the PC sample used by Ehlich and Sillescu was supplied by Bayer AG (trade name Macrolon). Its M_w is about 35 000. It has a broad molecular weight distribution and contains a trace amount of plasticizer, like Lexan 4. The polydispersity and the presence of a trace amount of plasticizer combine to suppress the rapid drop in the diffusion coefficient in the vicinity of T_g. Nevertheless, TTI is a somewhat elongated molecule, compared to CQ, whose effective shape is closer to a sphere. From the size and shape consideration, we do not expect to observe the same diffusion coefficient for these two different dye molecules. Since one generally expects the D value to decrease with an increasing probe size, the fact that the tracer diffusion coefficients for two o-nitrostilbene (ONS) dyes of different sizes have a similar magnitude and temperature dependence indicates a more complex picture for diffusion. The internal flexibility of one of the ONS probe molecules may play a role in affecting the tracer diffusion coefficient, and the same diffusion coefficient obtained for molecules with different sizes may be accidental. Thus, for probes with vastly varying sizes, shapes, or internal flexibilities, there seems at present to be no single method that can be used to correlate these factors with the tracer diffusion coefficient. The interaction of the probe with the polymer may also play an important role. Thus, the agreement between the Ehlich–Sillescu TTI diffusion data and the present data only suggests that both CQP and TTI have roughly the same effective local friction coefficient, and no more can be said about the molecular size difference.

Tracer diffusion data of CQP in PC previously published by Wang and Xia[13] from this laboratory are also included in Figure 3 for comparison. These data significantly differ from the present ones obtained for PC-w, PC-w′, and PC-n.

The data of ref 13 also have much less temperature dependence on both sides of T_g. In the present work we also prepared new samples of PC-n and PC-w′ using the same procedure that was used in ref 13 and repeated the experiment. The data obtained for the new samples are shown in Figure 3; interestingly, they are in agreement with the earlier results reported in ref 13. In addition, we have found that these results are reproducible as long as the samples are prepared and treated in the same way. Therefore, the difference in the data of ref 13 and the data presently obtained for PC-n and PC-w′ is entirely due to the sample preparation. The sample used in ref 13 and the present samples prepared approximately 2 years afterward were prepared by using the same technique, involving continuous heating of the PC/CQ mixture for about 3 days at 280 °C in an N_2 atmosphere. Undoubtedly, at this temperature CQ molecules have undergone chemical changes, as the sample appearance becomes more brownish than when it is freshly melted. To show that the degradation is not associated with the polymer, we have dissolved the final sample in dichloromethane and precipitated the polymer with methanol. The result of analysis shows that no degradation has occurred in PC. Thus, the chemical change occurs in CQ at high temperature. While we are not able to identify the reaction product, the smaller diffusion coefficient obtained in PC-n or PC-w′, prepared by the hydraulic press method, indicates that the diffusing species detected in the Wang and Xia sample involves a much greater size than CQ. The vastly different results obtained in the PC sample clearly indicate the importance of the sample preparation procedure. Thus, when the diffusion data are reported, the method of sample preparation must be clearly described so that the state of the sample can be defined to facilitate comparison.

Free volume theory is very useful to provide a description of the temperature dependence. In free volume theory the tracer diffusion coefficient D is assumed to vary with the fractional free volume, f, according to

$$D = AT\exp(-B_d/f) \tag{4}$$

where A and B_d are constants, independent of temperature. Because only a trace amount of CQ molecules is present, f is assumed to be determined only by the polymer host and the added plasticizer. The fractional free volume f changes with temperature according to

$$f = f_0 + \alpha(T - T_0) \tag{5}$$

where f_0 is the fractional free volume at the reference temperature T_0 and α is the thermal expansion coefficient.

The tracer diffusion coefficient may depend on the molecular weight of the polymer host. Our recent work shows that the tracer diffusion coefficient depends on the polymer molecular weight through the T_g value of the polymer, provided that the host polymer is of the same type.[19] As mentioned above, within the accuracy of our DSC instrument (Perkin-Elmer Delta series), the PC-w, PC-w′, PC-n, and PC-w′ plasticized with 0.8% DOP are found to have T_g values equal to 150 °C. Thus, without other complicating factors, we would expect the same CQP tracer diffusion coefficient for them. However, as one sees in Figure 3, at the temperature above T_g − 20, the tracer diffusion coefficient in PC-n (or PC-w′) is smaller by about a factor of 7 than that in PC-w or the DOP-plasticized PC. The difference is due to different aging behaviors of PC-n and PC-w. In the present HGR measurement, all data points are taken 4 h after the temperature reading of the thermocouple (attached to the sample holder) is stabilized. In other words, all samples are annealed isothermally for 4 h. For the PC-w sample, as well as the plasticized PC-w′ samples (to be discussed below), the isothermal annealing effect is found negligible for $T > T_g - 20$ °C. This is due to the enhanced chain mobility introduced by the plasticizer. Taking the diffusion data after 4 h of isothermal annealing is believed to be sufficient to achieve the thermodynamic equilibrium temperature in the plasticized or PC-w sample. On the other hand, in the PC-n or PC-w′ sample, no low molecular weight species are present to plasticize the polymer chain; the mobility of the polymer chain is gradually frozen as T is decreased to the vicinity of T_g; diffusion is significantly affected by the glass transition process in the unplasticized sample. The time duration needed for establishing thermodynamic equilibrium in the vicinity of or below T_g becomes long.

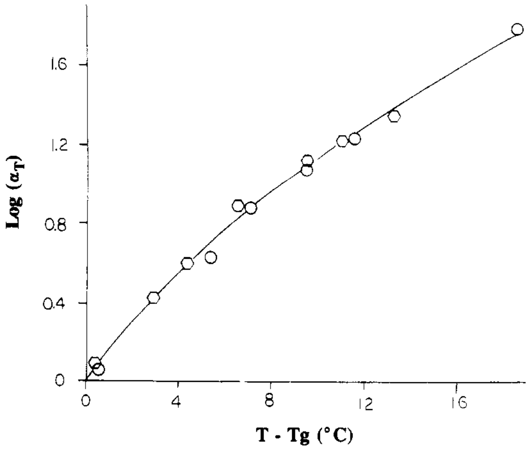

Figure 4. Shift factor defined in eq 4 for the PC-w′ sample and the PC-w′ sample plasticized 0.66% of 1,3-DCB plotted as a function of $T - T_g$. Circles (PC-w) and diamonds (plasticized PC-w) are experimental points, and the solid curve is the best fit to the data using the WLF equation (eq 4).

The effect of isothermal annealing in the vicinity of or below T_g is expected to play a significant role in affecting the tracer diffusion coefficient in PC-n. In the absence of other factors, the tracer diffusion coefficient should decrease with the annealing time.[22] This result is consistent with the physical aging effect on the tracer diffusion coefficient previously reported.[14,22] To study the effect of physical aging is very time-consuming, even with the HGR technique; however, we hope to carry out a more detailed investigation of the physical aging effect on the tracer diffusion coefficient in PC-n in the future using the 180° crossing angle. This should shorten the measurement time.

The shift factor a_T for diffusion is defined by the logarithm of the ratio of $D(T)/T$ to $D(T_g)/T_g$. On the basis of free volume theory, $\log a_T$ is proportional to $(1/f) - (1/f_g)$, where f and f_g are the fractional free volumes of the polymer at T and T_g, respectively. Using eqs 4 and 5, we obtain the Williams–Landel–Ferry (WLF) equation for diffusion, which for $T > T_g$ is given by

$$\log a_T = \frac{C_1^D(T - T_g)}{C_2^D + T - T_g} \tag{6}$$

where $C_2^D = f_g/\alpha$ and $C_1^D = 2.30B_d/f_g$. The shift factor obtained for the PC-w sample and PC-w plasticized with 0.66% 1,3-DCB is plotted in Figure 4 as a function of $T - T_g$. The WLF coefficient obtained for the fit is $C_1^D = 11.2$ and $C_2^D = 54.2$. Due to some freedom to vary C_2^D value and still obtain a good it, the C_2^D value is considered in

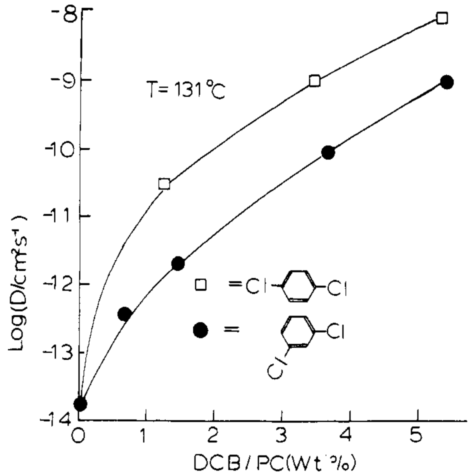

Figure 5. Change of the diffusion coefficients of CQP in PC-w at 131 °C as a function of additive concentration for two DCB.

agreement with the free volume parameter obtained in mechanical relaxation available in the literature, in which $C_2 = 51.6$K[23] is obtained. The good agreement between C_2 and C_2^D indicates that tracer diffusion is closely associated with the α-relaxation process of the polymer host.

It should be pointed out that C_1^D is in general smaller than the C_1 value obtained in the viscoelastic measurement. Again, using free volume theory, the zero shear viscosity η is given by the Doolittle equation[24]

$$\eta = A' \exp(-B/f) \qquad (7)$$

where A' and B are constants. The substitution of eq 5 into eq 7 gives the shift factor, $a_T(\eta) \equiv \eta(T)/\eta(T_g)$, as

$$\log a_T(\eta) = \frac{C_1(T - T_g)}{C_2 + T - T_g} \qquad (8)$$

where $C_2 = C_2^D$ and $C_1 = 2.30\, B/f_g = C_1^D/\zeta$. Here ζ ($=B_d/B$) is known as the coupling parameter.[14] The coupling parameter is in general less than 1. One expects ζ to increase with the probe size and approach the limit value of 1 at some particular size when the diffusion process is completely dictated by the viscoelastic property of the polymer host. Thus, when the tracer is of the same type of molecule as the polymer host, we expect to obtain the limiting value of $\zeta = 1$ and the Rouse model of polymer diffusion to become applicable. For the two samples, given in Figure 4, the ζ value is equal to 0.65. In accordance with the modified free volume theory,[25-27] the coupling parameter ζ is interpreted as the ratio of the critical molar volume of the probe and the polymer host jumping unit. The $\zeta = 0.65$ indicates that the probe size is about 65% of the segmental jumping unit in the PC host. While this is physically reasonable, in view of the difficulty in correlating D with the probe size, the result can only be taken qualitatively.

One notes in Table I that by adding 0.66% (by weight) 1,3-DCB to PC-w′ the T_g is depressed by nearly 7 °C and at the same time the tracer diffusion coefficient becomes greater than that for polydisperse PC-w. In Figure 5, we show the variation of the diffusion coefficients of CQP in PC-w′ at 131 °C as dichlorobenzene molecules are added to the PC/CQ sample. The presence of DCB significantly increases the tracer diffusion coefficient of CQP. Adding 5 wt % 1,4-DCB to the PC sample results in increasing the diffusion coefficient by nearly 5 orders of magnitude! Different structures of DCB also affect the diffusion coefficient differently. 1,3-DCB has a permanent dipole moment, but it causes a smaller increase in the diffusion coefficient than 1,4-DCB. The difference is due to different interactions between DCB and the polymer chain backbone. The interaction of 1,3-DCB with PC-w′ is not as effective in depressing the T_g of the plasticized polymer as that of 1,4-DCB with PC-w′.

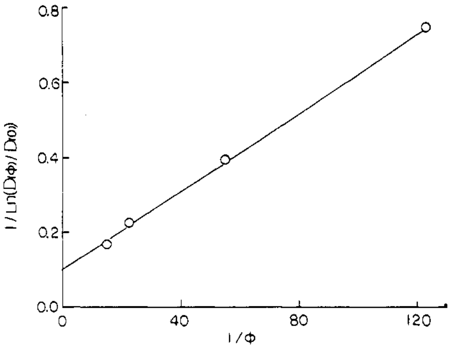

Figure 6. Plot of 1/ln $[D(C)/D_0]$ vs $1/C$.

Free volume theory can be used to provide a description of the concentration dependence of the diffusion coefficient.[24] We assume that by addition of a plasticizer (DCB in the present case) to the polymer host f is increased and the increase in f is proportional to the weight fraction of the plasticizer. Thus, we write[1,11]

$$f(T,C) = f(T,0) + \beta(T)C \qquad (9)$$

where $f(T,0)$ represents the fractional free volume in the pure polymer and $\beta(T)$ is a parameter independent of concentration. In eq 9, we used weight fraction instead of volume fraction as a convenience because at low concentration the two quantities are proportional to each other.

Substituting eq 9 into eq 4 and after some algebra, one finds

$$[\ln (D(C)/D_0)]^{-1} = \frac{f(T,0)}{B_d} + \frac{f(T,0)^2}{B_d\beta(T)}\frac{1}{C} \qquad (10)$$

where $D(C)$ is the diffusion coefficient when the dye concentration is equal to C and D_0 is the diffusion coefficient in the limit of dry-state polymer (zero concentration). In Figure 6 we plot $1/[\ln (D(C)/D_0]$ vs $1/C$; the linear plot confirms eq 10 and hence supports free volume theory.

As shown in Figure 2, the tracer diffusion coefficients in PC-w and in DCB-plasticized PC-w have no discerible change in the vicinity of the T_g. We have found that by normalizing $D(T)/T$ with respect to $D(T_g)/T_g$ for each plasticized sample (including both 1,3-DCB and 1,4-DCB), all data points (including data obtained at 25 °C below T_g) collapse to a single master curve, described by eq 6 (Figure 7). This result is surprising because the WLF equation (eq 6) is generally understood to be not applicable below T_g. However, since the free volume theory is phenomenological and does not give a detailed molecular picture for the effect of polymer segmental motion on the tracer diffusion, eq 6 can, at best, be considered a means for correlating the data. To improve the understanding of the difference between the PC-n and the plasticized PC-w′ results, where in one case the tracer discerns the effect of glass transition and in the others it goes completely unaffected, with only a smooth change across T_g, the

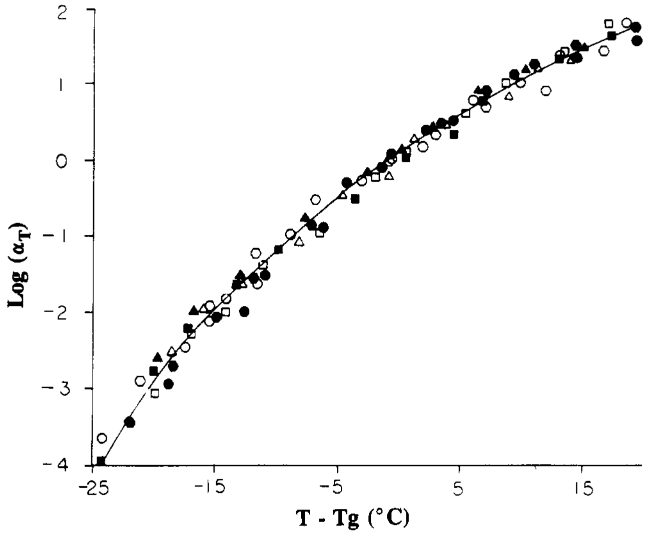

Figure 7. Master curve obtained for all diffusion data for obtained PC-w and plasticized C-w samples. The curve is given by eq 4, and the points are experimental values: (●) 1,3-DCB/P-w = 0; (■) 2,3-DCB/PC-w = 0.66; (●) 1,3-DCB/PC-w = 1.48; (▲) 1,3-DCB/PC-w = 3.63; (○) 1,3-DCB/PC-w = 5.42; (□) 1,4-DCB/PC-w = 1.08; (○) 1,4-DCB/PC-w = 3.43; (△) 1,4-DCB/C-w = 5.31.

development of a molecular theory including the interaction of additives and polymer chains is needed.

In conclusion, we have carried out an extensive measurement of the tracer diffusion coefficient of CQP in PC host. We have clarified the discrepancy that exists in the published tracer diffusion data in PC. We have examined the effect of plasticizer on the tracer (dye) diffusion coefficient. The experimental result shows that when plasticizer molecules such as DOP or DCB are added to PC, the local friction of the plasticized polymer is sharply reduced, resulting in a larger dye diffusion coefficient. The rapid decreased in the tracer diffusion coefficient in PC-n in the vicinity of T_g does not appear in PC-w or plasticizer PC. The β-suppression effect that is observed in the mechanical relaxation spectrum in the plasticized PC is also not manifested in the CQP tracer diffusion coefficient. The temperature and concentration dependence results can be described by empirical equations, provided by free volume theory.

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Registry No. PC (SRU), 24936-68-3; PC (copolymer), 25037-45-0; CQ, 465-29-2; DOP, 117-81-7; 1,3-DCB, 541-73-1; 1,4-DCB, 106-46-7.