

# Investigation of the Mass Diffusion of Camphorquinone in Amorphous Poly(methyl methacrylate) and Poly(*tert*-butyl methacrylate) Hosts by the Induced Holographic Grating Relaxation Technique

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**ABSTRACT:** Laser-induced holographic grating relaxation studies of camphorquinone (CQ) diffusing in poly(methyl methacrylate) (PMMA) and poly(*tert*-butyl methacrylate) (PtBMA) hosts are carried out. A decay-growth-decay curve is observed and can be fit to the expression given by  $I(t) = [A \exp(-t/\tau_1) - B \times \exp(-t/\tau_2)]^2$ . Fitting the diffracted intensity curve to this equation allows the diffusion coefficients of camphorquinone and its photoproduct to be determined. The temperature dependence of the diffusion coefficient above  $T_g$  for the two systems is found to follow the WLF equation. The influence of the polymer free volume on the mutual diffusion coefficients is discussed. The free volume interpretation for the diffusion process (in this very slow diffusion range varying from  $10^{-9}$  to  $10^{-14}$  cm<sup>2</sup>/s) in the solute-polymer system developed recently by Vrentas and Duda is found to be consistent with our data.

## Introduction

Studies of photochemical and photophysical processes of chromophores molecularly dispersed in matrices of transparent polymers are of fundamental and practical interest.<sup>1-3</sup>

One of the applications of these photoprocesses involving chromophore molecules is the measurement of very slow diffusion coefficients of dye molecules in transparent polymers via the technique of holography. Applying this technique, we have succeeded in obtaining the temperature dependence of the diffusion coefficients of camphorquinone (CQ) in poly(methyl methacrylate) (PMMA) [ $T_g < T < T_g + 50$  °C] and poly(*tert*-butyl methacrylate) (PtBMA) [ $T_g - 10$  °C  $< T < T_g + 40$  °C]. We have chosen the two polymer systems having the same glass transition temperature  $T_g$  (110 °C) so that the effects of  $T_g$  and free volume fluctuations due to side-group motion can be investigated. Our technique involves the employment of a single-frequency radiation from an Ar<sup>+</sup> laser that induces a holographic phase grating by photobleaching the dye molecules. The distance between dark and bright grating fringes ( $d/2$ ) is only 0.17  $\mu$ m (for the 90° bleaching angle). Diffusion of the dye molecules over a length shorter than  $d/2$  can be detected immediately, since it will decrease the amplitude of the grating modulation and consequently the diffracted intensity. In a typical permeation experiment, diffusants must at least diffuse over a distance of 0.1 mm = 100  $\mu$ m in order to be detected. Since  $t \propto d^2$ ,  $t$  being the time of diffusion and the distance  $d$  involved in the holographic diffusion technique being nearly equal to the wavelength of light ( $\approx 0.2$ – $0.5$   $\mu$ m), the time scale for observing the diffusion coefficient is reduced by at least 8 orders of magnitude, thereby making the detection of a very slow diffusion coefficient possible. Applying this technique, we have been able to obtain the mutual diffusion coefficients as low as  $10^{-14}$  cm<sup>2</sup>/s in a period of about 2 hours, compared with  $\sim 10^{-10}$  cm<sup>2</sup>/s, the smallest diffusion coefficient that conventional methods can obtain with a much longer period of time ( $> 1$  week).

This advantage enables us to test the adequacy of the free volume interpretation for the diffusion process in the solute-polymer system (i.e., small amount of small molecules dissolved in the polymer matrix) directly in the temperature range near  $T_g$ , in which the diffusion coefficients

are usually much smaller than  $10^{-10}$  cm<sup>2</sup>/s.

Our objective in this study is to check the validity of the free volume interpretation of the diffusion process in the solute-polymer systems<sup>5-10</sup> and to examine the influence of the polymer free volume on the mutual diffusion coefficients in these systems.

We have established that the diffusion coefficients show the WLF behavior [ $T > T_g$ ] both in PMMA and PtBMA and the size of free volume (determined by the size, shape, and stiffness of the side groups attached to a polymer main chain) has strong influence on the mutual diffusion coefficients.

## Theory

We consider here small molecules (solute) diffusing in the polymer host. A number of theories dealing with diffusion of the solute (or diluent)-polymer system exists in the literature;<sup>5-8,10-12,15-20,25</sup> most of them are based on the free volume theory. The first free volume theory of transport was initiated by Cohen and Turnbull, who considered molecular transport in a liquid of hard spheres and related the self-diffusion coefficient to the free volume in the liquid.<sup>9</sup> The free volume theory was later extended to the solute-polymer system.

In the free volume theory, a diffusant is assumed to vibrate about an equilibrium position until the combination of two events occurs: (1) the molecule attains sufficient activation energy to overcome the attractive potential holding it to its neighbors, and (2) a large enough void (free volume) is available in the neighborhood of the diffusant, into which it can jump. The possibility of a transition of the diffusant from one site to another is given by the expression:  $P_t = P_e P_v$ , where  $P_e$  is the probability for the diffusant to attain sufficient activation energy to overcome the attractive potential and  $P_v$  is the probability that a large enough void is created by local density fluctuations. [In the case of the solute-polymer system, the void is created by cooperative motions of several polymer segments. It has been shown that even for small gas diffusant molecules like H<sub>2</sub> and O<sub>2</sub>, cooperative motions of tens of polymer segments are needed to create a critical void.]<sup>11</sup> If  $P_e$  is given by the Boltzmann distribution and  $P_v$  is given by  $\exp(-\nu V_0/V_f)$ , derived from Cohen and Turnbull by maximizing the number of ways of distributing a finite

number of diffusants into a finite number of free volumes ( $V_f$ ),<sup>9</sup> the viscosity  $\eta$  can be written as

$$\eta = A/(P_e P_v) = A \exp(E/RT + \nu V_0/V_f) \quad (1)$$

where to obtain eq 1, it is assumed that the viscosity is inversely proportional to the diffusion jump probability.<sup>5,10</sup> In eq 1  $A$  is a constant,  $E$  is related to the potential barrier between adjacent sites,  $V_f$  is the average free volume per molecule,  $V_0$  is the molecular volume of the diffusant, and  $\nu$  is a numerical factor needed to correct for the overlap of free volume and lies between 0.5 and 1.

The self-diffusion coefficient of the diffusant is inversely proportional to the viscosity. Thus, we have

$$D = D_0 \exp(-E/RT - \nu V_0/V_f) \quad (2)$$

This is the result of the free volume theory for self-diffusion of simple liquids. A different version of free volume theory for diffusion in the solute-polymer system has been proposed by Paul.<sup>1</sup> In his theory, the translational self-diffusion coefficient of the solute in the polymer matrices is related to the properties of both the solute and the polymer. In Paul's version, the solute self-diffusion coefficient is expressed as<sup>7</sup>

$$D_1 = D_2 P + J D_{01} T^{1/2} \exp(-\nu \hat{V}_1^*/V_f) \quad (3)$$

with

$$\hat{V}_f = \hat{V} - \omega_1 \hat{V}_1^0(0) - \omega_2 \hat{V}_2^0(0) \quad (4)$$

where  $\hat{V}_f$  is the free volume per gram of the mixture,  $D_{01}$  is a constant preexponential factor,  $J$  is a jump-back factor,  $\hat{V}$  is the specific volume of the polymer solution, and  $\hat{V}_1^0(0)$  is the specific volume of the solute when it exists in the pure state at 0 K.  $D_2$  is the self-diffusion coefficient of the polymer and  $P$  is a probability that depends on the polymer volume fraction.  $\omega_1$  is the mass fraction of the solute.  $\omega_2$  is the mass fraction of the polymer. However, Paul's model predicts that at the zero solute concentration limit (as is the case in this study)  $D_1 = D_2$ . This is clearly inconsistent with the experimental result, as can be seen by comparing our diffusion coefficient data of CQ in polystyrene with the self-diffusion coefficients of polystyrene reported by Antonietti et al.<sup>13</sup> The latter show that  $D_2 \sim 10^{-12}$  cm<sup>2</sup>/s at  $T = 177$  °C, with the activation energy  $E = 167$  kJ/mol. The extrapolation of the data given in ref 13 will give an estimated value of  $D_2$  to be  $10^{-15}$  cm<sup>2</sup>/s at  $T = 132$  °C, whereas our CQ diffusion coefficient at this temperature is about  $10^{-10}$  cm<sup>2</sup>/s.

Vrentas and Duda have proposed another version of free volume theory for diffusion in the solute-polymer system.<sup>5,6,14-19</sup> Their result for the solute self-diffusion coefficient in the solute-polymer system is

$$D_1 = D_{01} \exp(-E/RT) \exp[-\nu(\omega_1 \hat{V}_1^* + \omega_2 \hat{V}_2^* \xi)/\hat{V}_{FH}] \quad (5)$$

where

$$\hat{V}_{FH} = \nu[K_{11}\omega_1(K_{21} + T - T_{g1}) + K_{12}\omega_2(K_{22} + T - T_{g2})] \quad (6)$$

and where  $E$  is the activation energy, the energy required to overcome the attracting potential holding the solute molecule to its neighbors.  $D_{01}$  is a preexponential factor.  $\hat{V}_1^*$  is the specific critical free volume of the solute required for making a jump.  $\hat{V}_2^*$  is the minimum or critical local free volume per gram of polymer segments required for the displacement of a jumping unit.  $\omega_1$  and  $\omega_2$  have the same definition as in eq 3.  $T_{g1}$  is the glass transition temperature of the solute in the pure state ( $T_{g1}$  is zero for solutes with no glass transition).  $T_{g2}$  is the glass transition temperature of the pure polymer,  $\hat{V}_{FH}$  is the average hole

free volume per gram of mixture, and  $\xi$  is the ratio of the critical molar volume of the solute jumping unit to the critical molar volume of polymer jumping unit.  $K_{11}$  and  $K_{21}$  are free volume parameters of the solute, and  $K_{12}$  and  $K_{22}$  are free volume parameters of the polymer.

Equation 5 is quite similar to eq 2, except for the different definition of the free volume  $\hat{V}_{FH}$ . In the solute-polymer case,  $\hat{V}_{FH}$  is the average hole free volume in the mixture consisting of solute molecules and polymer segments, instead of that in the pure liquid as in eq 2.

At the zero solute concentration limit ( $\omega_1 \rightarrow 0$ ), eq 5 becomes

$$D_1 = D_{01} \exp(-E/RT) \exp[-\nu \xi \hat{V}_2^*/\hat{V}_{FH}] = D_{01} \exp(-E/RT) \exp\left[\frac{-\xi \hat{V}_2^* \nu}{K_{12}(K_{22} + T - T_0)}\right] \quad (7)$$

where  $T_0$  is an arbitrary reference temperature.

One notes eq 7 is of the form of the WLF equation. It is thus useful to relate the above free volume parameters to the WLF constants, which have been extensively tabulated for many important polymer systems.<sup>12</sup> By identifying  $K_{22} = C_2^0$ ,  $\nu \hat{V}_2^*/K_{12} = (\ln 10)C_1^0 C_2^0$ , and  $T_0 = T_g$ , we can rewrite eq 7 as

$$D_1(T) = D_{01} \exp(-E/RT) \exp\left[\frac{-\xi(\ln 10)C_1^0 C_2^0}{C_2^0 + T - T_g}\right] \quad (8)$$

At vanishing solute concentration and at temperatures not much higher than  $T_g$  ( $T_g < T < T_g + 100$  °C), the vibrational frequency of the diffusant about its quasi-equilibrium site is much higher than the rate of creating a sufficiently large free volume in the neighborhood of the diffusant.<sup>11,12</sup> Under these conditions, the diffusant will have a sufficient number of vibrations in the proper direction during the existence time of the free volume for the diffusant to jump into this free volume. This suggests that diffusion of the solute molecules in the solute-polymer system at vanishing solute concentration and at temperature  $T$  such that  $T_g < T < T_g + 100$  °C is dominated mainly by the free volume fluctuation of the polymer rather than by the activation energy effect. Thus, as suggested in ref 15, from  $T_g$  to  $T_g + 100$  °C, it is possible to absorb the  $E$  term into the preexponential factor and rewrite eq 8 as

$$D_1 = D_{01} \exp\left(\frac{-\xi(\ln 10)C_1^0 C_2^0}{C_2^0 + T - T_g}\right) \quad T > T_g \quad (9)$$

where  $D_{01}$  is effectively a constant.

If the glass transition temperature of the polymer is chosen as the reference temperature, then eq 9 can be written as

$$\ln \left\{ \frac{D_1(T)}{D_1(T_g)} \right\} = \frac{\xi(\ln 10)C_1^0(T - T_g)}{C_2^0 + T - T_g} \quad (10)$$

Equations 9 and 10 are not only simpler than eq 7 they also avoid the uncertainty in obtaining free volume parameters.<sup>6</sup> As discussed in ref 5, suppressing the energy effect will of course introduce some degree of error in obtaining the free volume parameters, but this error is expected to be minimal when  $\omega_1 \rightarrow 0$  and when  $T$  is not much higher than  $T_g$ . One notes from Figure 6 of ref 6 that eq 9 describes the experimental data quite well in the  $\omega_1 \rightarrow 0$  region, whereas considerable error occurs when  $\omega_1 \rightarrow 20\%$ . We shall discuss our experimental results in the framework of eq 9 and 10.

It should be noticed that eq 9 describes the translational self-diffusion coefficient of the solute in the polymer host, whereas the holographic grating relaxation technique employed in the diffusion measurement gives in general the mutual translational diffusion coefficient of the solute with respect to the polymer host. However, in the limit of zero solute concentration, the self-diffusion coefficient of the solute and the mutual diffusion coefficient of the solute with respect to the polymer host became identical.<sup>20</sup>

For  $T$  below  $T_g$ , Vrentas and Duda suggest that<sup>14-19</sup>

$$D_1 = D_{01} \exp \left[ \frac{-\xi(\ln 10) C_1^0 C_2^0 / \lambda}{C_2^0 / \lambda + T - T_0} \right] \quad T < T_g \quad (11)$$

where the parameter  $\lambda$  describes the change in the volume expansion coefficient attributed to the onset of the glass transition.  $\lambda$  is less than 1.

This result is obtained by considering that fractional free volume is related to temperature by<sup>12</sup>

$$f \equiv V_f/V = f_0 + \alpha(T - T_0) \quad T > T_g \quad (12)$$

where  $T_0$  is an arbitrary reference temperature and  $\alpha$  is the expansion coefficient. As the glass transition region is traversed,  $\alpha$  will show a step change. Thus, the expansion coefficient below  $T_g$  can be expressed as

$$\alpha|_{T < T_g} = \lambda \alpha|_{T > T_g} \quad (13)$$

The WLF constant  $C_2^0$  is defined as<sup>12</sup>

$$C_2^0 = f/\alpha \quad (14)$$

Thus

$$C_2^0|_{T < T_g} = f/\alpha|_{T < T_g} = C_2^0|_{T > T_g}/\lambda \quad (15)$$

Equation 11 is obtained by replacing  $C_2^0$  in eq 9 with  $C_2^0/\lambda$ .

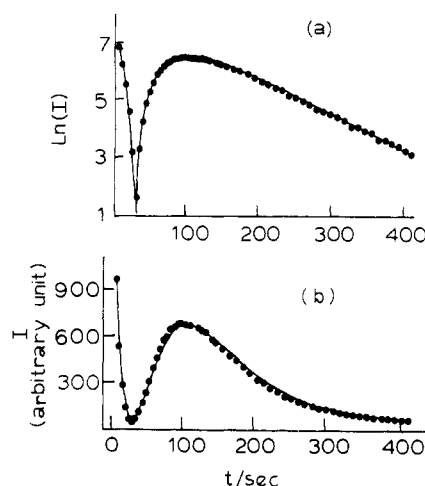
Equations 9 and 11 thus predict a discontinuity in the activation energy as  $T_g$  is traversed.

## Experimental Section

PMMA [MW = 460 000,  $M_w/M_n = 1.76$ ] and PtBMA [MW = 550 000,  $M_w/M_n = 1.24$ ] were both synthesized by Polymer Standard Inc., associated with the University of Mainz, West Germany. The CQ + PMMA and CQ + PtBMA mixtures are prepared by first dissolving CQ in petroleum ether, a nonsolvent for both polymers, and then adding PMMA [or PtBMA] powder in the solution. The mixture is then placed in a vacuum oven at a temperature higher than the boiling point of petroleum ether for several hours to remove the nonsolvent. The dried mixture is then pressed into a pellet with a modified infrared sample presser. The pellet is then placed in a vacuum oven at 175 °C for 3 days to anneal and to let the dye molecules diffuse in the sample so as to reach a homogeneous concentration distribution. The CQ concentration used varies only between 0.5% and 1% (by weight), to warrant the self-diffusion measurement.

CQ is chosen as dye because of its good stability at high temperature and its relatively small size to enable measurements of diffusion coefficients at lower temperatures.

The holographic grating is induced by crossing two equal intensity bleaching (writing) beams from an Ar<sup>+</sup> laser radiating at  $\lambda = 5145$  Å. The angle between bleaching beams is variable from  $\theta = 8.8^\circ$  to  $\theta = 90^\circ$ , so the grid spacing of the induced grating,  $d = \lambda/[2 \sin(\theta/2)]$ , can be varied to ensure that the relaxation time constant  $t = d^2/4\pi^2 D$  ( $D$  is the mutual diffusion coefficient)<sup>22</sup> falls into a convenient measurable range (5 s to 3 h).  $\theta$  is the crossing angle between two reading beams and is equivalent to the angle between the reading beam and the straight line connecting the holograph spot and the detector. The experimental setup is similar to that used in ref 4 and 24. The bleaching time used varies from  $1/2$  to  $1/15$  s, depending on temperature and the bleaching angle, to ensure that the maximum diffracted intensity is adequate for the detector. After the grating is induced, one

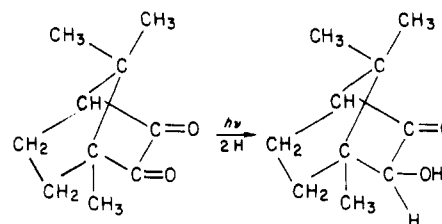


**Figure 1.** (a) Logarithm of the diffracted light intensity ( $I$ ) plotted as a function of time ( $t$ ) for the CQ-PMMA system at  $T = 418.7$  K, obtained with the bleaching angle  $\theta = 8.35^\circ$ . Note the linear feature at long times. (b) Diffracted light intensity ( $I$ ) vs. time ( $t$ ) plot. In both (a) and (b) the empty circles represent the experimental data points and solid lines the best fits of eq 17 to the experimental points. The slope of the linear portion in the  $\ln(I)$  vs.  $t$  plot gives  $d \ln(I)/dt|_{\text{linear part}} = 2/\tau_2 = 0.01254 \text{ s}^{-1}$ , or  $\tau_2 = 159.5 \text{ s}$ . This gives  $D = 1.78 \times 10^{-11} \text{ cm}^2/\text{s}$ .

of the bleaching beams is shuttered and the other attenuated by a factor of  $10^{-3}$  to  $10^{-4}$  immediately after the bleaching. The attenuated beam serves as a reading beam to monitor the decay of the diffracted intensity. Attenuation of the reading beam is necessary in order to avoid further photobleaching of the sample.

The signal from the photomultiplier and amplifier system is stored in a digital recorder. A data file (two-dimensional array) of diffracted intensity vs. time beginning from the end of bleaching is obtained.

The photochemistry of CQ is known to take place according to<sup>23</sup>



Abstraction of two hydrogen atoms from the polymer matrix will leave two free radicals on the polymer chains and hence may cause cross-linking and chain cleavage. Our GPC results in another system (polystyrene + CQ) before and after photobleaching show that chain cleavage indeed occurs.<sup>24</sup> However, the DSC results of the present CQ-PMMA and CQ-PtBMA systems before and after photobleaching show no change in  $T_g$ . This is probably due to the high molecular weight [MW  $\sim 500$  000] polymer samples used. A few chain cleavages in such a sample are not expected to cause any detectable change in  $T_g$ , and, consequently, the diffusion coefficients obtained in such samples should be identical with that in corresponding undisturbed systems.

## Results and Discussion

A typical  $\ln(I)$  vs.  $t$  (time) plot is shown in Figure 1a. The diffraction intensity curve  $I(t)$  consists of a rapid decay portion at short times followed by a growth portion and then a final slow decay at long times. When the curve is presented in the  $\ln I(t)$  vs.  $t$  (time) plot (Figure 1a), the decay portion at long times appear to be linear. This unusual line shape has been interpreted as due to the interference of two diffusion processes associated with two sets of gratings formed by CQ and its photoproduct, respectively.<sup>27</sup> It is well-known that the light intensity distribution in the crossing area of the beam interference

at the sample is given by  $I = I_0[\cos(\pi x/d)]^2$ , where  $x$  is the distance perpendicular to the fringes and  $d$  is the grid spacing of the induced phase grating. The distribution profiles of the photoproduct of CQ and the unreacted CQ molecules are thus proportional to  $[\cos(\pi x/d)]^2$  and  $[1 - \cos^2(\pi x/d)]$ , respectively. The change in the index of refraction  $\delta n$  then has the form

$$\delta n(x,t) = A \exp(-t/\tau_1)[1 - \cos^2(\pi x/d)] + B \exp(-t/\tau_2) \cos^2(\pi x/d) = [-A \exp(-t/\tau_1) + B \exp(-t/\tau_2)] \cos^2(\pi x/d) + A e^{-t/\tau_1} \quad (16)$$

where  $\tau_1$  and  $\tau_2$  are the relaxation time constants of CQ and its photoproduct, respectively, and  $t$  is the time measured from the moment when the writing beams are shut off. The last term represents an unmodulated index of refraction change and does not contribute to the diffracted light intensity.  $A e^{-t/\tau_1}$  and  $B e^{-t/\tau_2}$  represent the decay modulations of the induced phase grating. This decay is due to diffusion of CQ and its photoproduct; namely, unreacted CQ diffuses into the bright fringe area and its photoproduct diffuses into the dark fringe area until they are homogeneously distributed within the sample. The size of CQ is different from that of its photoproducts; hence, the diffusion coefficients and the corresponding relaxation time constants are also different.

The diffracted light intensity is proportional to the square of the index of refraction modulation; thus

$$I \propto (\delta n)^2 = [A \exp(-t/\tau_1) - B \exp(-t/\tau_2)]^2 \quad (17)$$

We may include in eq 17 a small incoherent background, but it is small and the main feature can be accounted for without it.

Shown in Figure 1 are fits of the above equation to the experimental points obtained at  $T = 418.7$  K. The best fit values are  $A = 107.0$ ,  $B = 66.64$ ,  $\tau_1 = 43.3$  s, and  $\tau_2 = 162.0$  s. One notes that the relaxation time  $\tau_2$  obtained from the fit is nearly the same as that determined from the slope measurement.

The corresponding diffusion coefficients of CQ and its photoproducts are respectively given by  $D_{CQ} = d^2/4\pi^2\tau_1 = 6.66 \times 10^{-11}$  cm<sup>2</sup>/s and  $D_{PP} = d^2/4\pi^2\tau_2 = 1.71 \times 10^{-11}$  cm<sup>2</sup>/s. Using the diffusion coefficient data, we can estimate the ratio of the molecular volume of CQ with respect to its photoproduct (PP). In eq 9, the quantity  $\xi$  is proportional to the molecular volume.<sup>26</sup> If we rewrite eq 9 as

$$\ln \left[ \frac{D_1(T)}{D_1(T_f)} \right] = -\xi(\ln 10)C_1^0 C_2^0 \left[ \frac{1}{C_2^0 + T - T_g} - \frac{1}{C_2^0 + T_f - T_g} \right] \quad (18)$$

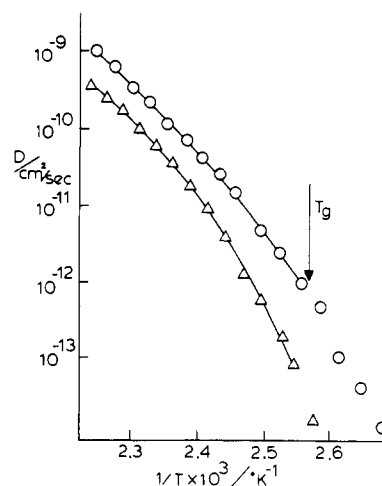
where  $D_1(T_f)$  is the diffusion coefficient reference temperature  $T_f$ .

If the diffusion coefficients of CQ and PP are determined at both  $T$  and  $T_f$ , then eq 18 gives

$$\ln \left[ \frac{D_{PP}(T)}{D_{PP}(T_f)} \right] / \ln \left[ \frac{D_{CQ}(T)}{D_{CQ}(T_f)} \right] = \frac{\xi_{PP}}{\xi_{CQ}} = \frac{V_{PP}}{V_{CQ}} \quad (19)$$

where  $D_{PP}(T)$  (or  $D_{CQ}(T)$ ) and  $D_{PP}(T_f)$  (or  $D_{CQ}(T_f)$ ) are diffusion coefficients of PP (or CQ) at temperatures  $T$  and  $T_f$ , respectively.

Using the data obtained for PP and CQ from our computer fitting of the diffracted intensity vs. time curve at  $T_f = 409.6$  K and  $T = 418.7$  K, we obtain  $D_{CQ}(T_f) = 1.67 \times 10^{-11}$  cm<sup>2</sup>/s,  $D_{PP}(T_f) = 3.84 \times 10^{-12}$  cm<sup>2</sup>/s,  $D_{CQ}(T) = 6.66$



**Figure 2.** Diffusion coefficients of the CQ-PMMA and CQ-PtBMA systems plotted as functions of  $1/T$ : ( $\Delta$ ) experimental points from CQ + PMMA; ( $\circ$ ) experimental points from CQ + PtBMA. Solid lines are the best WLF fit (above  $T_g$ ) to the experimental data. The best WLF constants obtained from the fits are  $C_1^0 \xi = 8.22$ ;  $C_2^0 = 54.24$  K for CQ-PMMA and  $C_1^0 \xi = 10.03$ ;  $C_2^0 = 119.2$  K for CQ-PtBMA.  $T_g$  for both systems is 117 °C.

**Table I**  
Temperature Dependence of the Self-Diffusion Coefficients of CQ in PMMA ( $T_g = 117$  °C)

$T$ , K	$D$ , cm <sup>2</sup> /s	$T$ , K	$D$ , cm <sup>2</sup> /s
388.9	$1.64 \times 10^{-14}$	418.7	$1.78 \times 10^{-11}$
393.5	$8.50 \times 10^{-14}$	423.3	$3.55 \times 10^{-11}$
396.0	$1.93 \times 10^{-13}$	427.8	$6.05 \times 10^{-11}$
401.2	$5.89 \times 10^{-13}$	432.3	$1.00 \times 10^{-10}$
405.1	$1.37 \times 10^{-12}$	436.9	$1.71 \times 10^{-10}$
409.6	$3.84 \times 10^{-12}$	441.4	$2.54 \times 10^{-10}$
414.2	$8.95 \times 10^{-12}$	446.0	$3.64 \times 10^{-10}$

**Table II**  
Temperature Dependence of the Self-Diffusion Coefficients of CQ in PtBMA ( $T_g = 117$  °C)

$T$ , K	$D$ , cm <sup>2</sup> /s	$T$ , K	$D$ , cm <sup>2</sup> /s
373.9	$1.34 \times 10^{-14}$	410.7	$2.23 \times 10^{-11}$
378.0	$4.35 \times 10^{-14}$	415.7	$4.04 \times 10^{-11}$
382.7	$1.06 \times 10^{-13}$	419.7	$7.10 \times 10^{-11}$
387.1	$4.82 \times 10^{-13}$	424.8	$1.14 \times 10^{-10}$
391.7	$9.41 \times 10^{-13}$	429.3	$2.20 \times 10^{-10}$
396.7	$2.30 \times 10^{-12}$	434.0	$3.38 \times 10^{-10}$
401.5	$5.67 \times 10^{-12}$	438.9	$6.18 \times 10^{-10}$
406.5	$1.28 \times 10^{-11}$	444.0	$9.48 \times 10^{-10}$

$\times 10^{-11}$  cm<sup>2</sup>/s,  $D_{PP}(T) = 1.71 \times 10^{-11}$  cm<sup>2</sup>/s. In accordance with eq 19, we obtain  $V_{PP}/V_{CQ} = \ln(1.71 \times 10^{-11}/3.84 \times 10^{-12})/\ln(6.66 \times 10^{-11}/1.67 \times 10^{-11}) = 1.08$ .

The calculation shows that PP is slightly larger than CQ by about 8%. This result is consistent with the geometric consideration based upon the photochemistry of CQ given above and is significantly different from the estimate based upon the Stokes-Einstein equation ( $D = kT/6\pi\eta a$ ,  $a$  being the radius of the diffusant). The Stokes-Einstein equation would predict  $V_{PP}/V_{CQ} = 389\%$ , which apparently overestimated the size of PP.

The excellent fit of eq 17 to the experimental data indicates that the unusual decay-growth-decay intensity relaxation curve is indeed due to the interference of two diffusive motions.

Diffusion coefficients extracted from the diffracted intensity curves obtained for the CQ-PMMA and CQ-PtBMA systems at two different bleaching angles are plotted vs.  $1/T$  in figure 2. The data are also shown in Tables I and II, respectively. Diffusion coefficients of these

two systems can be interpreted in terms of eq 10 and a least-squares fit of eq 10. The fits to the WLF equation are excellent and the resultant best fit values are  $C_1^0\xi = 8.22$ ,  $C_2^0 = 54.24$  K for the CQ-PMMA system and  $C_1^0\xi = 10.03$ ,  $C_2^0 = 119.2^\circ$  K for the CQ-PtBMA system. Note that the  $C_2^0$  value obtained here is about 26 K lower than that obtained from the viscosity data of PMMA.<sup>12</sup> This difference is due to the fact that our measurements cover a temperature range of  $T_g < T < T_g + 50^\circ$  C while the viscosity data used to extract the WLF parameters are obtained at considerably higher temperatures. As mentioned above, eq 9 is obtained by suppressing the activation energy term. Upon an increase of temperature, the activation energy term in eq 8 will become more important. Since the viscosity data that are used in ref 12 for the WLF equation fit are obtained at considerably high temperature, it is a simple matter to show that the fit to higher temperature data would result in a higher value of  $C_2^0$ .

One also notes in Figure 2 that for the PtBMA system the change in the activation energy across  $T_g$  is not observed, in contrast to the theoretical prediction.<sup>25,26</sup> There are several possible causes to account for the difference. First, the  $T_g$  value of  $117^\circ$  C determined by our DSC technique is with a heating rate of 10 K/min, whereas the diffusion of the dye molecules in the polymer host is a much slower process. Apparently with a slower heating rate, the  $T_g$  values is expected to be significantly lower than  $117^\circ$  C.<sup>4</sup> The discontinuity would probably be detected at a temperature lower than  $T_g$ . This indeed corresponds to what was previously found in the dye-polycarbonate system.<sup>4</sup> Second, the DSC result of PtBMA shows a rather strong subglass process that may render greater segmental motion to occur as the temperature is increased, thereby causing the higher-than-expected activation energy below  $T_g$  in this system. Third, the ratio  $\lambda = E_{\text{act}}(T_g^-)/E_{\text{act}}(T_g^+) = (\text{change in the volume contraction as } T_g \text{ is transverses})$  is estimated to be around 0.6 (see Figure 2 and Table II, ref 25) for this polymer glass. A change in  $E_{\text{act}}$  is difficult to detect at the temperature range, being not too far below  $T_g$ . However, in view of Figure 5 of ref 25, a change in the activation energy is difficult to detect for  $\lambda$  in the 0.6–1.0 range.

Finally one further notes that the diffusion coefficients of the CQ-PtBMA system is about 8–16 times higher than that of the CQ-PMMA system, despite both polymer samples have practically the same  $T_g$ . These results suggest that the diffusion of small solute molecules in the polymer matrix depends mainly on the creation of large enough free volumes in the polymer system in the neighborhood of the diffusants. The intrinsic nature of the Brownian motion of the solute molecules leading to diffusion in the<sup>9</sup> solvent of small molecules apparently does

not play any significant role. This result is consistent with the fact that the big and stiff  $\text{C}(\text{CH}_3)_3$  side group in PtBMA introduces a larger free volume than that of the methyl group does in PMMA, thereby facilitating the diffusion process to occur.

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