sterically more permissive than the analogous S_N2 attack of mechanism I.

Our calculations give results that are in complete accord with Penczek and Szymanski's conclusion that polymerization of 1,3-dioxolane (**2**) proceeds predominantly via mechanism I.[1,2] They also are in accord with a change to propagation via open carbenium chain ends (mechanism II) for polymerization of 2-alkylated cyclic acetals as some of us have suggested.[3,4] Since the critical energy differences are small, it appears that individual cases require consideration in detail.

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Supplementary Material Available: Extra data includes copies of AM1 Z-matrix format files for all structures and transition states shown in Figures 2–4 as well as vibrational modes for transition-state structures (24 pages). Ordering information is given on any current masthead page.

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Registry No. 1,3-Dioxolane, 646-06-0.

Dependence of the Mutual Diffusion Coefficient on the Dye Concentration in the Polymer/Dye System

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Introduction

In recent years, the holographic grating relaxation (or forced Rayleigh scattering) technique has been proven to be very valuable in measuring the slow translational diffusion coefficient of photoreactive organic dye molecules dissolved in amorphous solid-state polymer hosts.[1–7] In the vicinity of the glass transition temperatures of amorphous polymers, diffusion coefficients are on the order of 10^{-12}–10^{-15} cm^2/s, depending on the nature of the polymers being studied. When the polymer contains monomers not removed or additives intentionally added in as plasticizers, the translational diffusion coefficient of the photoreactive dye is significantly increased.[4] Thus, in reporting the diffusion data, the state of the polymer host must be clearly characterized and defined in order to facilitate comparison. When the concentration of dye molecules is very small, the translational diffusion coefficient is found to be determined only by the size of the dye molecule and the properties of the polymer that serves as a host.[1] In the low concentration limit, the dye molecules serve as tracers. Temperature-dependence studies of the tracer diffusion coefficient in the polymer host above T_g display a non-Arrhenius behavior and are found to follow the form of the Williams–Landel–Ferry (WLF) equation,[1–6] consistent with the free-volume theory proposed for the polymer/plasticizer system originally by Fujita[8] and further elaborated by Vrentas and Duda.[9–11]

The translational diffusion coefficient measured in the polymer/dye system is strictly a mutual diffusion coefficient, and, as such, its value will depend on the concentration of the photoreactive dye molecules that are present in the polymer. Mutual diffusion is concerned with the rate at which concentration gradients approach equilibrium; on the other hand, self-diffusion deals with the mobility of the molecule in a chemically uniform environment. At vanishing dye concentration, the mutual diffusion coefficient is the self-diffusion coefficient of the dye molecules in the polymer environment. In this limit, the self-diffusion coefficient of the dye molecules is entirely dictated by the density fluctuation of the amorphous polymer matrix; hence, the mutual diffusion coefficient in the limit of vanishing concentration of dye molecules can be used as a probe for studying the dynamics of polymer chains above and below the glass transition temperature when other techniques become inadequate due to very slow polymer dynamics involved. While in the literature there is an abundance of diffusion data for polymers in solvents of small molecules, concentration-dependence data for diffusion of small molecules in polymer hosts are quite scarce. In this communication, we report the results of the mutual diffusion coefficient (D) measurement on the poly(methyl methacrylate) (PMMA)/camphorquinone (CQ) system as a function of the CQ concentration. Our object is to show that D varies greatly with the concentration of CQ. A very small concentra-

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Table I
Effects on Molecular Weight[a] and Glass Transition Temperature[b] due to the Presence of Camphorquinone in PMMA

CQ concn, wt %	$\bar{M}_w \times 10^{-5}$, g/mol	$\bar{M}_w/\bar{M}_n$	T_g, °C
0.5	2.46	5.36	117.0
1.0	2.25	4.53	114.5
2.3	1.95	4.24	110.8
3.5	1.57	3.85	108.4
5.8	1.89	4.38	104.4
9.5	1.76	5.36	99.4
15.0	1.40	4.89	92.1

[a] Measured with Waters GPC equipment. [b] Measured with Perkin-Elmer DSC (Delta-7 Series).

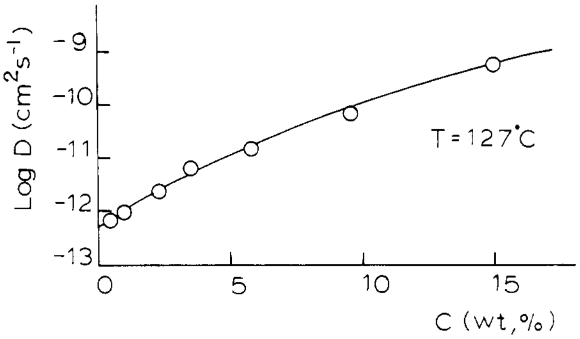

Figure 1. Dependence of the mutual diffusion coefficient or the CQ concentration for the PMMA/CQ system.

tion of the dye molecules (less than 0.5% by weight) is needed in order to obtain a reliable self-diffusion coefficient.

Experimental Section

To prepare the samples for the diffusion measurement, we synthesize PMMA samples containing various known amounts of CQ. We start with purifying MMA monomers (purchased from Aldrich Chemical Co.) by distillation to remove impurities and inhibitors. The purified MMA monomers are then added with 0.25% of initiator (benzoyl peroxide) and with a desired amount of CQ in test tubes (OD = 11.5 mm). The test tubes containing the samples are sealed and placed in an oven for controlled polymerization carried out by a gradual temperature increase (by 10 °C every 24 h raising from 40 to 150 °C). After 10 days of polymerization, yellowish transparent rods free from the presence of monomer are obtained. A slice is cut off from each rod and then polished into an optically clear pellet of about 2-mm thickness. The pellet is mounted on a specially designed temperature-controlled copper holder to carry out the diffusion measurement using the holographic grating relaxation technique. The optical set up in the holographic grating relaxation study is identical with that used previously[1-7] and will not be repeated here.

Molecular weights of PMMA rods are characterized by the gel permeation chromatography (GPC) technique, and the glass transition temperature of each PMMA rod containing a given amount of CQ is determined DSC. The results are shown in Table I. One notes that, by increasing the CQ concentration, the average molecular weight ($\bar{M}_w$) is gradually lowered. There seems to be no systematic change in the molecular weight distribution as the CQ concentration is changed. Increasing the CQ concentration also results in the depression of the glass transition temperature.

Results and Discussion

The diffusion coefficient of the photoproduct of CQ relative to the polymer host at 127 °C is shown in Figure 1 as a function of CQ concentration. At 15% CQ concentration D is 5.6×10^{-10} cm²/s and decreases to 7.1×10^{-13} cm²/s at 0.5% CQ concentration, a change of nearly 800-fold between two concentrations. Such a pronounced concentration dependence of the diffusion coefficient is not uncommon in the polymer/dye systems that have been studied in this laboratory.[12] The large increase in D as the CQ concentration is increased is closely related to the lowering of the glass transition temperature of the PMMA/CQ system associated with the plasticizing effect of the polymer by the dye molecules which enhance the chain mobility of the polymer and facilitates the translational diffusion of the dye molecules to take place.

One notes in Figure 1 that D increases linearly with increasing CQ concentration only at very low concentration (<2%). At higher concentration, it increases less rapidly than the linear extrapolation. This result can be understood by considering the concentration dependence of the mutual diffusion coefficient. In the laboratory-fixed coordinate system, the mutual diffusion coefficient is[13]

$$D = \Omega\left(\frac{\partial\mu_1}{\partial C_1}\right) \tag{1}$$

where Ω is the Onsager coefficient and μ_1 and C_1 are, respectively, the chemical potential and the molar concentration of dye molecules. If one assumes the Flory–Huggins expression for the free energy of mixing for the polymer/dye system,[14] then

$$\partial\mu_1/\partial C_1 = RT(X_2/C_1)(N_2\phi_1 + \phi_1)(\phi_2 + \phi_1/N_2 - 2\chi\phi_1\phi_2) \tag{2}$$

where X_2 is the mole fraction of PMMA, N_2 is the number of monomer in PMMA, ϕ_1 and ϕ_2 are, respectively, the volume fraction of CQ and PMMA, and χ is the Hildebrand interaction parameter and is negative. At low concentration, the Onsager coefficient can be written as[15]

$$\Omega = (\phi_1 C_1/N_o\xi_1)(1 - K_1\phi_1 + K_2\phi_1^2 + ...) \tag{3}$$

where ξ_1 is the friction of coefficient of dye molecules at infinite dilution, N_o is Avogadro's number, and K_1 and K_2 are empirical constants. The predicted value for K_1 is about 7 for a macromolecule in solvent of small molecules,[16] and K_2 is less than 1.[15] Substitution of eq 2 and 3 into eq 1 yields (for $N_2 \gg 1$)

$$D = X_2D_1^\circ\{1 + \phi_1(N_2 - K_1 - 2\chi - 2) + \phi_1^2[K_2 - K_1(N_2 - 2\chi - 2) - N_2(2\chi + 1) + 4\chi] + O(\phi_1^3)\} \tag{4}$$

where $D_1^\circ = kT/\xi_1$, the self-diffusion coefficient of dye molecules in the infinite dilution limit. Since N_2 is on the order of 10^3 in the present PMMA polymer, the coefficient associated with the ϕ_1 term is positive and that with the ϕ_1^2 term is negative. Due to the absence of K_1, K_2, and χ data, we cannot quantitatively compare the result with experiment. However, eq 4 is qualitatively in agreement with the concentration-dependence result shown in Figure 1.

Free-volume theory may also be used to provide a satisfactory description of the concentration dependence of the diffusion coefficient. In terms of the fractional free volume, f, the diffusion coefficient, D, can be written as[8]

$$D = RTA_d \exp(-B_d/f) \tag{5}$$

where A_d and B_d are constants, which are independent of temperature and dye concentration. The fractional free volume should be a function of both temperature and diluent concentration. We assume that by addition of a diluent (CQ in the present case) f is increased and the increase in f is proportional to the weight fraction of the diluent (in ref 8, it is assumed to be proportional to

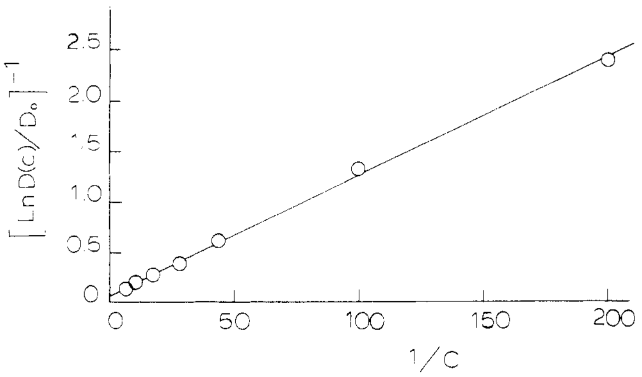

Figure 2. Plot of $1/[\ln D(C)/D_0]$ versus $1/C$. The intercept, $f(T,0)/B_d$, is 7.769×10^{-2}, and the slope, $[f(T,0)]^2/B_d\beta$, is 1.181×10^{-2}.

the volume fraction). Thus we write

$$f(T,C) = f(T,0) + \beta(T)\, C \qquad (6)$$

where $f(T,0)$ represents the fractional free volume in the pure polymer and $\beta(T)$ is a parameter independent of concentration.

Substituting eq 6 into eq 5 and doing some algebra, one finds

$$\{\ln [D(C)/D_0]\}^{-1} = f(T,0)/B_d + [f(T,0)^2/B_d\beta(T)](1/C) \qquad (7)$$

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 zero dye concentration. In Figure 2, we plot $1/\ln [D(C)/D_0]$ versus $1/C$; the linear plot confirms eq 7 and hence supports the free-volume theory of Fujita.[8] Using the assumption $f(T_g,0) = 0.025$, we have calculated $f(T = 127\ °\mathrm{C}, 0)$ to be equal to 0.030, also assuming the thermal expansion coefficient at T_g to be $4.82 \times 10^4\ \mathrm{K}^{-1}$, and this gives $B_d = 0.384$ and $\beta(T) = 0.128$. If eq 6 is expressed in terms of the volume fraction, B_d becomes 0.392 and $\beta(T) = 0.164$. These values are consistent with Fujita's results[8] and clearly show that the remarkable concentration dependence of the diffusion coefficient is due to the smallness of the $f(T,0)$ and $\beta(T)$ values.

One notes that even at 0.5% CQ concentration, D still has not reached the zero concentration self-diffusion limit, although the difference is about 6% in the present case. We expect that the difference increases as the temperature is brought toward T_g of the polymer. Thus, efforts must be taken to ascertain the dependence of D on the dye concentration when investigating the diffusion process in the vicinity of T_g. The presence of dye molecules tends to suppress the rapid change of D associated with the effect due to a large change in the chain motion that takes place in the vicinity of the glass transition region. To monitor the effect of the glass transition on the density fluctuation through the diffusion study, it is therefore essential to keep the dye concentration at a very small level.

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The Effective Interaction Coefficient Corresponding to Translational Diffusion of High Molecular Mass Polystyrene in Good Solvents

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Quasielastic laser light scattering (QELS) experiments,[2,3] in conjunction with applications of new theoretical achievements involving scaling theories,[4,5] have opened up a new stage in studying polymer dynamics. Despite considerable progress there are still unanswered questions related to some scaling exponents. QELS of polymer solutions is usually studied by using the photon correlation spectroscopy (PCS) technique.[2] In a PCS experiment the time autocorrelation function (ACF) of the scattered light intensity is measured. The observed decay rate Γ of the ACF is related to diffusion phenomena. In dilute solutions Γ depends on concentration c and scattering angle θ [or scattering vector $\mathbf{q}$, where $|\mathbf{q}| = q = (4\pi/\lambda) \sin (\theta/2)$ and λ is the wavelength of light in the scattering medium]. The concentration dependence is caused by effective polymer segment–solvent molecule and segment–segment interactions while the $\mathbf{q}$ dependence is related to the influence of chain internal modes of motion. The product qR_h (with the R_h Stokes-effective hydrodynamic radius) is closely related to the characteristics of diffusional movement measured in the experiment.[3-5] If $qR_h < 0.4$–0.5, translational diffusion of the macromolecular center-of-mass (characterized by the corresponding D_t diffusion coefficient) dominates the ACF.[6,7] In this scattering vector regime both the effec-

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