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Studies of the Diffusion Process of Camphorquinone in Poly(aryl ether ether ketone) by the Holographic Grating Technique

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ABSTRACT: The diffusion coefficients of a trace amount of camphorquinone (CQ) and its photoproduct (CQP) in poly(aryl ether ether ketone) (PEEK) are measured as a function of temperature by using the holographic grating relaxation technique. Above T_g the diffusion coefficients are non-Arrhenius, whereas they become Arrhenius below T_g. Comparison of the diffusion data with the dynamic shear modulus data of PEEK shows that diffusion of CQ (or CQP) in PEEK is completely determined by the molecular size (characterized by a parameter ξ) of CQ (or CQP) and by the viscoelastic property of PEEK. However, the ξ parameter is found to be host dependent.

Introduction

Studies of the translational diffusion process of trace amounts of low molecular weight organic dye molecules in molten and glassy polymers are of practical and fundamental interest. Recent work carried out by using the holographic grating relaxation technique[1-3] has shown that in the dye/polymer system the behavior of concentration fluctuations of the dye molecules is dictated by the dynamics of polymer chain motion, provided that the dye concentration is small such that the dye molecule undergoes self-diffusion in the polymer environment and that the lifetime of the excited dye molecule is much longer than the rate of dye diffusion. Under these conditions, the dye molecule serves as a probe of the polymer chain motion, and measurements of the mutual diffusion coefficient in the limit of vanishing dye concentration in the dye/polymer system should provide information about the motion of the polymer chains. When the polymer host is in the rubbery state, the segmental motion of the polymer chain is rapid and the diffusion of the probe can be studied either by using a conventional technique such as a radioactive isotope tracer or by using pulsed field gradient NMR. However, as the dye/polymer system is brought toward the glass transition temperature (T_g) of the polymer, the segmental motion is gradually frozen, and the diffusion process of the probe becomes very slow, thus rendering the conventional techniques ineffective.

The holographic method deals with the detection of the dye diffusion over a distance about the order of one optical wavelength, and consequently it decreases the measurement time by about a factor of 10^8, in comparison with the conventional technique, thereby making the measurement of a very slow diffusion coefficient (as small as 10^{-15} cm^2/s) feasible. This technique is especially useful for polymers with high T_g. In this paper, we apply the holographic grating relaxation technique to measure the diffusion coefficient of a photochromous dye, camphorquinone (CQ), in poly (aryl ether ether ketone) (PEEK).

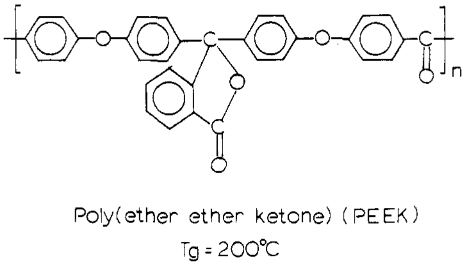

Figure 1. Molecular formula of poly(aryl ether ether ketone) (PEEK).

Due to its outstanding thermal and combustion characteristics and its resistance to a wide range of solvents, PEEK has received an increased attention as a high performance thermoplastic.[4,5] In order to gain a better understanding of the properties of this useful material as well as to certify the applicability of the holographic grating technique as a technique for characterizing the high T_g thermoplastic material, we have also measured the temperature dependence of the dynamic shear modulus for comparison.

Experimental Section

Poly(aryl ether ether ketone) (PEEK) (with its repeating unit shown in Figure 1) used in the present study was synthesized

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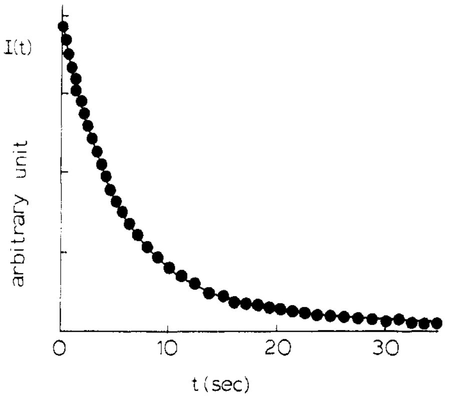

Figure 2. The diffraction intensity curve as a function of time for the sample at $T = 199$ °C and $\theta = 11.8°$. The dots correspond to the experimental data, and the curve is the fit to the experimental data according to eq 1. The parameters obtained in the fit are $a = 22.3$, $b = 9.8$, $\tau_1 = 22.6$ s, and $\tau_2 = 140.0$ s, where a and b are in arbitrary units.

in the Changchun Institute of Applied Chemistry, Academia Sinica, China.[6] The polymer is amorphous as confirmed by a broad halo in the wide-angle X-ray diffraction analysis. The glass transition temperature determined by a DSC (with a heating rate of 20 °C/min) is 200 °C. The number-average molecular weight is $M_n = 12\,000$, and $M_w/M_n = 2.6$, determined by using a gel permeation chromatographic (GPC) apparatus.

To prepare the CQ/PEEK sample for the holographic grating relaxation experiment, we first dissolved CQ in petroleum ether, a nonsolvent for PEEK, and then added PEEK powder to the CQ solution. The PEEK powder was prepared by dissolving a PEEK plastic sheet in CH_2Cl_2. The polymer in solution was precipitated out with CH_3OH and then dried. The CQ/PEEK mixture was next dried in a vacuum oven at a temperature higher than the boiling point of petroleum ether for several hours. The dried mixture was pressed into a film of about 0.4-mm thickness with a temperature-controlled press at 300 °C. The film sample was then placed in an oven at 250 °C for a week to anneal and to allow the dye molecules to diffuse into the sample and to reach a uniform distribution in dye concentration. The CQ concentration is less than 0.5% (by weight).

The apparatus used in the holographic grating experiment was similar to that used in the previous experiments.[1,2] The film was mounted in a copper holder which was placed in a temperature-controlled oven with glass windows to permit transmission of the laser beam. Holographic gratings were induced by crossing two equal intensity coherent beams split from a main beam of an Ar ion laser operating at $\lambda = 4880$ Å and at a power level of 30 mW. The laser power of the main beam was attenuated by a factor of about 150 before being incident on the sample. The laser writing time was about 1 s, controlled by an electronically actuated shutter. The crossing angle of the two coherent beams was varied from $\theta = 3.8$ to $\theta = 15°$. At $\theta = 3.8°$, the grid spacing $\Lambda = \lambda/[2 \sin (\theta/2)]$ is equal to 7.72 μm.

Camphorquinone (CQ) reacts photochemically by hydrogen abstraction.[7] The photochemical reaction is irreversible. Thus, the mechanism leading to the decay of the diffraction intensity curve is not complicated by the finite lifetime of the photoproduct.

The dynamic viscoelastic properties of a PEEK film with the dimension of a film strip equal to 3 cm × 0.5 cm × 1 mm were studied by using a DDV II rheovibron. The real and imaginary parts of the shear modulus at a frequency equal to 3.5 Hz were measured from 40 to 280 °C.

Results and Discussion

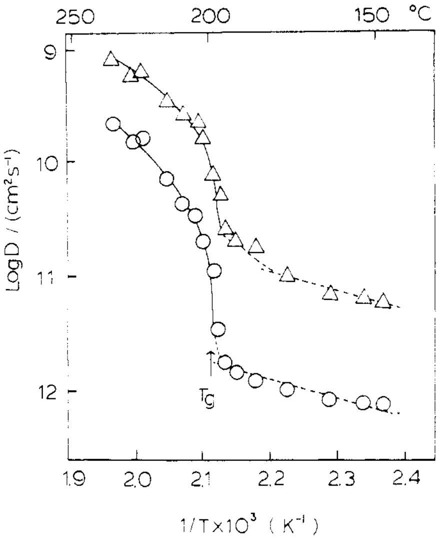

Figure 3. The logarithm of diffusion coefficients of CQ and CQP plotted as a function of $1/T$. Note the rapid decrease of the diffusion coefficient as the temperature is lowered toward T_g. Below T_g, the temperature dependence is approximately Arrhenius. The solid lines above T_g are fits to eq 6.

The diffraction light intensity curve observed at first order ($q = 2\pi/\Lambda$) at crossing angle $\theta = 11.8$ °C for a PEEK sample containing less than 0.5% CQ at 199 °C is shown in Figure 2. While the intensity curve displays a monotonous decay shape, the curve shape does not correspond to a single exponential. However, it can be fit to an equation involving the sum of two exponentials, as given by

$$I(t) = (ae^{-t/\tau_1} + be^{-t/\tau_2})^2 \tag{1}$$

where a and b are positive constants and τ_1 and τ_2 are the relaxation times associated with the diffusion coefficients D_1 and D_2 by

$$\tau_j = \frac{\lambda^2}{16\pi^2 D_j \sin^2 (\theta/2)} \tag{2}$$

where $j = 1$ is for the dye molecule and $j = 2$ for the photoproduct. Knowing λ (the wavelength of the writing laser) and θ (the crossing angle), one can determine the diffusion coefficient D_j from the measured relaxation times τ_j. Derivation of eq 1 has been given in recent publications.[2,8] Using eq 2, we have obtained the diffusion coefficient for CQ to be 6.31×10^{-11} cm^2/s and for CQP 1.02×10^{-11} cm^2/s for the sample near T_g (at 199 °C). Consistent diffusion coefficients D_j are obtained by using different crossing angles, thus certifying that the time dependence in the intensity curve arises from translational diffusion of the dye molecules.

Shown in Figure 3 are the temperature dependence of the diffusion coefficient of CQ (the top curve) and CQP (the bottom curve) in PEEK. One notes that the diffusion coefficients for both species decrease rapidly with decreasing temperature and decrease precipitously as the glass transition temperature (T_g) is traversed from above. Above T_g the temperature dependence cannot be described by an Arrhenius equation, whereas it is effectively Arrhenius below T_g, with an activation energy equal to 7.1 kcal/mol. This activation energy is close to the 9.1 kcal/mol activation energy obtained in the dielectric relaxation study.[9] The Arrhenius behavior below T_g is not unexpected because below T_g the diffusion of the organic dye molecules is assisted by the secondary β-relaxation process.

The non-Arrhenius behavior above T_g can be understood by free volume theory, by which the diffusion coefficient D is expressed in terms of the fractional free volume f by[10]

$$D = RTA_d \exp(-B_d/f) \tag{3}$$

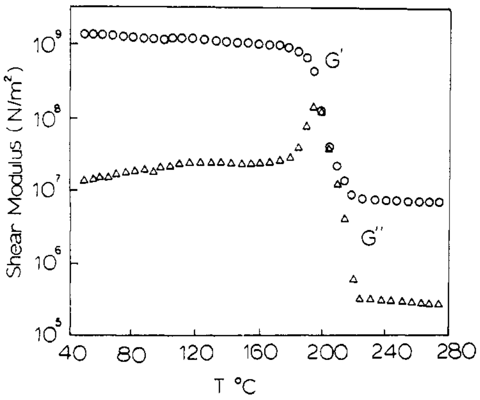

Figure 4. The real (G') and imaginary (G'') parts of the dynamic shear modulus plotted as a function of $1/T$. The solid line for G' is the fit to eq 9.

where A_d and B_d are parameters independent of temperature but may depend on the size and shape of the diffusant; R is the gas constant.

The ratio of the diffusion coefficient at $T > T_g$ and that at $T = T_g$ is thus given by

$$\ln\left\{\frac{D(T)/T}{D(T_g)/T_g}\right\} = -B_d\left(\frac{1}{f} - \frac{1}{f_g}\right) \tag{4}$$

By assuming that the fractional free volume varies with temperature as[10]

$$f = f_g + \alpha_f(T - T_g) \tag{5}$$

where f_g is the fractional free volume at T_g and α_f is the difference of the thermal expansion coefficient above and below T_g, we obtain by substituting eq 5 into eq 4 the Williams–Landel–Ferry (WLF) equation for diffusion as

$$\log\left\{\frac{D(T)/T}{D(T_g)/T_g}\right\} = -\frac{B_d C_1(T - T_g)}{C_2 + T - T_g} \tag{6}$$

where $C_1 = 1/2.30f_g$ and $C_2 = f_g/\alpha_f$.

The data above T_g shown in Figure 3 are fit to eq 6, using the measured $D(T_g)$ value for CQ ($=6.3 \times 10^{-11}$ cm²/s); the fit gives $C_2 = 45.3 \pm 2.9$ K and $C_1B_d = 5.8 \pm 0.8$. If the $D(T_g)$ value for CQP ($=1.18 \times 10^{-11}$ cm²/s) is used, then we obtain $C_1B_d = 7.3 \pm 0.8$, with practically the same value for C_2.

The fact that the same C_2 value is obtained for CQ and CQP is a clear indication that C_2 depends only on the volumetric properties of the polymer. Hence it suggests that the diffusion of the dye molecules is dictated by the dynamics of segmental motion of the polymer host, in addition to the size effect of the dye molecule (related to the parameter B_d) which also plays a role. The rapid decrease in the diffusion coefficient as temperature is decreased toward T_g apparently is related to the slowing down of the segmental motion of the PEEK chain. As the temperature is lowered below T_g, the configurational rearrangement of polymer chain backbones become extremely slow, resulting in a very slow fluctuation in the free volume for the dye diffusion process to take place.

To correlate the viscoelastic property of PEEK with the dye diffusion coefficient, we have measured the dynamic shear modulus at 3.5 Hz as a function of temperature. The temperature dependence of the real (G') and imaginary (G'') parts of the dynamic shear modulus is shown in Figure 4. The prominent peak at 200 °C in G'' (or a rapid change in G') is clearly associated with the glass transition process arising from the rapid change in the segmental motion of the polymer main chain.

Assuming that the temperature dependence of the dynamic shear modulus is also due to the change in free volume, we write

$$G' = A\exp(B/f) \tag{7}$$

where A and B are constants independent of temperature. The ratio of G' at T to that at T_g can then be written as

$$\ln\left[\frac{G'(T)}{G'(T_g)}\right] = B\left(\frac{1}{f} - \frac{1}{f_g}\right) \tag{8}$$

Substituting eq 5 into eq 8 and converting the result to base 10 logarithm, we obtain the WLF equation for dynamic shear modulus as

$$\log\left[\frac{G'(T)}{G'(T_g)}\right] = \frac{BC_1(T - T_g)}{C_2 + T - T_g} \tag{9}$$

where as before $C_2 = f_g/\alpha_f$ and $C_1 = 1/2.30f_g$. We fit the dynamic data of Figure 4 to eq 9 and obtain $C_2 = 40.5 \pm 3.0$ K and $C_1B = 13.8$.

Comparing the WLF coefficients obtained from the viscoelastic data with the diffusion data, we have found that the C_2 values obtained from both data agree (within the experimental uncertainty) with each other. This agreement lends a strong support to the idea that the diffusion of the trace amount of dye molecules in polymer is completely determined by the free volume of the polymer host. Since this aspect of the viscoelastic behavior is also controlled by the polymer free volume, the self-diffusion process of the dye molecule is thus closely related to the polymer viscoelasticity. The temperature dependence of both G' (or G'') and D near T_g results from the reduction of segmental chain mobility as the temperature falls, which slows the fluctuation in free volume. We can now divide the value $C_1B_d = 5.8$ obtained from the diffusion data of CQ by $C_1B = 13.8$ obtained from the viscoelastic data of the pure polymer and obtain $B_d/B = 5.8/13.8 = 0.42$. The parameter C_1 drops out of the equation.

The theory of diffusion in concentrated polymer solutions or in polymer–plasticizer systems formulated in the framework of free volume theory by Fujita[11] is similar to that presented above. The free volume theory for diffusion is extended by Vrentas et al.,[12] who have strongly argued that the ratio $\xi = B_d/B$ is equal to the ratio of the critical molecular volume of the diffusant (V_d^*) to that of the polymer segment (V_p^*) that undergoes motion to initiate the free volume fluctuation. In the CQ/PEEK system we obtain $\xi = 0.42$, as given above. The result thus indicates that the critical molecular volume of CQ in PEEK is about 42% of the polymer segmental volume. This result is consistent with our intuition expected for the diffusion process to occur. Whether or not V_d^* is a fixed quantity independent of the matrix can be tested by determining ξ of two different diffusants in two different polymer hosts since V_p^* cancels in the relation $\xi_1/\xi_2 = V_{d_1}^*/V_{d_2}$.

The fact that the diffusion coefficients of CQ and CQP in PEEK can simultaneously be measured by using the holographic grating technique allows us to carry out such a test. Using the C_1B_d values obtained from the WLF equation fits, we find $\xi(\text{CQP})/\xi(\text{CQ}) = 1.20$, indicating that in PEEK the size of CQ is smaller than that of CQP. This is consistent with the geometric model of the molecules. However, whether or not the size of CQP is indeed increased by 20% after CQ undergoes hydrogen abstraction is, of course, dictated by the accuracy of the theory.

However, in our previous work we have found that in PMMA the $\xi(\mathrm{CQ})/\xi(\mathrm{CQP})$ ratio is equal to 1.03, and in polycarbonate[14] it is equal to 1.34. These results thus demonstrate that the ξ value and hence for the critical molecular volume $V_d{}^*$ of the dye dependents on the nature of the polymer host.

Using eq 6, we find that above T_g the effective activation energy

$$E_D = RT^2\left(\frac{\partial \ln D}{\partial T}\right)_p = RT + \frac{2.3\xi C_1 C_2 R T^2}{(C_2 + T - T_g)^2} \qquad (10)$$

Equation 10 indicates that the effective activation energy increases rapidly as T is decreased toward T_g. Furthermore, one notes that E_D is linearly proportional to ξ. Thus, given the same polymer environment, the rate of dye diffusion in a polymer is strongly affected by the size of the dye molecule.

In conclusion, we have carried out diffusion measurements of a trace amount of CQ in PEEK as a function of temperature. We have shown that the diffusion coefficient of CQ in PEEK is closely associated with the viscoelastic property of PEEK. The main-chain segmental motion that affects the dynamic shear modulus data also dominates the diffusion process of camphorquinone and its photoproduct in PEEK.

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Registry No. CQ, 465-29-2; PEEK, 40883-84-9.

Chain Architecture in the Hydrodynamic Scaling Picture for Polymer Dynamics[†]

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ABSTRACT: The hydrodynamic scaling picture of polymer dynamics is extended to treat the consequences of chain architecture on tracer diffusion by linear and star polymers in a matrix of linear polymers. From hydrodynamic scaling, one clearly predicts: (i) whereas in comparing linear and many-armed star polymers of equal *total* molecular weight, a given large concentration of matrix polymer is modestly more effective (smaller D/D_0) at retarding a linear polymer than at retarding a star polymer; (ii) with linear and star polymers of equal *arm* molecular weight, a large concentration of matrix polymer is far more effective at retarding a star than at retarding a linear polymer. Contrary to the claims of their authors, recent experiments of Lodge, Wheeler, et al. (*Macromolecules* 1989, *23*, 3409) on tracer diffusion of linear and star polystyrenes in poly(vinyl methyl ether) matrices are consistent with predictions of the hydrodynamic scaling model.

Introduction

Wheeler, Lodge, and Markland[1,2] have recently reported an extensive experimental study on the tracer diffusion coefficient D of linear and star polystyrenes (PS) through poly(vinyl methyl ether) (PVME)/*o*-fluorotoluene, comparison being made with the reptation-scaling,[3] reptation-Mori,[4,5] dynamic entanglement,[6,7] and hydrodynamic scaling[8-10] models of polymer dynamics. Lodge et al.[2] concluded "...star-branched polymers are retarded significantly relative to linear polymers...the observation that branched polymers move less rapidly is consistent only with the reptation-based picture." A reader might reasonably conclude from the latter phrase that Lodge et al.[2] viewed their findings to be *inconsistent* with the hydrodynamic scaling[8-10] and dynamic entanglement[6,7] models. Since neither of these models had hitherto been

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