ifluorinated *n*-alkanes in the solid state and that, furthermore, its vibrational frequency is characteristic of the entire extended molecule. Thus no decoupling of the chain vibration occurs at the juncture between the helical and planar zigzag conformations.

In the melt state, however, the molecular picture is quite different. A disordering of the hydrocarbon segment of the F12H*m*F12 molecule occurs at the melting point, effectively decoupling the longitudinal oscillations of F12 segments. Hence the observed Raman frequency reflects the LAM of the much shorter F12 segment. At short lengths (small *m* values) of the disordered hydrocarbon, the LAM frequency of the F12 segment is perturbed due to a slight coupling with the other attached F12 segment. When this length exceeds 10 CH_2 groups, there is no further perturbation on the LAM frequency.

Acknowledgment. J.F.R. acknowledges partial support of this work by the NSF Division of Materials Research. We acknowledge the assistance of R. L. Siemens in obtaining the thermal measurements and W. Fleming, C. Wade, and C. Gettinger for the NMR determinations.

Registry No. $F_{12}H_6F_{12}$, 114221-77-1; $F_{12}H_8F_{12}$, 100550-09-2; $F_{12}H_{10}F_{12}$, 100550-10-5; $F_{12}H_{12}F_{12}$, 100550-11-6; $F_{12}H_{20}F_{12}$, 114221-78-2; $F_{12}H_{22}F_{12}$, 114221-79-3; $F_{12}H_6F_{12}I_2$, 114221-75-9; $F_{12}H_{22}F_{12}I_2$, 114221-76-0; $F(CF_2)_{12}I$, 307-60-8; $H_2C{=}CH(CH_2)_2CH{=}CH_2$, 592-42-7; $H_2C{=}CH(CH_2)_{18}CH{=}CH_2$, 53057-53-7; $F(CF_2)_{24}F$, 1766-41-2.

References and Notes

(1) Mizushima, S. I.; Shimanouchi, T. *J. Am. Chem. Soc.* **1949**, *71*, 1320.
(2) Peticolas, W. L.; Hibler, G. W.; Lippert, J. L.; Peterlin, A.; Olf, H. *Appl. Phys. Lett.* **1971**, *18*, 87.
(3) Rabolt, J. F. *CRC Crit. Rev. Solid State Mater. Sci.* **1985**, *12*, 165.
(4) Twieg, R. J.; Rabolt, J. F. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 901.
(5) Minoni, G.; Zerbi, G. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 533.
(6) Rabolt, J. F.; Russell, T. P.; Twieg, R. J. *Macromolecules* **1984**, *17*, 2786.
(7) Russell, T. P.; Rabolt, J. F.; Twieg, R. J.; Siemens, R. L.; Farmer, B. L. *Macromolecules* **1986**, *19*, 1135.
(8) Brace, N. O. *J. Am. Chem. Soc.* **1964**, *86*, 523.
(9) Brace, N. O. *J. Org. Chem.* **1966**, *31*, 2879.
(10) Rabolt, J. F.; Fanconi, B. *Polymer* **1977**, *18*, 1258.
(11) Broadhurst, M. G. *J. Res. Natl. Bur. Stand. Sect. A* **1962**, *66A*, 241.
(12) Starkweather, H. *Macromolecules* **1986**, *19*, 1131.
(13) Olf, H. G.; Fanconi, B. *J. Chem. Phys.* **1973**, *59*, 534.
(14) Hannon, M. J.; Boerio, F. J.; Koenig, J. L. *J. Chem. Phys.* **1969**, *50*, 2829.
(15) Masetti, G.; Cabassi, F.; Morelli, G.; Zerbi, G. *Macromolecules* **1973**, *6*, 700.
(16) Rabolt, J. F.; Fanconi, B. *Macromolecules* **1978**, *11*, 740.
(17) Clark, E. S. *J. Macromol. Sci., Phys.* **1967**, *B1*, 795.
(18) Bunn, C. W.; Howells, E. R. *Nature (London)* **1954**, *174*, 549.
(19) Shimanouchi, T.; Tasumi, M. *Indian J. Pure Appl. Phys.* **1971**, *9*, 958.
(20) Kobayashi, M.; Tashiro, K.; Tadokoro, H. *Macromolecules* **1975**, *8*, 158.
(21) Zabel, K.; Schlotter, N. E.; Rabolt, J. F. *Macromolecules* **1983**, *16*, 446.

Effect of Plasticization on Mass Diffusion of Camphorquinone in Polystyrene

J. Zhang and C. H. Wang*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

Received May 15, 1987; Revised Manuscript Received November 13, 1987

ABSTRACT: Mass diffusion coefficients of camphorquinone (CQP) in the polystyrene–dioctyl phthalate (plasticizer) system are measured at various temperatures and concentrations of dioctyl phthalate (DOP) by using the laser-induced holographic grating relaxation technique. The mass diffusion coefficient of CQP shows a strong dependence on the concentration of DOP, which is explained in terms of the free volume increase introduced by the plasticizer. At a given temperature, the diffusion coefficient of CQP in polystyrene (PS) containing 12.4% of DOP is more than 10^4 times higher than that in pure PS. The apparent activation energy is found decreasing as the plasticizer concentration increases.

Introduction

The study of the diffusion process of small molecules in macromolecular matrices is fundamental to the basic understanding of the diffusion mechanism and many operations of polymer processing. It is of key importance to many diffusion-controlled processes such as permeation, diffusion-controlled chemical reactions, and controlled drug delivery. In these processes, it is desirable to control, either to increase or to decrease, the diffusion rate. One of the ways to accomplish this is by altering the polymer matrices. In our previous work, we have reported reducing the diffusion coefficient by forming cross-links in the polymer hosts.[1,2] In this study, we report increasing the diffusion rate by plasticizing the polymer host. Plasticization is the process in which the plasticizer molecules neutralize secondary valence bonds or van der Waals force between polymer molecules. It then increases the chain mobility and the fractional free volume of the polymer. As a result, it reduces moduli or stiffness, increases the ability for elongation and chain flexibility, and lowers the glass transition temperature of the polymer.

Since plasticization increases the chain mobility and fractional free volume of the polymer,[3] we expect the diffusion rate of the probe molecule to increase. It is the objective of this work to carry out a quantitative study of the dependence of the diffusion coefficient on the degree of plasticization and temperature of the plasticized polymer. The plasticizer used is dioctyl phthalate (DOP), a member of the most important plasticizer family. It is an external plasticizer that interacts with the polymer without undergoing the chemical reaction. The organic diffusant and the polymer used are camphorquinone (CQ) and polystyrene (PS), respectively.

In the vicinity of the glass transition temperature of PS, the diffusion coefficient of CQ is in the range of 10^{-14}–10^{-10} cm^2/s, depending on the plasticizer concentration and the

0024-9297/88/2221-1811$01.50/0

Table I
The Change of the Glass Transition Temperature as a Function of Plasticizer Concentration

plasticizer concn, %	T_g, °C	plasticizer concn, %	T_g, °C
0.00	99.3	5.26	77.2
1.01	92.2	12.36	58.9
3.09	88.6		

temperature of the sample. Such diffusion coefficients are too low to be measured by the conventional tracer technique. The laser-induced holographic grating relaxation (LIHGR) technique is capable of measuring very low diffusion coefficient[1] and allows such measurements to be carried out. In this experiment, the concentration of the photochromophore CQ is less than 1%. This low concentration of CQ does not affect the polymer matrix appreciably. On the other hand, DOP does not undergo the photochemical reaction upon laser radiation; therefore, the effect of DOP can be considered together as part of the polymer matrix. Thus, the roles of these two additives, CQ as diffusant and DOP as plasticizer, are well-separated. We show that the increase of the diffusion coefficient and the decrease of the apparent activation energy of the organic diffusant can be fully accounted for by the free volume increase caused by the plasticization.

Experimental Section

Polystyrene (PS) samples containing various concentrations of dioctyl phthalate (DOP) are synthesized in our laboratory. Pure styrene monomers are purchased from Aldrich Co. and purified by distillation to remove impurities and inhibitors. The purified styrene monomers are added with 0.25% of initiator (benzoyl peroxide) and 1% of camphorquinone (CQ) (by weight) in a 300-cm^3 beaker and stirred well. The solution is then distributed into seven test tubes (o.d. = 11.5 mm), each containing desired amount of DOP. The test tubes are then sealed with flame and put in an oven for polymerization. Seven yellowish, transparent rods are obtained after about 14 days of polymerization (10 °C per step from 40 to 170 °C, 24 h per step). Slices are cut from the rods and polished into pellets with a thickness of 2–3 mm. The pellet (one at a time) is mounted on a specially designed copper holder that is then placed in a temperature-controlled oven with glass windows to permit the transmission of laser beams. After the thermal equilibrium is reached, a holographic grating is formed by crossing two equal intensity, coherent bleaching beams from an Ar$^+$ laser operating at 4880 Å. The experimental set up is similar to that used in ref 1. The angle between the bleaching beams is varied from $\theta = 5.28°$ to $\theta = 44.6°$. The grid spacing

$$d = \lambda/(2 \sin(\theta/2))$$

(λ being the wavelength of the laser radiation in vacuum) then varies from 5.29 to 0.642 μm. This ensures that the relaxation time $\tau = d^2/4\pi^2 D$ (D being the diffusion coefficient of CQP) falls into a conveniently measurable range of our experimental setup. The detailed procedures of experimental operation, data acquisition, and the photochemistry of CQ have been discussed in detail in our previous works[2,4,5] and will not be repeated here.

The plasticizer increases the free volume and soften the polymer. It, therefore, lowers the glass transition temperature of the polymer. The glass temperature of each plasticized sample is measured with Perkin-Elmer Delta-7 DSC. The result as a function of x [x = (DOP/PS)(weight)] is shown in Table I. The uncertainty of all diffusion values is below 15%.

Results and Discussion

The time dependence of the light intensity, $I(t)$, diffracted from the induced gratings shows an unusual decay–growth–decay shape. We have shown in ref 2, 4, and 5 that this time dependence arises from the simultaneous decay of two sets of gratings with their phase shifted by π and its curve shape can be precisely described by

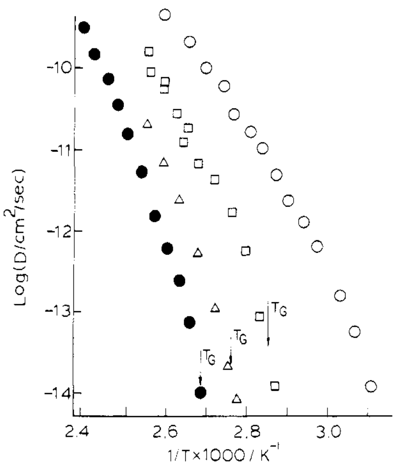

Figure 1. Temperature dependence of the diffusion coefficient of the photoproduct of camphorquinone in the polystyrene–dioctyl phthalate system, at different DOP concentrations: ●, DOP/PS = 0%; △, DOP/PS = 3.1%; □, DOP/PS = 5.3%; ○, DOP/PS = 12.4%.

$$I(t) = [Ae^{-t/\tau_1} - Be^{-t/\tau_2}]^2 \tag{1}$$

It can be shown that τ_2, the relaxation time constant associated with the diffusion of the photoproduct of CQ (CQP), is related to the slope (s) of the linear portion of the curve (see, for example, Figure 1b of ref 4) by $\tau_2 = |2/s|$; τ_2 is, in turn, related to the diffusion coefficient of CQP by $D = d^2/4\pi^2\tau_2$, where D is the coefficient of CQP and d is the grid spacing of the induced grating. We have determined all values of D by measuring s.

The temperature dependence of the diffusion coefficient of CQP in PS containing various concentrations of DOP is shown in Figure 1. The presence of plasticizer molecules causes a drastic increase in the diffusion coefficient. For example, the diffusion coefficient in PS containing 12.4% of DOP is more than 10^4 times higher than that in pure PS. This is due to the increase in free volume caused by the plasticizing effect. Further, one notes that the apparent activation energy decreases as the concentration of DOP increases.

According to the free volume concept, in a temperature range not too much higher than T_g, where the apparent activation energy E_{app} is dominantly determined by the polymer segmental motion, E_{app} can be shown to be[6]

$$E_{app} = -R\frac{\partial \ln D}{\partial (1/T)} = T^2\frac{A}{(V_{FH})^2}\frac{\partial V_{FH}}{\partial T} \tag{2}$$

where R is the gas constant and A is a constant. V_{FH} is the average size of the free volume. On the basis of eq 2, one expects a decrease in E_{app} as a concentration of the plasticizer increases.

Shown in Figure 2 is the diffusion coefficient at T = 103.3 and 107.4 °C as a function of x. One sees a drastic increase of D at small x; but as x gradually increases, the influence of the plasticizer becomes less. The dependence of D on the plasticizer concentration can be quantitatively described by free volume theory.

Ferry pointed out that at two states, 1 and 2, of the same polymer system, the shift factor a_{12}, defined as the ratio of two specific relaxation times, can be described in terms of fractional free volume f as

$$\log a_{12} = \frac{B}{2.3}\left(\frac{1}{f_2} - \frac{1}{f_1}\right) \tag{3}$$

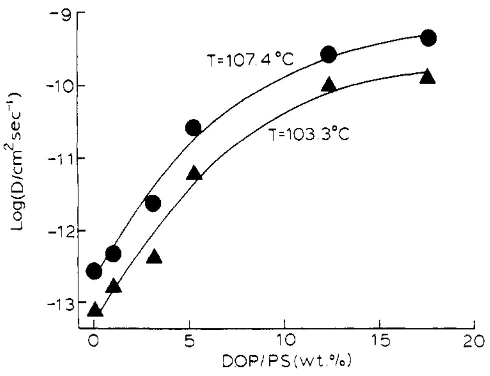

Figure 2. Diffusion coefficients of camphorquinone in the DOP–PS system, as a function of DOP concentration, at two temperatures.

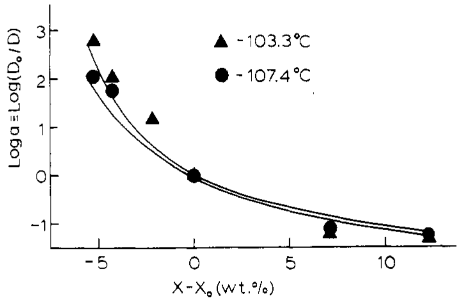

Figure 3. Fit of experimental diffusion coefficients as a function of x_0 (DOP concentration–reference DOP concentration) to the WLF equation (modified for plasticizer induced free volume increase): the reference concentration is 5.3%; ▲, T = 103.3 °C; ●, T = 107.4 °C.

where B is a constant close to unity and f_1 and f_2 are the fractional free volumes at states 1 and 2, respectively. States 1 and 2 can be due to difference in temperature, pressure, or any other quantities as long as it is associated with the change of free volume and no glass transition or any phase change is involved. In the present case, states 1 and 2 differ only in the degree of plasticization.

When the concentration of the plasticizer is not too high, it is reasonable to assume fractional free volume linearly increases with the concentration of the plasticizer or

$$f_2(T,x_2) = f(T,x_1) + \alpha(x_2 - x_1) \qquad (4)$$

where α is a proportional constant that is determined by the plasticizer's effectiveness in increasing the free volume. Inserting eq 4 to eq 3, we obtain for constant temperature

$$\log (a_x) = \log \left(\frac{D(x)}{D_0}\right) = \frac{+B}{2.3f_0}\left\{\frac{x - x_0}{f_0/\alpha + (x - x_0)}\right\} \qquad (5)$$

where a_x is the shift factor for the plasticizer concentration equal to x, x_0 is the reference concentration of the plasticizer, and D_0 is the diffusion coefficient of CQP at $x = x_0$. The fractional free volume $f(x_0) = f_0$ at $x = x_0$ is a function of temperature.

Shown in Figure 3 is the fit of the experimental points at T = 103.3 and 107.4 °C to eq 5, with x_0 being 5.26%. The fit is satisfactory and shows that eq 5 can be used to describe the change of D with the plasticizer concentration. The best fit yields values: $B/2.303f(x_0) = 6.35$, $f(x_0)/\alpha = 0.103$ for the T = 103.3 °C curve and $B/2.303f(x_0) = 6.21$, $f(x_0)/\alpha = 0.116$ for the T = 107.4 °C curve. These best fit values are qualitatively correct as B and a are constants and are not expected to change appreciably with T and x. We thus expect a lower value of $B/(2.303f(x_0))$ and a higher value of $f(x_0)/\alpha$ as T increases. This is consistent with the fit results. Due to the uncertainty in the diffusion data, we cannot determine quantitatively the change in $f(x_0)$ over the small temperature difference. However, this change is expected to be only about 10%.

Acknowledgment. Financial support from ONR and the National Science Foundation, Material Division, Polymer Program (DMR 8606884), is appreciated.

Registry No. DOP, 117-81-7; PS, 9003-53-6.

References and Notes

(1) Zhang, J.; Wang, C. H.; Chen, Z.-X. *J. Chem. Phys.* **1986**, *85*, 5359.
(2) Zhang, J.; Wang, C. H. *Macromolecules*, in press.
(3) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(4) Zhang, J.; Wang, C. H.; Ehlich, D. *Macromolecules* **1986**, *19*, 1390.
(5) Zhang, J.; Wang, C. H. *J. Phys. Chem.* **1986**, *90*, 2286.
(6) See for example: Vrentas, J. S.; Duda, J. L.; Ling, H. C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 275 and references therein.

Effect of an Inhomogeneity on Local Chain Dynamics: Conformational Autocorrelation Function

Valérie Veissier* and Jean-Louis Viovy

Laboratoire de Physico-chimie Structurale et Macromoléculaire, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France.
Received June 9, 1987; Revised Manuscript Received November 9, 1987

ABSTRACT: The influence of an inhomogeneity such as a fluorescence or ESR label on local polymer main chain dynamics is investigated theoretically by using a bistable conformational model including isolated transitions and correlated pair transitions. The conformational autocorrelation function is determined by a perturbative treatment within the limit of a far chain end inhomogeneity. The model suggests two types of behavior according to the dynamic properties of the inhomogeneity. A flexible inhomogeneity yields a decrease of the cooperative relaxation time and an increase of the main-chain mobility while the opposite case is obtained with a rigid one. The results are compared with Hall–Helfand's model, generalized diffusion and loss model, and the recent study of Pant et al. relative to the effect of a probe on polymer chain dynamics.

I. Introduction

Many studies have dealt with local dynamics in polymers since 1960. With this aim in view, correlation functions which are statistical quantities directly available to experiments have been exploited as a useful intermediary between theory and experiment. Techniques such as NMR, Kerr effect, dielectric relaxation, picosecond holographic grating spectroscopy, and fluorescence anisotropy

0024-9297/88/2221-1813$01.50/0