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Application of the Laser-Induced Holographic Grating Relaxation Technique to the Study of Physical Aging of an Amorphous Polymer

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ABSTRACT: The temperature dependence of the diffusion coefficient of diacetyl (DA) in poly(methyl methacrylate) (PMMA) in the temperature range from 96 to 130 °C is obtained by the laser-induced holographic grating relaxation technique. The relaxation time is found to increase by a factor of about 2000 as the temperature is lowered by 10 °C from 117 to 107 °C. The angular dependence study of the relaxation time at constant temperature (at 121.3 °C) indicates that, at this temperature and hence below, the relaxation of the induced grating is due to translational diffusion of DA and its photoproduct. The diffusion coefficient of DA in PMMA is measured at various isotherms below the glass transition temperature as a function of time. The results clearly show the effect of physical aging.

Introduction

When the temperature of a polymer is quenched from above to below T_g, the thermodynamic equilibrium is not established immediately. The volume and entropy of such a system are greater than what they should be in the equilibrium state. As time elapses, the thermodynamic equilibrium will eventually be established. This gradual transition to equilibrium is known as physical aging, which is to be distinguished from chemical aging.

Physical aging in polymers can proceed from minutes to years, depending on temperature and nature of the material. Physical aging affects all temperature-dependent properties which change drastically and abruptly at T_g. Many important plastic-processing techniques (e.g., extrusion and injection molding) yield products subject to effects of physical aging. Therefore, studies of physical aging are of both practical and fundamental importance.

Numerous methods have been employed to study physical aging. Among them are volume relaxation,[1] mechanical,[2] dielectric,[3] and sorption measurements.[4] Recently, Sung et al. used the rate of trans–cis photoisomerization of azo label to monitor the free volume contraction.[5] Since the diffusion coefficient is strongly affected by the free volume contraction, we report here results of the diffusion measurement using the laser-induced holographic grating relaxation (LIHGR) technique. (This technique is also referred to as forced Rayleigh scattering or holographic grating relaxation by other authors.) The principle of the LIHGR technique is given elsewhere.[6,7] The present measurements cover a range of diffusion coefficients varying from 10^{-14} to 10^{-9} cm^2/s; this is difficult to accomplish with the conventional technique. To the best of our knowledge, this is the first study of physical aging of an amorphous polymer by the LIHGR technique.

Experimental Section

The poly(methyl methacrylate) (PMMA) sample containing 0.9% diacetyl (DA) (by weight) is synthesized in our laboratory by using the free radical polymerization method. The average molecular weight is about four million, with $M_w/M_n \sim 4.3$. The glass transition temperature (T_g) is 115 °C. The polymerization and the sample preparation procedures are similar to those reported in ref 8, with the exception that DA, rather than camphorquinone (CQ), is presently used as the photochromic dye. The experimental setup and the data acquisition procedures are identical with those employed in ref 8.

For the physical aging experiments, the PMMA–DA sample is first kept at T = 135 °C for 1 day to reach thermodynamic equilibrium. The temperature of the system is then lowered and kept at a constant temperature of 114.2 °C for 1 h. Afterward, the phase grating is formed in the sample and the relaxation of the diffracted intensity is recorded at appropriate times without disturbing the temperature of the system. After the isothermal measurement at 114.2 °C is finished, the sample is reheated to 135 °C and kept at that temperature for 1 day before the temperature is lowered. The LIHGR experiment, at 110.0 and 117.8 °C are carried out in the same way.

For temperature-dependent measurements, the system is also first kept at 135 °C for 1 day. The temperature of the system is then lowered to the temperature of interest and then kept there for 1 h before the LIHGR measurement is made. Above T_g, 1 h is sufficient to ensure thermal equilibrium of the system. Below T_g, because the reach of the true thermodynamic equilibrium may be very long, the diffusion coefficients are also measured after the system is thermally stabilized (usually takes less than 1 h).

For the angular-dependent measurements, the system is equilibrated at 121.3 °C for 2 days. The relaxation time is then measured at different crossing angles.

Results and Discussion

The diffracted intensity $I(t)$ as a function of time (t) in the LIHGR measurement are well represented by two exponentials by the equation

$$I(t) = [A \exp(-t/\tau_1) + B \exp(-t/\tau_2)]^2 \qquad (1)$$

where τ_1 and τ_2 are the relaxation times associated with the diffusion of DA and its photoproduct, respectively.[6,9]

The angular dependence of τ_2 at T = 121.3 °C is shown in Figure 1; the straight line that goes through the origin suggests that the relaxation time is due to the translational mass diffusion of the photoproduct of DA. Thus, relaxations of holographic gratings below 121.3 °C are also due to mass diffusion.

According to the free volume interpretation for organic molecules diffusing in polymer hosts,[10,11] the diffusion coefficient (D) is related to the free volume by

$$\ln (D) = \ln (D_0) - K/V_f \qquad (2)$$

where D_0 is a preexponential constant corresponding to the limiting diffusion coefficient at high temperature, K is a combination of constants whose definitions are given in ref 11, and V_f is the average size of the free volume. Volume shrinkage in the physical aging process decreases V_f, which in turn results in a decrease in D, according to eq 2. Therefore, the change in D can be used to monitor the process of physical aging.

Shown in Figure 2 are the diffusion coefficient data taken at three isotherms as a function of time. For T = 114.2 °C, thermodynamic equilibrium is reached in less than 1 day, as indicated by the leveling off of the diffusion coefficient after 24 h. However, for T = 111.7 °C, it takes about 2 days to reach thermodynamic equilibrium. For

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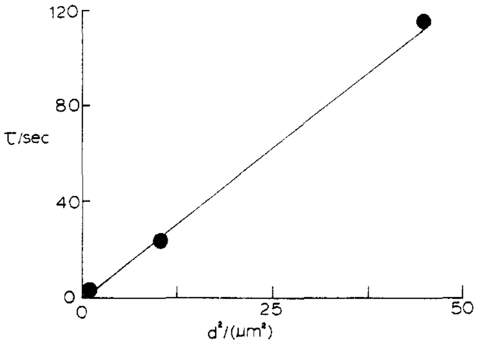

Figure 1. Angular dependence of the relaxation time τ_2 (defined in the text) measured at T = 121.3 °C. The quantity of d is the grid spacing, given by $d = (\lambda/2) \sin(\theta/2)$, where λ is the wavelength of the excitation laser and θ is the angle between two bleaching beams.

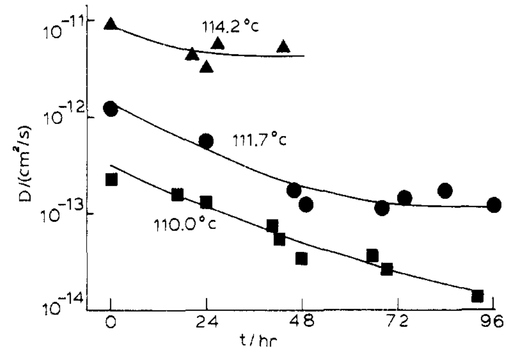

Figure 2. Diffusion coefficients taken at three isotherms as a function of time.

T = 110.0 °C, thermodynamic equilibrium is not reached even after 4 days. These isothermal results closely resemble the volume contraction measurement results of Kovacs.[1] In Figure 2, the horizontal axis is labeled with t, instead of the usual log t because of the limited time duration in the present case. However, the feature showing the effect of physical aging is apparent.

Shown in Figure 3 is the temperature dependence of the diffusion coefficient of DA in PMMA above and below T_g. In a previous paper, we reported the temperature dependence diffusion coefficient of camphorquinone (CQ) in PMMA.[6] If there is no other effect (such as hydrogen bonding), the diffusion coefficient of DA at the same temperature in the same polymer host is expected to be larger than that of CQ, due to the fact that the size of CQ is larger than that of DA. In the previous work,[6] it was difficult to obtain the diffusion coefficient of CQ in PMMA at temperatures lower than T_g, due to the fact that at T_g, the diffusion coefficient is already as low as 1.6 × 10^{-14} cm^2/s, which is about the lower limit of the measurement that can be accomplished by the present experimental setup. Like CQ, DA and its photoproducts also have good thermal stability at high temperature. Thus, in the pesent PMMA–DA system, we are able to obtain the diffusion coefficient of DA at 20 °C below T_g. This makes it possible to examine the behavior of the temperature dependence of the diffusion coefficient as T_g is traversed.

One sees in Figure 3 a sharp decrease in D in the temperature range 107.7–117.8 °C. Clearly, the sharp decrease is associated with the onset of the glass transition, which gradually freezes the mobility of the chain backbone and segmental motion. The freezing of the segmental and chain backbone motion slows down molecular diffusion on account of the retardation of free volume fluctuations. When the temperature is decreased about 10 °C from 117 to 107.7 °C, the diffusion coefficient decreases more than 3 orders of magnitude from 8.5 × 10^{-11} to 3.43 × 10^{-14} cm^2/s. Below 107.7 °C, the diffusion coefficient changes slowly with temperature.

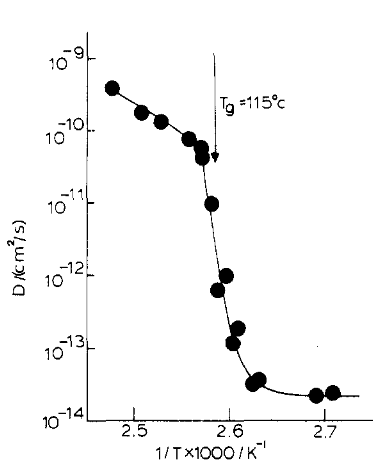

Figure 3. Temperature dependence of the diffusion coefficient of DA in PMMA.

The glass transition temperature of PMMA, as determined by DSC, is approximately 115 °C.

The rapid decrease of the mass diffusion coefficient D over the temperature range 108–118 °C is consistent with the fact that the glass transition does not occur as a point, but rather is over a range in the temperature scale. The result above and below the glass transition region (108–118 °C) is also consistent with the prediction that the activation energy above T_g is higher than that below T_g.

The unusual decrease in the diffusion coefficient observed in this system is in contrast to that of ref 12, in which no obvious change appears at T_g. However, similar phenomena have been observed in ESR studies of polymer transitions.[14,15] In an ESR experiment, one observes the line width associated with the rotational mobility of the paramagnetic probe, which is closely related to the relaxational properties of the polymer host. The sharp decrease in the rotational mobility has been observed in many polymer–probe systems.[15] The transition region from low to high mobility could be wide or narrow, depending on the size of the paramagnetic probe. Although ESR measures the rotational mobility of the paramagnetic probe and LIHGR measures the translational mobility of the diluent, the sharp increase of both types of mobility near T_g have the same origin—a combination of effects associated with a sharp decrease in the segmental mobility of the polymer host in the glass transition region and the size of the probe. One notes that the "transition region" is about 10 °C wide, which is wider than one would expect. This is probably due to the physical aging effect, since every point is taken 1 h after thermal equilibrium is reached, instead of waiting until true thermodynamic equilibrium is reached. The diffusion coefficient obtained this way is larger than that one would obtain after the true thermodynamic equilibrium is reached, resulting in a less abrupt decrease in D, or a wider transition region.

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References and Notes

(1) Kovacs, A. *J. Polym. Sci.* **1958**, *30*, 131.
(2) Petrie, S. E. B. *J. Macromol. Sci., Phys. B* **1976**, *12* (2), 225.
(3) Uchidoi, M.; Adachi, K.; Ishida, Y. *Polym. J. (Tokyo)* **1978**, *10*, 161. Guerdoux, L.; Marchal, E. *Polymer* **1981**, *22*, 1199.
(4) Chan, A. H.; Paul, D. R. *Polym. Eng. Sci.* **1980**, *20*, 87.

(5) Sung, C. S. P.; Lamarre, L.; Chung, K. H. *Macromolecules* **1981**, *14*, 1839.
(6) Zhang, J.; Wang, C. H.; Ehlich, D. *Macromolecules* **1986**, *19*, 1390.
(7) Zhang, J.; Yu, B. K.; Wang, C. H. *J. Phys. Chem.* **1986**, *90*, 1299.
(8) Zhang, J.; Wang, C. H., unpublished.
(9) Zhang, J.; Wang, C. H.; Chen, Z.-X. *J. Chem. Phys.*, in press.
(10) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(11) Vrentas, J. S.; Duda, J. L. *AIChE* J. **1979**, *25*, 1. Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 407. Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 417. Vrentas, J. S.; Duda, J. L. *Macromolecules* **1976**, *9*, 785. Ju, S. T.; Liu, H. T.; Duda, J. L.; Vrentas, J. S. *J. Appl. Polym. Sci.* **1986**, *26*, 3735.
(12) Coutandin, J.; Ehlich, D.; Sillescu, H.; Wang, C. H. *Macromolecules* **1985**, *18*, 589.
(13) The actual drop in D above and below T_g is larger than that shown in Figure 3 on account of the fact that below T_g, the system is in the nonequilibrium state and D decreases with increasing time due to physical aging.
(14) Buchachenko, A. L.; Kovarskil, A. L.; Vasserman, A. M. *Adv. Polym. Sci.* **1974**, 26.
(15) See, for example: (a) Kausler, P. L.; Foyer, R. F. *Macromolecules* **1976**, *9*, 903. (b) Rabold, G. P., *J. Polym. Sci., Part A-1* **1969**, *7*, 1203. (c) Gross, S. C. *J. Polym. Sci., Part A-1* **1971**, *9*, 3327.

Assessment of Bond Rotation Interdependence in Polymer Chains: An Information Theory Approach

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ABSTRACT: Measures of randomness from information theory are adapted so that they test the correlation of rotational states in a chain molecule. One term measures the equiprobability of the rotational states. This term is simply the well-known expression for the entropy of mixing of an ideal solution, recast in the jargon of information theory. The more interesting second term measures the interdependence of the bond rotations. This term arises from the contribution of preferential nearest-neighbor interactions to the entropy of mixing of a nonideal one-dimensional system. The behavior of these two terms is examined in detail for infinitely long simple chains in which bonds are subject to symmetric threefold rotation potentials. In the special case of linear polyethylene, the distribution becomes more equiprobable upon an increase in temperature, but there is virtually no change in interdependence due to the nearly exact compensation of two competing effects. Illustrative calculations for poly(vinyl acetate) demonstrate that microstructure can have a large influence on both the equiprobability and the interdependence of the distribution of rotational states.

Introduction

Many configuration-dependent physical properties of unperturbed chains are successfully rationalized by application of the rotational isomeric state approximation.[1-3] The most common situation, in which rotations about consecutive bonds are interdependent, can be treated to any desired degree of approximation by formulation of the configuration partition function as a product of statistical weight matrices. Bonds are independent in the special case where each statistical weight matrix has identical rows.

While it is easy to distinguish between chains with independent and interdependent bonds, it is often a more difficult task to assess which of two real chains has the greater degree of interdependence of bond rotations. For example, in which member of the following pairs of chains are the bond rotations more interdependent: Polyethylene with 10 and 20 bonds? Long polyethylene chains at 300 and 400 K? *meso*- and *rac*-poly(vinyl acetate)? Poly(vinyl bromide) and poly(vinyl chloride)? Poly(oxyethylene) and poly(vinylidene chloride)? Unambiguous answers to these questions are possible if there is access to a singe quantitative measure of the interdependence of bond rotations that can be applied to *all* of these chains. An appropriate measure can be formulated by utilization of concepts from information theory. The formulation is accomplished here. Illustrative applications are made to simple chains with threefold rotation potentials and to poly(vinyl acetate).

Measures of Equiprobability and Interdependence

Rotational States as Characters of an Alphabet. The discussion is in terms of a chain that has ν rotational states for each internal bond. Several common chains have $\nu = 3$, with the rotational states designated as t (trans), g^+ (gauche$^+$), and g^- (gauche$^-$). Each real chain of n bonds may be mapped as a sequence of $n - 2$ characters selected from ν possibilities. This map bears an analogy to an information message encoded by a string of characters (such as the present text), where the maximum number of distinguishable characters is ν. However, this analogy is limited, because the information in the conformation of a polymer chain is not targetted to a receiver, in contrast with a DNA sequence, which contains a measurable quantity of information in the sequence of nucleotides that is transmitted to the cellular protein synthetic machinery throuch the messenger RNA.

Measures of Randomness from Information Theory. The a priori probability for a specified pair of rotational states at bond $i - 1$ and i, denoted by $p_{\xi\eta;i}$, is easily extracted from Z by matrix methods that evaluate the partial derivative shown in eq 1.[2,3] In eq 1 $w_{\xi\eta;i}$ is the

$$p_{\xi\eta;i} = \partial \ln Z / \partial \ln w_{\xi\eta;i} \tag{1}$$

statistical weight for bond i in state η when bond $i - 1$ is in state ξ. The first-order probability, $p_{\eta;i}$, that bond i is in state η is given by eq 2, and the second-order conditional probability, $q_{\xi\eta;i}$, is given by eq 3. Averages over all choices

$$p_{\eta;i} = \sum_{\xi=1}^{\nu} p_{\xi\eta;i} \tag{2}$$

$$q_{\xi\eta;i} = p_{\xi\eta;i} / p_{\xi;i-1} \tag{3}$$

for the subscript i are denoted more simply by p_η and $q_{\xi\eta}$.

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