Physical Aging Effects on Molecular-Scale Polymer Relaxations Monitored with Mobility-Sensitive Fluorescent Molecules

J. Scot Royal[†,‡] **and John M. Torkelson***[‡,§]

Departments of Materials Science and Engineering and of Chemical Engineering, Northwestern University, Evanston, Illinois 60208-3120

Received September 10, 1992; Revised Manuscript Received November 30, 1992

ABSTRACT: The fluorescence response of a mobility- or free volume-sensitive molecule, julolidenemalononitrile (JMN), is shown to be affected by the relaxations that occur on the molecular scale during physical aging in various glassy polymers including polystyrene, polycarbonate, poly(methyl methacrylate), and poly(isobutyl methacrylate). In general, the change in fluorescence intensity is approximately linear with logarithmic aging time as has been found in bulk volume and enthalpy relaxations. Near the glass transition temperature, JMN monitors the relaxations until equilibrium is reached where the fluorescence response maintains a constant value. Additionally, the physical aging rate was found to depend on temperature in all polymers as has been observed in bulk specific volume behavior. The temperature trends found in polystyrene, poly(methyl methacrylate), and polycarbonate with the molecular fluorescence technique agree well with those from specific volume relaxation. These results provide experimental evidence of how the molecular environments contribute to the traditionally observed bulk properties.

Introduction

When an amorphous material is quenched from the liquid state to a temperature below the glass transition temperature, T_g, and held there, the resulting nonequilibrium glass will attempt to relax toward equilibrium in a process referred to as "physical aging".[1] As with chemical aging (e.g., degradation), physical aging results in time-dependent changes in the properties of materials. Quantities known to change during physical aging of polymers include specific volume, enthalpy, and mechanical behavior such as creep rate or ultimate elongation. However, the effects of physical aging may be erased completely by heating the sample above T_g into the rubbery state for a time which brings the system back to an equilibrium liquid; thus, physical aging is thermoreversible.

Greiner and Schwarzl[2] demonstrated that the specific volume decreases approximately linearly with logarithmic aging time during physical aging of polystyrene (PS) at various temperatures below T_g. Near T_g, the volume decreases for a time and then reaches a plateau indicating that the bulk specific volume has relaxed to equilibrium. They demonstrated clearly that equilibrium is not reached on useful experimental time scales when physical aging is performed at temperatures much below T_g. For example, the specific volume of polystyrene does not reach equilibrium at 90 °C after 4 months of aging (dilatometric T_g = 95 °C at a cooling rate of 1 K/min).[2] Similar volume responses have been observed in many amorphous polymers including poly(methyl methacrylate) (PMMA),[2,3] polycarbonate (PC),[2,4] poly(vinyl acetate) (PVAc),[5] and poly(vinyl chloride) (PVC).[2] Kovacs[5] also showed that physical aging affects the specific volume of many glass-forming materials including small-molecule glucose and borosilicate glasses.

Many authors have shown that the effects of physical aging on specific volume are dependent on the aging temperature.[1,2,4,5] At temperatures very near T_g, the volume relaxes to equilibrium on accessible time scales to produce an equilibrium plateau. At temperatures far below T_g, the volume changes little at early times, producing an "initial plateau" which has been observed in PS,[2,6] PC,[2,4] and PVAc.[5] This initial plateau is not associated with a slow attainment of thermal equilibrium after the thermal quench as it can last up to 1 day at 25 °C in PS.[2]

The slope of the volume change between the initial and equilibrium plateaus is associated with the rate of physical aging (r) which has been defined[1,2,4] as

$$r = -\frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}\log t_A} \qquad (1)$$

where v is the specific volume at aging time t_A. Plotting the aging rate, r, versus the aging temperature after 12 days of aging, Greiner and Schwarzl[2] constructed temperature-dependent aging rates for PS, PMMA, PC, and PVC. In general, as the temperature decreases below T_g, the aging rate increases to a maximum and then decreases. This temperature dependence of the aging rate is due to a competition between the thermodynamic driving forces promoting aging and the mobility that allows the volume relaxations to occur. Near T_g, the thermodynamic driving force from the thermal quench is small, and the mobility is large relative to that at a lower temperature. The small thermodynamic driving force dominates the large mobility to produce a slow aging rate. Deeper thermal quenches below T_g increase the thermodynamic driving force but decrease the mobility to give a slow aging rate. Somewhere, a synergism occurs between the thermodynamics and kinetics to produce a maximum in the aging rate. Greiner and Schwarzl[2] found that the maximum aging rates are within 25 °C, of T_g for PS, PC, and PVC. However, they reported that the maximum aging rate for PMMA occurred near its secondary transition temperature around 30 °C (T_g - 75 °C).

As with volume, other thermodynamic state variables such as the enthalpy are affected by the relaxation behavior of amorphous materials. Similar to volume relaxation, the enthalpy in excess of the equilibrium value relaxes approximately linearly with logarithmic physical aging times in PS[7] and PMMA[8] but apparently with longer relaxation times than volume relaxation.[9,10] The volume and enthalpy will relax to equilibrium on useful time scales if physical aging is performed at temperatures very near the phenomenological T_g.[6] Enthalpy relaxation has also

---

[*] To whom correspondence should be addressed.

[†] Present address: Monsanto Co., Springfield, MA 01101.

[‡] Department of Materials Science and Engineering.

[§] Department of Chemical Engineering.

0024-9297/93/2226-5331$04.00/0

been monitored in other polymer systems including PVAc[5,11-13] and PC,[14] as well as in nonpolymer glasses.[14]

Monitoring the time-dependent specific volume, enthalpy, or mechanical properties during physical aging provides useful information for the changes occurring on the macroscopic scale but does not provide any direct information on the molecular-scale behavior of the system. Many techniques have been employed to study the molecular or microscopic origins of macroscopic responses during behaviors such as physical aging including positron annihilation spectroscopy,[15-17] dielectric relaxation,[11,18,19] X-ray scattering,[3] and probe techniques (electron spin resonance,[4,20,21] photochromic,[22,23] second-order nonlinear optical,[24,25] and fluorescence[13,26-28]). It should be noted that the applicability of one of these techniques, positron annihilation spectroscopy, to monitor physical aging effects has recently come into question.[29,30]

In previous publications,[13,28] we demonstrated the sensitivity of the fluorescence probe julolidenemalononitrile (JMN) to polymer relaxation behavior from a molecular perspective. Behaviors such as asymmetry,[5] the τ_{EFF} paradox,[5] memory effects,[5] and plasticization were all reproduced with very good agreement with the general relaxation behavior traditionally monitored on the bulk scale.[13] In this study, the effects of physical aging on the molecular-scale behavior of various polymer glasses were studied and compared to bulk specific volume results in order to provide further insight into the molecular contributions to bulk-scale polymer relaxation behavior.

Experimental Section

Most polymers used in this study were purchased and used as received. Nearly monodisperse polystyrene (PS; nominal MW = 625 000; $M_w/M_n \leq 1.06$; T_g = 103 °C) and poly(methyl methacrylate) (PMMA; nominal MW = 265 000; $M_w/M_n \leq 1.15$; T_g = 105 °C) were purchased from Pressure Chemical. A polydisperse Bisphenol A polycarbonate secondary standard (PC; nominal MW = 28 800; $M_w/M_n = 1.66$; T_g = 145 °C) was purchased from Scientific Polymer Products, Inc., and gave optically clear films above 275 nm. Commercially available poly(isobutyl methacrylate) (PiBMA) caused photobleaching of the fluorescent probes. Therefore, PiBMA was synthesized by free-radical polymerization at 70 °C for 1 h with benzoyl peroxide as initiator and cleaned by reprecipitation from acetone and methanol five times. Gel permeation chromatography of PiBMA in benzene at 25 °C gave a peak molecular weight of about 1×10^6, and differential scanning calorimetry gave an onset glass transition temperature of 60 °C. The fluorescent probe, julolidenemalononitrile (JMN; Molecular Probes), was used as received.

All polymer films were solution cast onto 2 in. × 2 in. H-grade (transparent above 275 nm) or Q-grade (transparent above 220 nm) quartz slides from 7-10 wt % polymer solutions in spectrophotometric-grade dichloromethane (Aldrich) containing appropriate amounts of fluorescent probe. Films were dried in the following manner. After solutions were poured onto quartz slides, the slides were covered with a Petri dish to slow the evaporation process. (Fast evaporation of the dichloromethane can lead to a very rough film surface and segregation of the probe to the outer edges of the film.) PS and PC films were dried under the Petri dish (in the dark) at room temperature for 1 day and PiBMA and PMMA films for 1 week before drying in a vacuum oven at 80 °C for 3 days to remove residual solvent. Probe concentrations ranged from 0.004 to 0.007 wt % in dry polymer films. Bulk properties such as T_g or enthalpy were unaffected by the presence of this low concentration of probe.

Steady-state fluorescence spectra of sample films in a specially designed film holder were recorded as a function of time with a SPEX Fluorolog-2 DM1B fluorimeter in a front-face mode. The wavelength of light used to excite the sample is selected with a monochromator positioned between the sample and a xenon arc lamp light source. The irradiation wavelength used for JMN was the absorbance maximum of 450 nm (Figure 1 was obtained with an irradiation wavelength of 430 nm); emission intensities were monitored at the emission maximum in each polymer system. Two improvements have been made to the instrument to reduce systematic errors from scan to scan. This instrument uses the fluorescence of a rhodamine B/propylene glycol (8 g/L) reference to correct for lamp intensity fluctuations. Since fluorescence intensity is sensitive to temperature, the temperature of the rhodamine B reference has been stabilized by placing the solution in a water-jacketed quartz cuvette and connected to a circulating water bath with temperature control of ±0.5 °C. Additionally, the mirrors have been focused to give the largest possible signal to noise ratio when sample films are studied. With these improvements to the fluorimeter, the fluorescence intensity errors become equal to or less than ±0.2% when the system has stabilized.

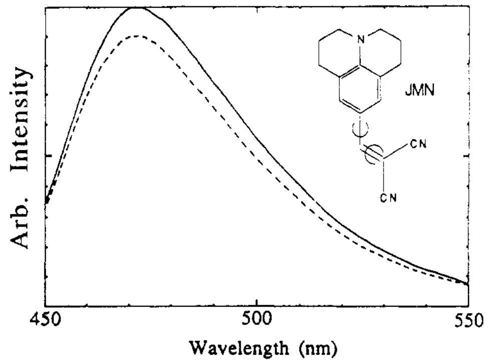

Figure 1. Chemical structure (illustrating potential internal conversion pathways) and fluorescence emission spectrum of JMN in polystyrene after (- - -) 1 min or (—) 6 h of physical aging at 60 °C.

Temperature jumps were accomplished in two ways. For polymers with T_g > 100 °C, the thermal history was erased in an oven with no vacuum at T_g + 20 °C for at least 30 min. The film was then removed, placed into the temperature-controlled cell, and quenched with the water bath (Neslab Endocal RTE-9 with ±0.05 °C temperature control). Thermal equilibrium occurred in less than 5 min. For polymers with T_g < 100 °C, the thermal history was erased above T_g for at least 30 min in the film holder using one water bath. The temperature was changed by rapidly switching to another water bath at the desired relaxation temperature. Thermal equilibrium was attained in less than 30 s for jumps smaller than 15 °C and in less than 1 min for jumps smaller than 50 °C.

All glass transition temperatures were taken as the onset temperature[31] of a heat capacity change of each polymer in hermetically sealed pans in a Perkin-Elmer DSC-2 differential scanning calorimeter using 40 K/min cooling rates and 10 K/min heating rates.

Results and Discussion

Loutfy[32] first described the excited molecular rotation of JMN (shown in Figure 1) and other similar molecules. After absorbing light and being elevated to a singlet excited state, JMN has two major pathways for returning to the ground state. The preferred deactivation route is nonradiative rotational deactivation involving bond rotations around the bond joining the phenyl and vinyl group or the isomerization-like motion of the malononitrile around the vinyl group. Hindering these rotations causes the probes to deactivate by fluorescence. Thus, the probe fluorescence intensity, quantum efficiency, and lifetime will increase when the local rigidity surrounding the probe increases. Physical aging is known to decrease the mobility of polymers[1] and would therefore be expected to affect the probe rotation abilities.

Figure 1 shows the fluorescence emission spectrum of the probe JMN in PS 1 min and 6 h after a quench from 120 °C (T_g + 20 °C) to 60 °C. After 6 h, the fluorescence intensity at the emission maximum increases by 10%

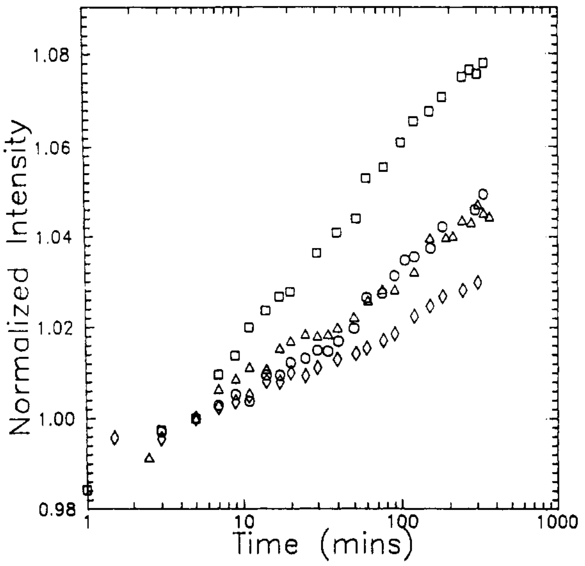

Figure 2. Normalized fluorescence intensity of JMN in polystyrene (T_g = 103 °C) at the emission maximum as a function of physical aging time after thermal quenches from 120 °C to (△) 90, (□) 60, (○) 30, or (◇) 20 °C. The slopes are related to the polymer physical aging rate.

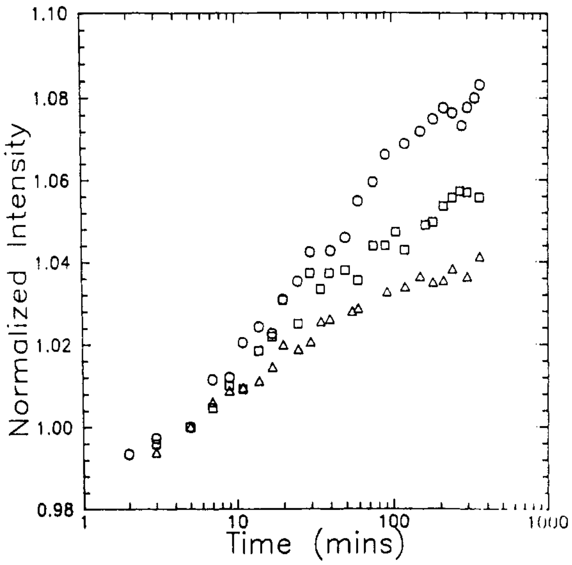

Figure 3. Temperature dependence of the physical aging rate of poly(methyl methacrylate) (T_g = 105 °C) as sensed by JMN after thermal quenches from 125 °C to (○) 30, (□) 60, or (△) 15 °C.

compared to the sample aged for just 1 min. The intensity depends on temperature and mobility, as does the quantum efficiency. For this particular experimental setup, the intensity also depends on probe concentration and film thickness. Since these two emission spectra were recorded from the same film at the same temperature, the only contribution to changes in intensity would be changes in the mobility or free volume surrounding the JMN probes. Thus, structural changes taking place in the polymer film during 6 h of physical aging increasingly hinder the intramolecular motions of JMN, causing a 10% increase in the fluorescence intensity. In addition to the magnitude of polymer relaxation reported by the JMN fluorescence, the time-dependent fluorescence response during polymer relaxations provides a measure of the rate of physical aging of the polymer.

Figure 2 is a plot of the time-dependent fluorescence intensity at the emission maximum of JMN in PS during physical aging at different temperatures. The responses were normalized to a value of 1 after 5 min of aging to ensure thermal equilibrium had been established after the quench from above T_g. In addition, normalizing the data allows the relative intensity changes that occur during physical aging at different temperatures and in different films to be compared directly. Such comparison is possible since absolute intensity differences for a given polymer caused by different temperatures, film thicknesses, and/or probe concentrations between experiments are normalized out.

The fluorescence response to physical aging is approximately linear with logarithmic time similar to specific volume[2] and enthalpy[7] responses. A total 6 h of aging at 60 °C causes an 8% increase in the fluorescence intensity relative to the reference state at 5 min of aging. Greiner and Schwartz[2] found that the specific volume decreased only 0.002 cm^3/g in 6 h which is only about a 0.2% change. From this comparison, it would appear that the JMN probe is more sensitive to physical aging effects than dilatometry. However, a more meaningful comparison of the sensitivity to physical aging of the two techniques may be made by defining a sensitivity ratio as the uncertainty in each data point divided by the overall change that occurs in a given aging time. Kovacs[5] has reported the smallest error in specific volume measurements at $\pm 1 \times 10^{-5}$ cm^3/g. Assuming the uncertainty in Greiner and Schwarzl's data is this low, the sensitivity ratio of the specific volume for physical aging of PS at 60 °C for 6 h is 0.005 (10^{-5} cm^3 g^{-1}/0.002 cm^3 g^{-1}). The uncertainty in the fluorescence data at 60 °C is ±0.2% (from a linear least-squares fit), giving a sensitivity ratio of 0.05. The second smallest uncertainties in specific volume measurements were recently reported by Santore et al.[33] at 2×10^{-5} cm^3/g. Therefore, assuming the best specific volume conditions ever reported and an average case for the fluorescence technique in PS, specific volume may detect changes 5–10 times smaller than this fluorescence technique during physical aging. While both techniques have higher sensitivities to aging than other techniques commonly used to monitor relaxation such as viscoelastic methods, the fluorescence technique requires <0.5 g of the polymer sample and is less tedious to use than dilatometry.

Figure 2 also shows that the slope of the JMN fluorescence response to physical aging depends on the aging temperature in a nonstraightforward manner. The slopes are related to the physical aging rate of the polymer as discussed previously. Thus, these data indicate that, for the aging temperatures studied, PS ages fastest at 60 °C, slower at 30 or 90 °C which are similar, and slowest at 20 °C. This temperature dependence of the physical aging rate sensed by JMN is in excellent agreement with the bulk specific aging rate–temperature trend for PS reported by Greiner and Schwarzl.[2] Hence, this technique that senses changes in mobility and free volume on the molecular scale gives the same aging–rate temperature trend as a technique that monitors macroscopic properties. These results are direct experimental evidence that bulk relaxations are manifestations of molecular-scale processes.

Greiner and Schwarzl[2] also found temperature-dependent aging rates in other polymers as well. Figure 3 shows the normalized intensity of JMN as a function of aging time in PMMA at various aging temperatures. The slopes are approximately linear and depend on the aging temperature as was found in PS. The aging rate sensed by JMN in PMMA decreases in the order 30 °C > 60 °C > 15 °C which agrees well with the bulk dilatometric findings.[2] Larger error in the fluorescence intensity from one data point to another is seen in PMMA than in PS because PMMA films detach easily from the quartz slides.

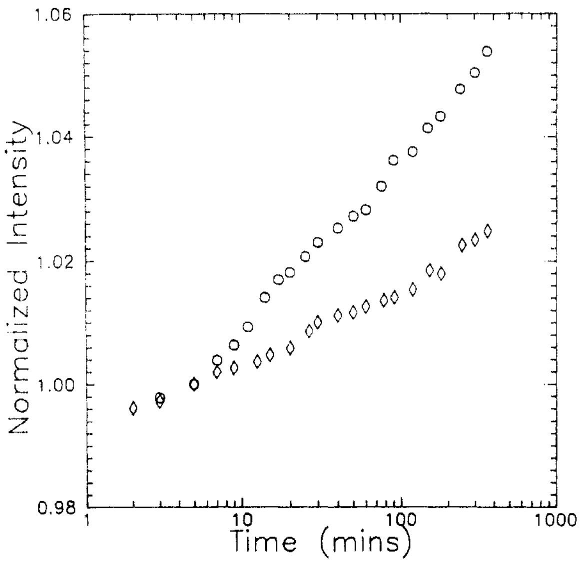

Figure 4. Temperature dependence of the physical aging rate of polycarbonate (T_g = 145 °C) as sensed by JMN after thermal quenches from 165 °C to (○) 95 or (◇) 30 °C.

While the results in Figures 2 and 3 clearly show a simple, strong correlation between fluorescence intensity and specific volume aging data as a function of aging temperature in a given polymer, the correlation between polymers is more complex. For example, the ratio of specific volume aging rate[2] in PS to that in PMMA at 60 °C is approximately 1.4; the ratio of fluorescence aging rates at 60 °C is approximately 1.3. The similarity in ratios despite potential differences in polymers might be used to suggest a simple, direct correlation across polymer types. However, a comparison of aging rates at 30 °C reveals that such a simple, direct correlation is not valid. While the ratio of specific volume aging rates in PS to that in PMMA is slightly greater than 1, the ratio of fluorescence intensity aging rates is almost 2. Given that the fluorescence behavior of a charge transfer probe such as JMN is expected to be a function of matrix polarity[32,34] and is a reflection of the local conformational arrangement and rigidity of its environment on time scales related to its excited-state lifetime (less than 1 ns in these glassy polymer matrices[35]), it is logical that a simple correlation across polymer types may not exist. Further study will be required to assess how fluorescence sensitivity in different polymers may allow for comparison of polymer properties.

Figure 4 shows the fluorescence response of JMN during physical aging of PC at 30 and 95 °C. The temperature dependence of the physical aging rate for these two data sets agrees well with dilatometric results[2,4] for the temperature range studied. The errors are much smaller in PC since it produces better films. The maximum dilatometric aging rate is reported to be near 125 °C.[2,4] However, in situ monitoring of aging could not be performed with the fluorescence technique above 96 °C since water was used for temperature control. Figure 4 also shows that the fluorescence technique senses aging effects in PC at T_g - 115 °C. While specific volume may detect physical aging effects on PC at these low temperatures after a few days of aging, other techniques such as enthalpy relaxation[36] have been shown to be insensitive at such deep quenches, leading to the conclusion that PC does not age at low temperatures. Thus, the fluorescence technique appears to be very sensitive to subtle polymer relaxation behavior that may be difficult to follow with traditionally employed techniques.

Figure 5 shows the JMN fluorescence response to physical aging in poly(isobutyl methacrylate) (PiBMA) (DSC onset T_g = 60 °C) at various aging temperatures. These data have been normalized to a value of 1 after 1 min of aging since thermal equilibrium is attained in less than 1 min when temperature jumps are performed with two water baths. As was seen in PS, PMMA, and PC, the aging rate given by the slope of the fluorescence response depends on the aging temperature (T_A). For the temperature range studied here, Figure 5 shows that the aging rate in PiBMA increases as the value of $T_g - T_A$ increases and that JMN is able to detect aging rate differences near the DSC T_g even when the aging temperatures differ by only 2 °C. Generally, the data are linear with logarithmic aging time as was seen in other polymers.

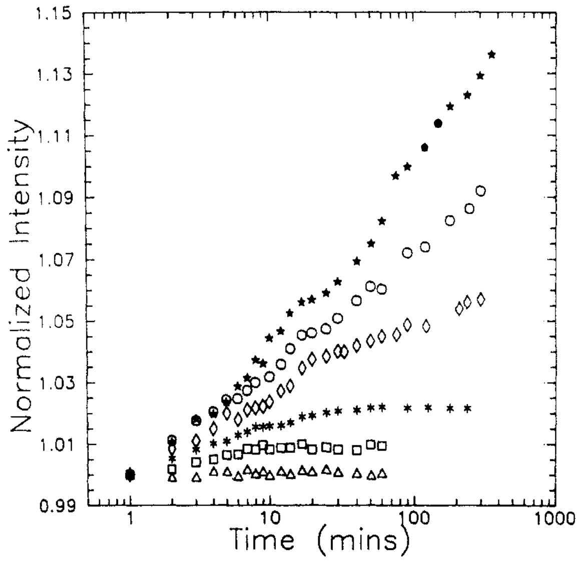

Figure 5. Temperature dependence of the physical aging rate of poly(isobutyl methacrylate) (T_g = 60 °C) as sensed by JMN after thermal quenches from 65 °C to (△) 62, (□) 60, (*) 58, (◇) 50, (○) 40, (★) 25 °C.

The temperature where the maximum aging rate occurs has not been identified in PiBMA because aging experiments were not carried out to low enough temperatures where the aging rate would begin to slow due to the loss of mobility from the deep quench below T_g. It is perhaps not surprising that the maximum aging rate was not found in this temperature range considering the specific volume results of Greiner and Schwarzl.[2] In their study, the temperatures of the maximum aging rate for PS, PC, and PVC fall between T_g - 20 °C and T_g - 30 °C. Thus, the maximum aging rate for PiBMA may be near 25 °C. However, PiBMA and PMMA are both methacrylates, so it is possible that the maximum aging rate could occur at much lower temperatures relative to T_g as with PMMA (T_g - 75 °C).

Figure 6 shows in greater detail the physical aging responses near the T_g of PiBMA. Although the overall changes in fluorescence intensity with aging are small, the point-to-point errors are much smaller, about ±0.1%, allowing for easy interpretation of aging effects. Results of the temperature-dependent aging studies at 58, 60, and 62 °C indicate that at some time the fluorescence responses level off, suggesting that the environments sensed by the JMN probes have reached equilibrium. These results are very similar to those reported previously[13] for the fluorescence response of JMN near the T_g of PVAc. Actually, the fluorescence response after a jump from 65 to 62 °C in PiBMA remains constant throughout the experiment, showing that the structural rearrangement after the jump reached equilibrium before 1 min of aging. This is not surprising since Kovacs[5] showed that the specific volume

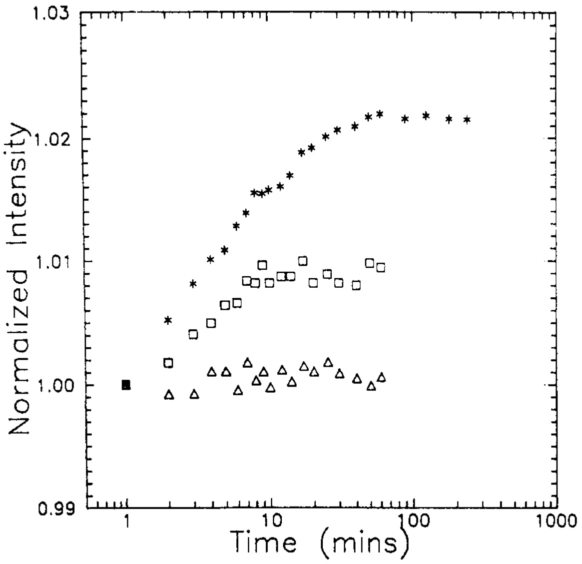

Figure 6. Fluorescence response of JMN near the T_g of PiBMA after thermal jumps from 65 °C to (△) 62, (□) 60, (*) 58 °C. For jumps near T_g of PiBMA, equilibrium is monitored by JMN.

reached equilibrium in under 6 min after jumps from $T_g + 30$ °C to $T_g + 5$ °C in PVAc. The fluorescence responses of JMN at 60 and 58 °C show that the times required to reach equilibrium become longer as $T_g - T_A$ becomes larger in agreement with bulk specific volume results.[2,5]

In this study, the mobility or free volume sensitivity of the probe JMN to physical aging processes has been displayed in many polymer glasses. As was found for other relaxation behaviors such as asymmetry and memory effects,[13,28] physical aging affects the molecular-scale polymer behavior monitored by JMN in manners similar to that observed on the bulk scale. Photochromic studies in polymers[23] indicate that the rate of motion of a probe is determined in part by the size of its rotating substituents. Thus, probes that require different amounts of free volume to perform their various mobility- or free volume-sensitive motions will sample different fractions of the free volume distribution. With such sensitivity, the shape and behavior of the free volume distribution during polymer relaxations may be better characterized, and concepts such as thermorheological simplicity may be addressed from a molecular perspective. Results of such studies will be the subject of a subsequent manuscript. Comparison of the excited molecular rotation of JMN (monitored by fluorescence) to the rotational diffusion of JMN (monitored by second-harmonic generation[37]) in amorphous polymers is also underway.

Acknowledgment. The authors acknowledge the support of IBM in the form of a graduate fellowship (J.S.R.) and the National Science Foundation in the form of support from the Northwestern University Materials Research Center (J.S.R., J.M.T.) and from a Presidential Young Investigator Award (J.M.T.).

References and Notes

(1) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, The Netherlands, 1978.
(2) (a) Greiner, R.; Schwarzl, F. R. *Rheol. Acta* **1984**, *23*, 378. (b) Greier, R.; Schwarzl, F. R. *Colloid Polym. Sci.* **1989**, *267*, 39.
(3) (a) Curro, J. J.; Roe, R.-J. *Polymer* **1984**, *25*, 1424. (b) Roe, R.-J.; Curro, J. J. *Macromolecules* **1983**, *16*, 428–434.
(4) Bartos, J.; Muller, J.; Wendorff, J. H. *Polymer* **1990**, *31*, 1678.
(5) Kovacs, A. J. *Fortschr. Hochpolym., Forsch. Bd.* **1963**, *3*, 394.
(6) Adachi, K.; Kotaka, T. *Polym. J.* **1982**, *14*, 959.
(7) Marshall, A. S.; Petrie, S. E. B. *J. Appl. Phys.* **1975**, *46*, 4223.
(8) Yoshida, H.; Kobayashi, Y. *J. Macromol. Sci., Phys.* **1982**, *B21*, 565.
(9) Petrie, S. E. B. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 1255.
(10) Bauwens-Crowet, C.; Bauwens, J.-C. *Polymer* **1986**, *27*, 709.
(11) Baer, H. E.; Johnson, G. E.; Anderson, E. W.; Matsuoka, S. *Polym. Eng. Sci.* **1981**, *21*, 930.
(12) Wang, C.-H.; Filisko, F. E. *Polym. Mater. Sci. Eng.* **1990**, *60*, 782.
(13) Royal, J. S.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 1705.
(14) Hodge, I. M. *Macromolecules* **1987**, *20*, 2897.
(15) Kobayashi, Y.; Zheng, W.; Meyer, E. F.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *Macromolecules* **1989**, *22*, 2302.
(16) Hill, A. J.; Jones, P. L.; Lind, J. H.; Pearsall, G. W. *J. Polym. Sci., Polym. Phys.* **1988**, *26*, 1541.
(17) (a) Malhorta, B. D.; Pethrick, R. A. *Eur. Polym. J.* **1983**, *19*, 457. (b) Malhorta, B. D.; Pethrick, R. A. *Polymer* **1983**, *24*, 165.
(18) Matsuoka, S.; Williams, G.; Johnson, G. E.; Anderson, E. W.; Furakawa, T. *Macromolecules* **1985**, *18*, 2652.
(19) Schlosser, E.; Schönhals, *Polymer* **1991**, *32*, 2135.
(20) Tsay, F. D.; Hong, S. D.; Moacanin, J.; Gupta, A. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *20*, 763.
(21) Bartos, J.; Szöcs, F.; Klimova, M.; Müller, J. *J. Polymer* **1992**, *33*, 3536.
(22) (a) Lamarre, L.; Sung, C. S. P. *Macromolecules* **1983**, *16*, 1729. (b) Yu, W. C.; Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355.
(23) (a) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 3490. (b) Royal, J. S.; Victor, J. G.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 729. (c) Royal, J. S.; Victor, J. G.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 4792.
(24) (a) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 3648. (b) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 625. (c) Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. *ACS Symp. Ser.* **1991**, *455*, 294.
(25) Hayden, L. M.; Sauter, G. F.; Ore, R.; Pasillas, P. L.; Hoover, J. M.; Lindsay, G. A. *J. Appl. Phys.* **1990**, *68*, 456.
(26) Guo, R. K.; Tazuke, S. *Macromolecules* **1989**, *22*, 3286.
(27) Meyer, E. F.; Jamieson, A. M.; Simha, R.; Palmen, J. H. M.; Booij, H. C.; Maurer, F. H. J. *Polymer* **1990**, *31*, 243.
(28) Royal, J. S.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 3536.
(29) O'Connor, P. J.; Kocher, C. W.; Landes, B. G.; Anderson, S. L.; Delassus, P. T.; Grulke, E. A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1992** *33* (2), 308.
(30) Welander, M.; Maurer, F. H. J. *Mater. Sci. Forum* **1992**, *105–110*, 1811.
(31) Rabek, J. F. *Experimental Methods in Polymer Chemistry*; Wiley: New York, 1980, p 565.
(32) (a) Loutfy, R. O.; Law, K. Y. *J. Phys. Chem.* **1980**, *84*, 2803. (b) Loutfy, R. A. *Macromolecules* **1981**, *14*, 270. (c) Loutfy, R. O.; Arnold, B. A. *J. Phys. Chem.* **1982**, *86*, 4205. (d) Loutfy, R. O. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 825. (e) Loutfy, R. O.; Teegarden, D. M. *Macromolecules* **1983**, *16*, 452. (f) Loutfy, R. A. *Pure Appl. Chem.* **1986**, *58*, 1239.
(33) Santore, M. M.; Duran, R. S.; McKenna, G. B. *Polymer* **1991**, *32*, 2377.
(34) van Ramesdonk, H. J.; Vos, M.; Verhoeven, J. W.; Mohlmann, G. R.; Tissink, N. A.; Meesen, A. W. *Polymer* **1987**, *28*, 951.
(35) Royal, J. S. Ph.D. Thesis, Northwestern University, Evanston, IL, 1992.
(36) Muller, J.; Wendorff, J. H. *J. Polym. Sci., Polym. Lett.* **1988**, *26*, 421.
(37) Dhinojwala, A.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 7395.