Molecular-Scale Asymmetry and Memory Behavior in Poly(vinyl acetate) Monitored with Mobility-Sensitive Fluorescent Molecules

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ABSTRACT: A fluorescence technique employing a mobility-sensitive fluorescence molecule (julolidenemalononitrile, JMN) is shown to sense the molecular relaxations occurring after temperature jumps in glassy and rubbery poly(vinyl acetate) (PVAc). Results suggest that molecular environments relax in a manner similar to bulk relaxations. After temperature jumps near T_g, the technique senses when the local probe environments reach equilibrium, and bulklike "asymmetry" behavior is shown to occur on the local level. The molecular mobility sensor, JMN, reproduces all details found in bulk volume or enthalpy asymmetry, including the τ_{eff} paradox. After multiple temperature jumps, the fluorescence technique also detects "memory effects" on the molecular scale. In addition, this technique senses the increase in mobility caused by the plasticization of PVAc by water which decreases the times needed to reach fluorescence equilibrium at a particular temperature. However, these equilibrium times are constant for a given value of $T_g - T_a$ (T_a = annealing temperature) regardless of water content. Since a short exposure to humid air can severely plasticize PVAc, it is concluded that T_g is a very important reference point for making comparisons of PVAc properties or attempting to extract meaningful parameters from theoretical fits of relaxation data. The sensitivity of the fluorescence technique to the relaxation time scales in PVAc is similar to that of dilatometry and bulk enthalpy relaxation.

Introduction

A glass-forming system cooled from above to below its glass transition temperature (T_g) has a nonequilibrium structure that continually relaxes toward thermodynamic equilibrium.[1,2] Since relaxation times in the glassy state are much longer than in the liquid or rubbery state,[3] glasses may not reach equilibrium on easily accessible experimental time scales even if the system is relatively near T_g. For example, the specific volume of polystyrene requires approximately 5 months to reach equilibrium after a simple temperature jump from above T_g to 90 °C (5 °C below T_g measured by dilatometry at 1 K/min).[4] Furthermore, relaxation behavior becomes very complex if a system is disturbed while relaxing from prior perturbations.[1,5] Relaxations in liquids and glasses may be induced in many ways including temperature[1,4,5] and pressure[6-8] jumps, strains,[9-11] plasticization,[3,11,12] and blending.[13,14]

Kovacs[1] studied extensively the volume relaxation behavior of various glass-forming systems after single and multiple temperature jumps. Using single jumps to a temperature T_e, Kovacs found that volume contraction (downward jump) required less time to reach equilibrium than expansion (upward jump) if the jumps were the same absolute magnitude. This "asymmetry" of approach to equilibrium may be explained qualitatively as follows. Contraction requires less time to reach equilibrium because the system is able to begin relaxing immediately after the downward temperature jump since the mobility is higher initially after the jump than it will be at equilibrium. In contrast, there is little volume change during early times of expansion due to the lower initial system mobility compared to that at equilibrium. These evolving mobilities also cause the volume to approach equilibrium during contraction in a different manner than during expansion. Mobility decreases as a system contracts, causing the contraction rate to slow continually, which is known as autoretardation.[2] As volume expands, mobility is gained, and the expansion rate increases in an autocatalytic manner.[2] Asymmetry behavior has also been observed in enthalpy[15-17] and dielectric[15] relaxations.

"Memory effects" are more complex relaxation behavior that are observed after two temperature jumps. Experimentally, the temperature of a system at volume equilibrium (T_0) is first lowered to T_1 for a time (t_1) that is insufficient to reach equilibrium. A second jump raises the temperature from T_1 to T_2 where $T_0 > T_2 > T_1$. After a poly(vinyl acetate) (PVAc) sample reached thermal equilibrium at T_2, Kovacs[1] found that the volume increased for a time (the peak amplitude and time depend upon T_1 and t_1 for a given T_0) and then decreased to the same equilibrium volume at the same time as a sample that had undergone a single jump from T_0 to T_2.

The memory behavior may be explained qualitatively by invoking the concept of multiple environments in a glass possessing various mobilities. Immediately after the first jump, all environments begin relaxing or contracting toward equilibrium at T_1. During the time at T_1, higher mobility environments relax more quickly and arrive closer to their equilibrium values at T_1 than do lower mobility environments. After the jump from T_1 to T_2, some higher mobility environments must recover (expand) to reach equilibrium at T_2 since they relaxed (contracted) past their T_2 equilibrium values during the time at T_1. Lower mobility environments would not have reached their T_2 equilibrium values while at T_1 and would still be relaxing (contracting) downward. Therefore, immediately after the second jump to T_2, the higher mobility environments dominate the relaxation process until they expand to equilibrium at T_2, after which the lower mobility environments (still relaxing downward) control the observed volume decrease. Memory effects have also been observed in enthalpy[5,16,17] and dielectric[18,19] relaxations.

The asymmetry and memory effects found in PVAc[1] have become a testing ground for theoretical models attempting to explain amorphous relaxations. Various phenomenological[20,21] and molecular[22-24] models have described asymmetry qualitatively with a single relaxation time or free volume element. None of the models involving

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a distribution of relaxation times has been able to reproduce the memory effects even qualitatively without at least two relaxation times (or free volume elements), and all of these models require the equivalent of a distribution of relaxation times to describe quantitatively the asymmetry or memory effects.[25] Only the "coupling" model[26] has reproduced the "τ_{eff} paradox".

Examples of the many techniques used to monitor relaxations or their manifestations include dilatometry[1,4,5] (specific volume), differential scanning calorimetry[15,27-29] (enthalpy), microcalorimetry[16,17] (continuous enthalpy), positron annihilation spectroscopy,[30] dielectric relaxation,[15,18,19] Brillouin scattering,[31] X-ray scattering,[8,32] and probe techniques (electron spin resonance,[33] photochromic,[34,35] second-order nonlinear optical,[36,37] and fluorescence[38-40]). In a previous publication, we reported preliminary results showing that a group of mobility-sensitive fluorescent probes were able to monitor polymer relaxations during physical aging of polystyrene and poly(methyl methacrylate).[40] This approach was based on earlier work by Loutfy[41] indicating that certain fluorescent molecules, such as (dialkylamino)malononitriles are sensitive to molecular mobility. After absorbing light and being elevated to singlet excited states, these probes have two major pathways for returning to the ground state. The preferred deactivation route is a nonradiative internal conversion mechanism involving various bond rotations in the probes. Hindering these rotations causes the probes to deactivate by emitting a photon or fluorescing. Therefore, the probe fluorescence intensity, quantum efficiency, and lifetime increase when the local mobility decreases.

In this study, we present further evidence of the mobility-sensitivity of these probes and results indicating that the polymer physics governing asymmetry and memory effects in bulk relaxations also regulate the molecular behavior on the probe size scale. The molecular technique reproduces every attribute of asymmetry and memory behavior found with traditional bulk techniques[1,15-17] and has similar sensitivity. In addition, the molecular effects of trace plasticizers in PVAc are detected.

Experimental Section

Poly(vinyl acetate) (PVAc; secondary standard, M_w = 194 800; M_n = 47 700; Aldrich) and the fluorescent molecule julolidenemalononitrile (JMN; Molecular Probes) were used as received. Polymer films were prepared and tested in the following manner to ensure that the films were as dry as possible. PVAc was dissolved in dry dichloromethane (Aldrich, spectrophotometric grade) containing the fluorescent probe JMN to produce a 7 wt % polymer solution. Films were solvent cast onto quartz plates in a nitrogen-filled glovebox, allowed to dry for 8 h, and then dried for 3 days in a vacuum oven at 70 °C over desiccant to remove residual solvent. Just before testing, the films were heated to 120 °C for 4 h under vacuum to remove bound water. Films contained less than 0.004 wt % probe.

The films were removed from the oven under dry nitrogen and desiccant and placed into a nitrogen-filled glovebox where they were loaded into a specially designed fluorescence cell whose temperature was controlled with circulating water baths (Neslab Endocal RTE-9) within ±0.05 °C. This apparatus was then placed into a nitrogen-filled sample chamber of a SPEX Fluorolog-2 DM1B spectrofluorimeter to record the steady-state fluorescence spectra in a front-faced geometry with 1.25-mm excitation and emission slits (band-pass of 4.5 nm) at an excitation wavelength of 450 nm. Flowing dry N_2 gas and having desiccant in the sample chamber kept samples dry during experiments. The fluorescence reference (Rhodamine B in propylene glycol, 8.0 g/L) was maintained at 30 ± 0.5 °C with a circulating water bath and a water-jacketed fluorescence cell to avoid variations in corrected fluorescence intensity due to instrument thermal changes.

The thermal history of each film was erased in the temperature-controlled cell by heating the sample above T_g (T_g + 5 °C) for 30 min before each experiment. A second water bath was used to change the sample temperature rapidly, and thermal equilibrium was attained in under 30 s. Changes in the fluorescence intensity were recorded at various intervals of time after a temperature jump. Except when recording a spectrum, the samples were shielded from irradiation to minimize any photodegradation of the probe (we have found[42] this effect to be negligible after 6 h of continuous irradiation of JMN in PVAc at the excitation wavelength used in this study).

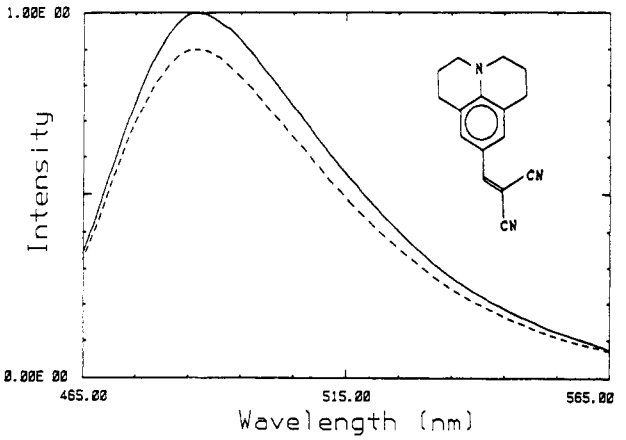

Figure 1. Structure of JMN and fluorescence emission spectra in dry PVAc (onset T_g = 39.5 °C) after a temperature jump from above T_g (45 °C) to below T_g (35 °C). Dashed and solid lines are 1 and 1440 min after the jump, respectively. Physical aging causes an increase in the fluorescence intensity of the probes.

Glass transition temperatures of films and bulk enthalpy relaxations were measured with a Perkin-Elmer differential scanning calorimeter DSC-2 in hermetically sealed pans with a cooling rate of 40 °C/min and a heating rate of 10 °C/min. After completing the fluorescence studies, some of the polymer film was removed (under dry N_2) from the quartz slide and placed in the pans for determining the T_g and the enthalpy relaxation. T_g's were taken as the onset of the heat capacity change, and the degree of enthalpy relaxation was determined by the method described by Marshall and Petrie.[27] The T_g of dry, pure PVAc was identical to that of dry, JMN-doped PVAc indicating that the probes' presence does not affect the bulk properties of PVAc.

Results and Discussion

Figure 1 illustrates the chemical structure and emission spectra of JMN in dry PVAc (T_g = 39.5 °C) after jumping the temperature from 45 to 35 °C. The dashed and solid lines were recorded 1 and 1440 min after the jump, respectively. As the polymer loses mobility, the probe fluorescence intensity increases. Conversely, an increase in mobility of the environments surrounding the probes would produce a decrease in the fluorescence. Local polarity changes around these probes cause the emission peak to shift wavelengths.[41] As Figure 1 demonstrates, no polarity changes occur during 24 h of polymer relaxation.

In Figure 2 the fluorescence intensity of JMN at the emission maximum is plotted as a function of logarithmic time after jumping the temperature of a PVAc film (T_g = 39.5 °C) from above T_g (45 °C) to near or below T_g. The data have been normalized to an intensity of 1.0 at 1 min to eliminate absolute intensity differences caused by slight probe concentration and film thickness variations between films. More importantly, the normalization allows us to compare the relative isothermal intensity changes caused by losses or gains in local polymer mobility at any relaxation temperature.

These fluorescence intensity changes are related to the polymer physical aging rates, and we reported previously that the fluorescence aging rate increases as the aging temperature approaches T_g.[40] We have since found that this

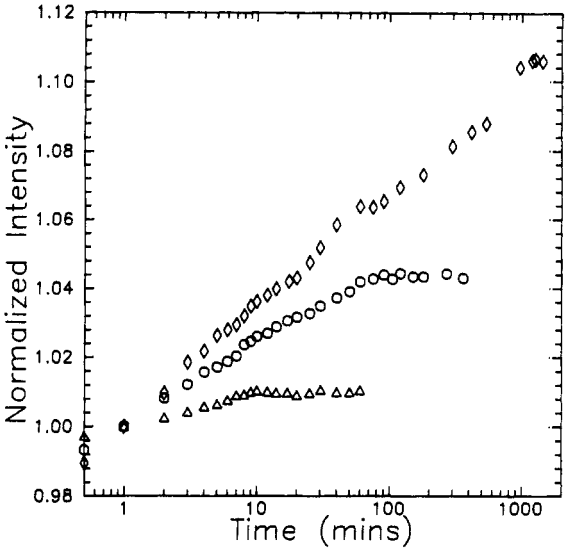

Figure 2. Normalized JMN fluorescence intensity at the emission maximum versus logarithmic time in dry PVAc (onset T_g = 39.5 °C) after temperature jumps from 45 °C to various temperatures near T_g. The probes sense when the environments come to equilibrium which depends upon the depth of the temperature jump below T_g. (△) T = 40 °C; (○) T = 37.5 °C; (◇) T = 35 °C.

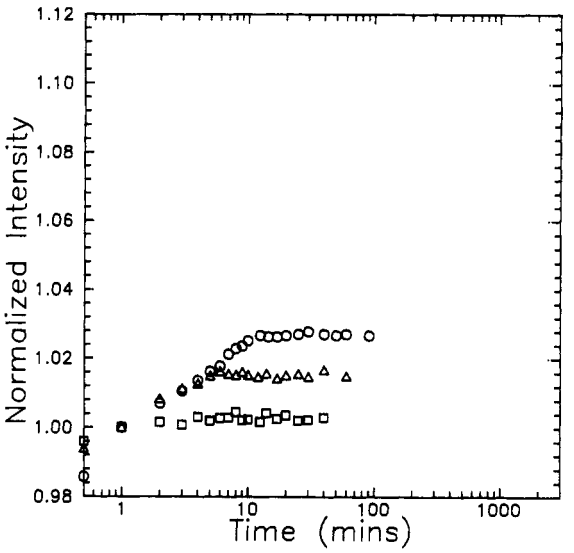

Figure 3. Normalized JMN fluorescence intensity at the emission maximum versus logarithmic time in wet (0.7 wt % H_2O) PVAc (onset T_g = 34.5 °C) after temperature jumps from 45 °C to various temperatures near T_g. A small amount of water can severely plasticize PVAc, depress T_g, and increase polymer mobility. Molecular-scale plasticization effects can be monitored with the fluorescent probes. (□) T = 40 °C; (△) T = 37.5 °C; (○) T = 35 °C.

aging rate-temperature trend was influenced significantly by instrumental thermal variations that affected the fluorescence reference.[43] We have reported recently[44,45] that the fluorescence aging rate-temperature trend closely matches the bulk polymer aging rate-temperature trend found with dilatometry in many amorphous polymers. Comparing the initial slopes of the curves in Figure 2, the aging rate is shown to increase as $T_g - T_a$ increases where T_a is the aging temperature. This trend is reasonable for the small temperature range studied since the bulk polymer aging rate generally increases as $T_g - T_a$ increases in a temperature range near T_g.[4,11,45] Figure 2 also shows that JMN in dry PVAc is able to detect aging rate differences caused by aging temperatures that differ by only 2.5 °C.

The fluorescence responses at 40 and 37.5 °C increase for a time and then level off, indicating that the local molecular environments have reached equilibrium. The relative intensity values and times required to reach equilibrium depend on the value of $T_g - T_a$. Both the relative equilibrium intensity and equilibrium time increase as $T_g - T_a$ increases, which is very similar to what Kovacs[1] observed while monitoring the bulk volume of PVAc relaxing to equilibrium after temperature jumps.

Figure 3 shows the normalized fluorescence response versus logarithmic time at various temperatures for plasticized PVAc plotted on the same intensity and time scales as the dry PVAc in Figure 2. This film was exposed to humid air (approximately 70% humidity) at a temperature of 26 °C (laboratory conditions on a particular day) for 20 min and absorbed approximately 0.7 wt % water. This small amount of water depressed the T_g by 5 °C to an onset T_g of 34.5 °C (midpoint T_g = 39.0 °C) which agrees well with the findings of Bair et al.[15] for the T_g depression of PVAc by water. Polymer plasticization by small-molecule diluents is a well-known phenomenon that depresses T_g because the mobility of the system is increased.[3,46,47] Therefore, at a particular temperature, the time required to reach equilibrium will be less for a plasticized sample than an unplasticized sample.

Figure 3 clearly illustrates that the probes sense the plasticization effects at all temperatures studied, and the equilibrium times at a given temperature are indeed smaller for the more mobile, wet PVAc than for the dry PVAc seen in Figure 2. The relative intensity changes at a given temperature in Figure 3 are smaller than those in Figure 2 because the structure of the wet sample is able to relax more significantly than the dry sample during the small thermal equilibration time after a temperature jump (before any meaningful measurements can be made since only isothermal changes are of interest). Note that all experimental temperatures in Figure 3 are above the DSC T_g of the plasticized sample, and the times required to reach equilibrium would be expected to be shorter in the rubbery region.

Comparing the experiments at 40 °C in Figure 2 and 35 °C in Figure 3, it is interesting to note that both relaxations reach equilibrium in approximately 10 min. Since these experiments were performed very near the DSC T_g's of these films, the results indicate that the equilibrium times depend largely on the distance of the "aging" temperature (T_a) from T_g. Bair et al.[15] found that the equilibrium times for enthalpy relaxation were identical in dry and wet (1.8 wt % H_2O) PVAc samples at aging temperatures equal to T_g - 9 °C. They concluded that the time-dependent relaxation behavior as well as the absolute enthalpy change was independent of the water content as long as $T_g - T_a$ was fixed. The relative fluorescence change of the 35 °C experiment in Figure 3 is not equal to the 40 °C experiment in Figure 2 because the former was a 10 °C jump (45 to 35 °C) while the latter was a 5 °C jump (45 to 40 °C).

The effects of water plasticization on PVAc relaxation behavior have been noted in many studies.[2,15,48,49] The relaxation dependence on $T_g - T_a$ found by Bair et al.[15] and supported by this study shows that it is critical to report the T_g and how it was determined if the relaxation results are to be compared to other PVAc relaxation data or if meaningful theoretical parameters are to be extracted. If the water content must be tightly controlled or dry PVAc is desired, the results in Figures 2 and 3 indicate that seemingly excessive environmental control around the PVAc samples must be practiced. Experimental details such as the relaxation time scales or the size of the "expansion gap" found at particular temperatures should

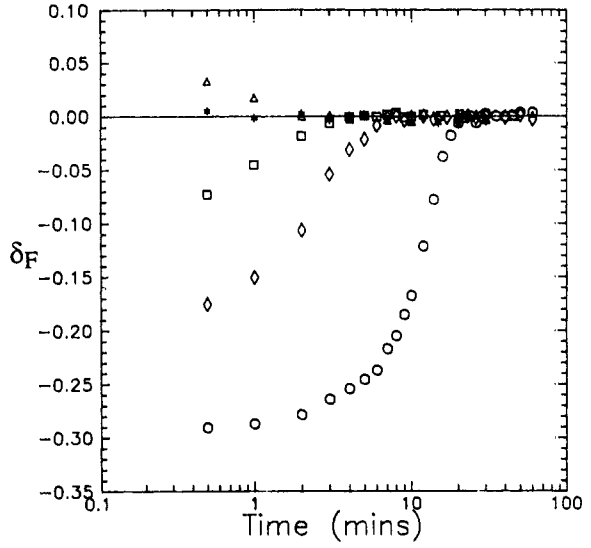

Figure 4. Molecular asymmetry behavior of wet PVAc (onset T_g = 34 °C) at 40 °C monitored with JMN. The fluorescence behavior was monitored after jumping the temperatures to 40 °C from the temperatures indicated below. The general behavior is very similar to bulk volume behavior found by Kovacs.[1] (△) T_0 = 70 °C; (*) T_0 = 50 °C; (□) T_0 = 35 °C; (◇) T_0 = 30 °C; (○) T_0 = ~25 °C.

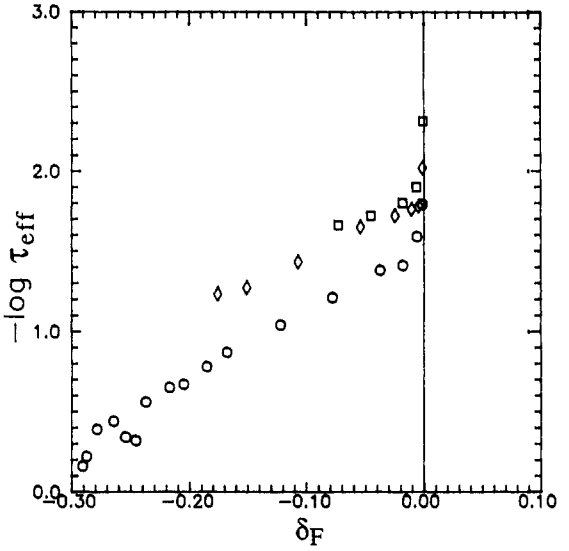

Figure 5. Molecular asymmetry data at 40 °C from Figure 4 has been plotted as a function of τ_{eff} versus δ_F. This plot accentuates the "expansion gap" in the asymmetry curves. The fluorescence behavior was monitored after jumping the temperature to 40 °C from the following: (○) T_0 = ~25 °C; (◇) T_0 = 30 °C; (□) T_0 = 35 °C.

not be taken as universal for PVAc unless the T_g is reported.

Kovacs[1] defined a parameter, δ, that describes the distance from the volume equilibrium of the system at time t:

$$\delta = (V_t - V_\infty)/V_\infty \quad (1)$$

where V_t and V_∞ are the volumes at time t and equilibrium ($t = \infty$), respectively. Therefore, during volume contraction $\delta > 0$, during expansion $\delta < 0$, and at equilibrium $\delta = 0$. A δ parameter similar to that of Kovacs may be defined for the distance from the equilibrium fluorescence intensity, δ_F

$$\delta_F = -(I - I_\infty)/I_\infty \quad (2)$$

where I and I_∞ are the intensities at time t and equilibrium, respectively, and the minus sign is due to the inverse relationship between volume and fluorescence responses to polymer structural change. Since the probes monitor when the local environments reach equilibrium after downward temperature jumps, it is possible that the same may be done for upward jumps, and asymmetry behavior on the molecular scale may be studied.

Figure 4 shows the results of asymmetry experiments in plasticized PVAc (T_g = 34 °C) monitored on the molecular scale with the fluorescent probe JMN. The samples were allowed to come to equilibrium at the indicated temperatures and then jumped to 40 °C (it is uncertain whether the 25 °C film attained equilibrium after annealing for 4 weeks). As with volume relaxation, relaxation after a downward temperature jump requires less time to come to equilibrium than after an upward jump of the same absolute magnitude. Qualitatively, every attribute found in the dilatometric asymmetry results of Kovacs for PVAc at 40 °C[1] is reproduced with the molecular-scale fluorescence technique. These results provide strong support for the idea postulated in many relaxation models that a distribution of molecular environments in amorphous materials controls bulk behavior.

It is important to note that the times required to come to equilibrium in Figure 4 appear to be temperature independent for the contraction results ($\delta_F > 0$) but not for the expansion results ($\delta_F < 0$). Kovacs[1] defined an effective relaxation time, τ_{eff}, that accentuates this behavior:

$$\tau_{eff}^{-1} = -\delta^{-1}(d\delta/dt) \quad (3)$$

While the volume contraction curves from Kovacs[1] appear to converge to equilibrium ($\delta = 0$) at the same τ_{eff}, the expansion curves do not, which produces an apparent effective relaxation time "gap" between expansions from different temperatures. This phenomenon is also known as the τ_{eff} paradox.[2,50] The word "paradox" is used because one would expect the mobilities of the expanding systems ($\delta < 0$) to become comparable as the volume nears its equilibrium value at 40 °C. Therefore, the effective relaxation times would become comparable near $\delta = 0$, and the expansion curves would converge on the same value of τ_{eff}. The volume results suggest that this concept is incorrect and is one reason why relaxation models, with the exception of the coupling model,[26] fail to model the expansion gap.

Due to the small amount of data on the expansion gap, there has been some discussion as to whether the presence of the gap is due to polymer physics or is an experimental artifact. Figure 5 contains the expansion data from Figure 4 plotted as a function of the τ_{eff} parameter. At values of δ_F between -0.01 and 0, there is a "τ_{eff} gap" between the expansion curves, although nothing as dramatic as those found from dilatometry.[1] Nevertheless, the molecular environments sensed by JMN relaxing to equilibrium from differential initial structures do not appear to reach equilibrium at the same effective relaxation time.

Figure 6 contains the fluorescence results of asymmetry experiments plotted as δ_F versus logarithmic time at 35 °C for JMN in plasticized PVAc (T_g = 34 °C). Qualitatively, the relaxation behavior at 35 °C is similar to that at 40 °C. Since these systems relaxed to equilibrium at T_g + 1 °C instead of T_g + 6 °C (40 °C experiments in Figure 4), the relaxation times are longer for a temperature jump of a given magnitude. For example, the upward 5 °C jump from 35 to 40 °C in Figure 4 requires less than 3 min to reach equilibrium while the 5 °C jump from 30 to 35 °C in Figure 6 needs at least 30 min. As in volume

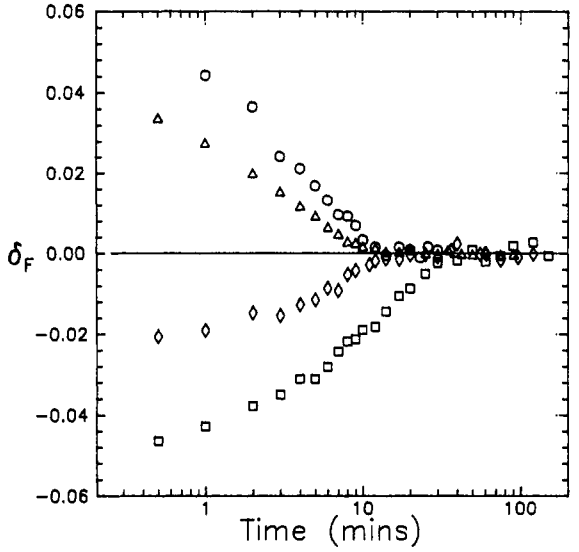

Figure 6. Molecular asymmetry behavior of wet PVAc (onset T_g = 34 °C) at 35 °C monitored with JMN. The fluorescence behavior was monitored after jumping the sample temperature to 35 °C from these temperatures: (○) T_0 = 55 °C; (△) T_0 = 40 °C; (◇) T_0 = 32.5 °C; (□) T_0 = 30 °C.

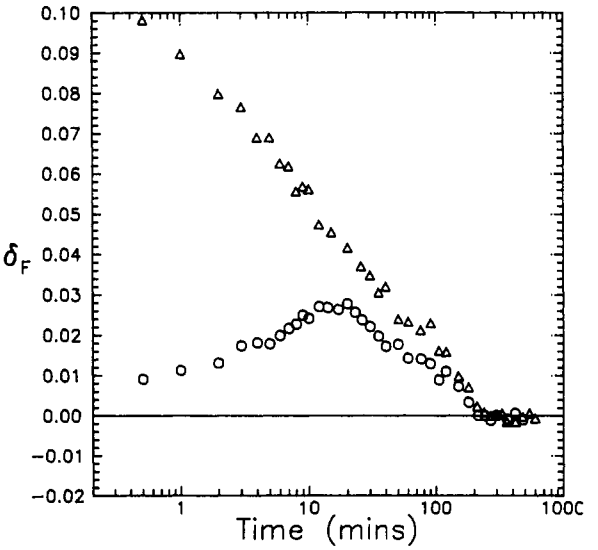

Figure 7. Molecular memory effects in wet PVAc (onset T_g = 34 °C) monitored by JMN. T_0 = 40 °C (initial temperature) and T_2 = 30 °C (final temperature) for both curves. (△) Single-temperature jump from 40 to 30 °C. (○) Double-temperature-jump experiment. The first jump was from 40 to 20 °C and held there for 2 h. The second jump was from 20 to 30 °C. The fluorescence behavior was monitored after the second temperature jump.

relaxation,[1] the fluorescence responses after the downward temperature jumps in Figure 6 reach equilibrium at approximately the same time.

Figure 7 compares the fluorescence response after a single-temperature jump to the response after a two-temperature jump memory effect experiment. After a single jump from 40 to 30 °C, volume contraction-type behavior would be expected and is seen in the fluorescence response. For the memory experiment, the system temperature was jumped from 40 to 20 °C, held there for 2 h, and then rapidly raised to 30 °C, after which data gathering began. The δ_F parameter increases initially, indicating an increase in the local mobility for about 15 min and then a loss of mobility down to δ_F = 0 in a similar time frame as the simple contraction after a single jump from 40 to 30 °C. This behavior is very similar to the dilatometric memory effect results reported by Kovacs.[1] Recall the fact that

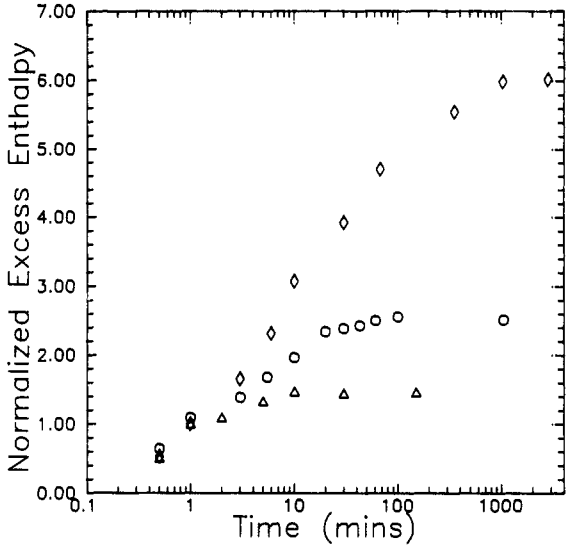

Figure 8. Enthalpy relaxations (normalized to a value of 1 at 1 min) performed on dry PVAc (onset T_g = 39.5 °C) in a DSC. The PVAc was from the films used to obtain the fluorescence data in Figure 2. The bulk, enthalpic time scales are similar to those found from the fluorescence probes. Relaxation temperatures: (△) T = 40 °C; (○) T = 37.5 °C; (◇) T = 35 °C.

many relaxation theories require a distribution of environments to account for memory effects. Therefore, in the language of these models, the probes measure a distribution of mobilities or environments in the polymer matrix, and their combined behavior produces a bulklike response.

The sensitivity of the fluorescence technique has been compared to those of bulk techniques traditionally employed to measure polymer relaxation kinetics. While it would be interesting to compare the fluorescence asymmetry and memory behaviors to the dilatometric results of Kovacs,[1] the unknown differences in water content between our PVAc samples and those studied by Kovacs would make such a comparison meaningless. Therefore, bulk enthalpy relaxation studies of dry PVAc were carried out with a differential scanning calorimeter, and the results were compared to the fluorescence responses in dry PVAc. Bair et al.[15] found a midpoint T_g of 43.5 °C for dry PVAc which agrees well with our midpoint T_g of 44.0 °C (onset T_g = 39.5 °C).

Figure 8 shows the normalized excess enthalpy versus logarithmic time for the same temperature jumps as performed in the fluorescence experiments in Figure 2. The times required to reach equilibrium at 40 and 37.5 °C for the enthalpy are very similar to the fluorescence equilibrium times at those temperatures in Figure 2, and both techniques show that longer experimental times are required to reach equilibrium at 35 °C. From this comparison, the JMN probe has nearly the same sensitivity as DSC to the relaxation time scales of PVAc near T_g. While the two techniques possess similar sensitivity, the fluorescence technique has a major advantage in that it allows for continuous, in situ, nondestructive monitoring of relaxations. We have also found that the molecular technique has a similar sensitivity to the physical aging of polystyrene as the most sensitive dilatometric measurements made by Kovacs.[45]

Photochromic and fluorescence probe studies have shown that the size of the mobile probe element is an important factor in determining the ability of a probe to change conformation in a polymer matrix.[35] Basically, the larger the volume needed for motion, the lower the

probability that motion occurs. For example, after quenching polystyrene to room temperature from above T_g, 1,3-bis(1-pyrene)propane cannot rotate to form intramolecular excimers,[35] but the probe JMN continues to sense relaxations in polystyrene under the same aging conditions for longer than 6 h.[40,45] Therefore, all else being equal, the size of the rotating probe element should determine the extent of the mobility sensitivity in a matrix and the equilibrium time during asymmetry experiments. Such probe size comparisons are currently underway in our laboratory.

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References and Notes

(1) Kovacs, A. J. *Fortschr. Hochpolym.-Forsch.* **1963**, *3*, 394.
(2) McKenna, G. B. In *Comprehensive Polymer Science*, 2nd ed.; Booth, C., Price, C., Eds.; Pergamon: Oxford, 1989; p 311.
(3) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(4) (a) Greiner, R.; Schwarzl, F. R. *Rheol. Acta* **1984**, *23*, 378. (b) Greiner, R.; Schwarzl, F. R. *Colloid Polym. Sci.* **1989**, *267*, 39.
(5) Adachi, K.; Kotaka, T. *Polym. J.* **1982**, *14*, 959.
(6) Prest, W. M.; O'Reilly, J. M.; Roberts, F. J.; Mosher, R. A. *Polym. Eng. Sci.* **1981**, *21*, 1181.
(7) Tribone, J. J.; O'Reilly, J. M.; Greener, J. *J. Polym. Sci., Polym. Phys.* **1989**, *27*, 837.
(8) (a) Roe, R.-J.; Song, H.-H. *Macromolecules* **1985**, *18*, 1603. (b) Song, H.-H.; Roe, R.-J. *Macromolecules* **1987**, *20*, 2723.
(9) Yee, A. *J. Polym. Sci., Polym. Phys.* **1988**, *26*, 2463.
(10) Smith, T. L.; Levita, G.; Moonan, W. K. *J. Polym. Sci., Polym. Phys.* **1988**, *26*, 875.
(11) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, The Netherlands, 1978.
(12) Cameron, G. G.; Miles, I. S.; Bullock, A. T. *Polymer* **1988**, *29*, 1282.
(13) Kambour, R. P. *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. S., Maconnachie, A., Eds.; NATO Series E89: Applied Sciences; Martinus Nijhoff Publishers: Dordrecht, The Netherlands 1985; p 333.
(14) Cowie, J. M. G.; Ferguson, R. *Macromolecules* **1989**, *22*, 2312.
(15) Bair, H. E.; Johnson, G. E.; Anderson, E. W.; Matsuoka, S. *Polym. Eng. Sci.* **1981**, *21*, 930.
(16) Wang, C.-H.; Filisko, F. E. *Polym. Mater. Sci. Eng.* **1990**, *60*, 782.
(17) Gusev, A. A.; Beshenko, S. I.; Oleinik, E. F. *Dokl. Acad. Nauk. SSSR* **1986**, *288*, 1143.
(18) Matsuoka, S.; Williams, G.; Johnson, G. E.; Anderson, E. W.; Furakawa, T. *Macromolecules* **1985**, *18*, 2652.
(19) Pathmanathan, K.; Johari, G. P.; Faivre, J. P.; Monnerie, L. *J. Polym. Sci., Polym. Phys.* **1986**, *24*, 1587.
(20) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, A. R. *J. Polym. Sci., Polym. Phys.* **1979**, *17*, 1097.
(21) DeBolt, M. A.; Easteal, A. J.; Macedo, P. B.; Moynihan, C. T. *J. Am. Ceram. Soc.* **1976**, *59*, 16.
(22) (a) Robertson, R. E.; Simha, R.; Curro, J. G. *Macromolecules* **1984**, *17*, 911. (b) Robertson, R. E.; Simha, R.; Curro, J. G. *Macromolecules* **1985**, *18*, 2239. (c) Robertson, R. E.; Simha, R.; Curro, J. G. *Macromolecules* **1988**, *21*, 3216.
(23) Grest, G. S.; Cohen, M. H. *Adv. Chem. Phys.* **1981**, *48*, 455.
(24) Curro, J. G.; Lagasse, R. R.; Simha, R. *Macromolecules* **1982**, *15*, 1621.
(25) Kovacs, A. J. *Ann. N.Y. Acad. Sci.* **1981**, *371*, 38.
(26) Rendell, R. W.; Ngai, K. L.; Fong, G. R.; Aklonis, J. J. *Macromolecules* **1987**, *20*, 1070.
(27) Marshall, A. S.; Petrie, S. E. B. *J. Appl. Phys.* **1975**, *46*, 4223.
(28) Hodge, I. M. *Macromolecules* **1987**, *20*, 2897.
(29) Tribone, J. J.; O'Reilly, J. M.; Greener, J. *Macromolecules* **1986**, *19*, 1732.
(30) Kobayashi, Y.; Zheng, W.; Meyer, E. F.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *Macromolecules* **1989**, *22*, 2302.
(31) Patterson, G. D.; Jue, P. K.; Stevens, J. R. *J. Polym. Sci., Polym. Phys.* **1990**, *28*, 481.
(32) (a) Roe, R.-J.; Curro, J. J. *Macromolecules* **1983**, *16*, 428. (b) Curro, J. J.; Roe, R.-J. *Polymer* **1984**, *25*, 1424.
(33) Tsay, F. D.; Hong, S. D.; Moacanin, J.; Gupta, A. *Bull. Am. Phys. Soc.* **1982**, *27*, 393.
(34) (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.
(35) (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.
(36) (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.
(37) Hayden, L. M.; Sauter, G. F.; Ore, R.; Pasillas, P. L.; Hoover, J. M.; Lindsay, G. A. *J. Appl. Phys.* **1990**, *68*, 456.
(38) Guo, R. K.; Tazuke, S. *Macromolecules* **1989**, *22*, 3286.
(39) Meyer, E. F.; Jamieson, A. M.; Simha, R.; Palmen, J. H. M.; Booij, H. C.; Maurer, F. H. J. *Polymer* **1990**, *31*, 243.
(40) Royal, J. S.; Torkelson, J. M. *Macromolecules* **1990**, *23*, 3536.
(41) (a) Loutfy, R. O.; Law, K. Y. *J. Phys. Chem.* **1980**, *84*, 2803. (b) Loutfy, R. O. *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. O. *Pure Appl. Chem.* **1986**, *58*, 1239.
(42) Royal, J. S.; Torkelson, J. M., unpublished results.
(43) See the Experimental Section for a description of how the temperatures of both the sample and fluorescence reference are now maintained at a constant temperature to ensure measurement of fluorescence changes under isothermal conditions.
(44) Royal, J. S.; Torkelson, J. M. *Bull. Am. Phys. Soc.* **1991**, *36* (3), 788.
(45) Royal, J. S.; Torkelson, J. M., in preparation.
(46) Kelly, F. N.; Bueche, F. *J. Polym. Sci.* **1961**, *50*, 549.
(47) Braun, G.; Kovacs, A. J. In *Proceedings of the Conference on Physics of Noncrystalline Solids*; Prins, A. J., Ed.; North Holland: Amsterdam, The Netherlands, 1965; p 303.
(48) Plazek, D. J. *Polym. J.* **1980**, *12*, 43.
(49) Ngai, K. L.; Mashimo, S.; Fytas, G. *Macromolecules* **1988**, *21*, 3030.
(50) The τ_{eff}-paradox data in ref 1 and 2 were plotted with an anomalous negative sign in the y-axis but have been corrected in refs 20, 22, and 26.

Registry No. PVAc (homopolymer), 9003-20-7; JMN, 58293-56-4; H_2O, 7732-18-5.