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Structural Recovery in a Model Epoxy: Comparison of Responses after Temperature and Relative Humidity Jumps

Y. Zheng and G. B. McKenna*

Texas Tech University, Lubbock, Texas 79409-3121

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ABSTRACT: One cause of long-term dimensional changes in glassy polymers is the gradual evolution of the viscoelastic behavior through aging processes in the glassy state. Many applications involve changes in relative humidity (RH), under which the materials exhibit aging processes that may differ from those in constant RH conditions. In this work, we report results from a study of a glassy epoxy subjected to isothermal RH-jumps. Similar to the temperature jump experiments of Kovacs,[6] we obtain the volume recovery responses in different histories as intrinsic isopiestics (constant RH), memory effect, and the asymmetry of approach. Our results qualitatively support the hypothesis that water has an effect similar to that of temperature on the structure (volume, enthalpy) of the glass-forming material. However, quantitatively, at the same RH−temperature states, the glasses formed by RH-jumps are different from those formed by temperature jumps. The implications of this difference for structural recovery are discussed. We have also extended the TNM−KAHR model to fit the experimental results of isothermal RH-jump experiments, and the outcome is also discussed in this paper.

I. Background and Introduction

An increase of relative humidity (RH) depresses the glass transition temperature (T_g) of polymers due to the plasticizing effect upon sample moisture uptake. It is well-known that small molecules or plasticizers depress the glass transition temperature and the magnitude of the depression can be estimated from configurational entropy[1,2] and free volume[3,4,5] models. As a result, common knowledge in the field of polymers is that plasticizing molecules act similarly to temperature in altering the viscoelastic response of the material at a given temperature T simply because the distance ($T_g - T$) from the glass transition temperature T_g is altered. The objectives in this paper are to examine the volume recovery in a model epoxy glass after relative humidity jumps (RH-jumps) from equilibrium and compare these results with those of Kovacs' temperature jump (T-jump) experiments[6] to test our hypothesis that the change of relative humidity has an effect similar to that of temperature change on structural recovery and physical aging. The meaning of this hypothesis is illustrated in Figure 1, where a three-dimensional plot of $V-T-$RH is presented. In the figure, at a constant relative humidity (isopiestic), one traverses the glass transition as temperature is reduced. Similarly, at each temperature (isotherm), one traverses the glass transition as relative humidity decreases. Furthermore, in traversing the glass transition (RH or T) the material is out of equilibrium and is expected to recover into equilibrium. Therefore, T-jump and RH-jump experiments should exhibit similar structural recovery behaviors.

To test this hypothesis, we performed a series of experiments: (a) intrinsic isopiestic (constant relative humidity), (b) asymmetry of approach, and (c) memory. These experiments are analogous to Kovacs' kinetic experiments after temperature jumps: (a) intrinsic isotherm, (b) asymmetry of approach, and (c) memory.[6]

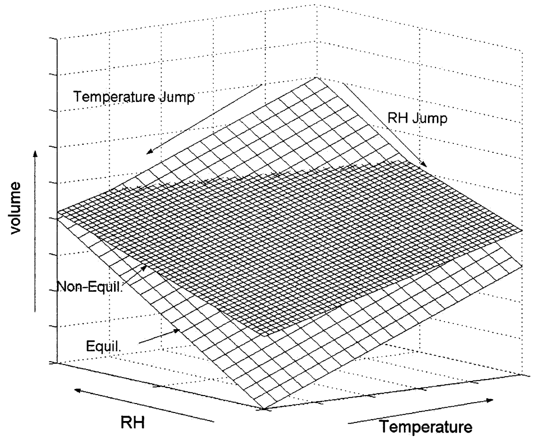

Figure 1. Three-dimensional schematic of the $V-T-$RH behavior for a glass-forming material.

We have also extended the TNM−KAHR (Tool[7,8,9]−Narayanaswamy[10]−Moynihan[11,12]−Kovacs−Aklonis−Hutchinson−Ramos[13]) model to relative humidity jump conditions.

Kovacs' Thermal Experiments and the TNM−KAHR Model. An important feature of the glass transition is the dramatic reduction of molecular mobility during cooling, which results in relaxation times that are larger than the experimental time scale. Since the glass exists in a nonequilibrium state, a rich set of kinetic phenomena is associated with the evolution of the glassy structure toward equilibrium. These were probed by Kovacs through a classic set of dilatometric experiments where he established the main features of structural recovery: (a) intrinsic isotherms, (b) asymmetry of approach, and (c) memory effect.[6]

The experimental protocol to obtain a family of intrinsic isotherms is illustrated in Figure 2a, and typical results are shown in Figure 2b. Because the glassy state is a nonequilibrium state, the material evolves continuously to reach equilibrium. Kovacs re-

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* Corresponding author. E-mail: greg.mckenna@coe.ttu.edu.

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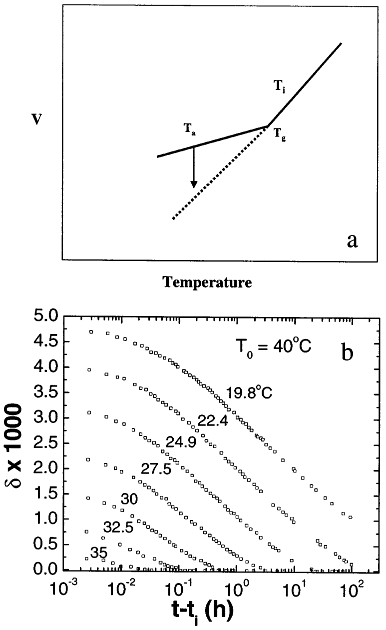

Figure 2. (a) Schematic of intrinsic isotherm experiment. (b) Experimental results (data from Kovacs[6]).

ferred to the volume or structural recovery response after temperature down jumps from a single starting temperature T_0 to a series of test temperatures as intrinsic isotherms. He defined the departure from equilibrium $\delta(t)$

$$\delta(t) = (V(t) - V_\infty)/V_\infty \qquad (1)$$

where V_∞ is the equilibrium volume at the temperature of interest and $V(t)$ is the volume at time t. As seen in Figure 2b, the isotherms take longer to attain equilibrium as temperature decreases. In our subsequent discussions, data obtained in isothermal relative humidity jumps from a single relative humidity will produce a family of curves that is similar to the Kovacs intrinsic isotherms shown in Figure 2b and which we refer to throughout this work as intrinsic isopiestics.

The protocol for the asymmetry of approach experiment is illustrated in Figure 3a, and the results are shown in Figure 3b. In this experiment, the up and down jumps to the final temperature are of equal magnitude and, were the material response linear, the volume recovery curves would be mirror images. Kovacs[6] showed the responses to be highly asymmetrical, and the nonlinear kinetics are interpreted in terms of the material mobility, depending on the instantaneous state of the glass.[6,8,11] Later we show that similar results are obtained after RH-jumps in nominally symmetric RH-jump magnitude conditions.

The protocol for the memory experiment is illustrated in Figure 4a, and typical results are shown in Figure 4b. Here the sample is subjected to a temperature down jump and is allowed to partially recover toward equilibrium. The recovery proceeds to a point such that, upon increasing temperature to the final testing temperature, the sample has (approximately) its equilibrium volume. In this case, the material “remembers” the prior history and the volume increases through a maximum before asymptotically approaching equilibrium. The memory effect is used to support the physical picture that there exists a distribution of relaxation times or other nonexponential kinetics in the structural

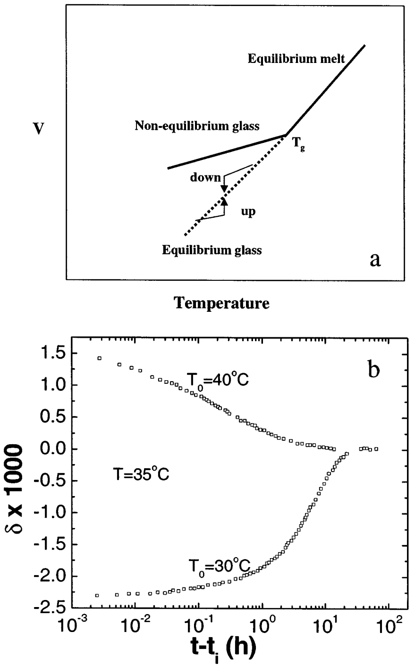

Figure 3. (a) Schematic of asymmetry of approach experiment. (b) Experimental results (data from Kovacs[6]).

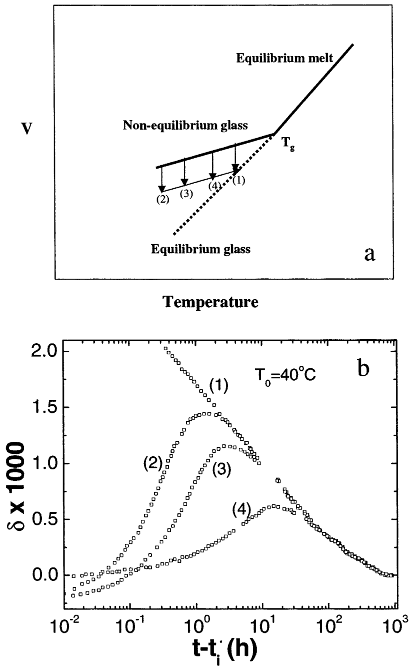

Figure 4. (a) Schematic of memory experiment. (b) Experimental results (data from Kovacs[6]).

recovery response.[11] We illustrate subsequently similar experimental results in two-step RH-jumps. Intrinsic isotherms, asymmetry of approach, and memory effect are the major manifestations of structural recovery and provide a basis to form a model that contains the essential ingredients for its description.[14]

The TNM−KAHR model[7−13] is known to provide a good representation of the structural recovery behavior of glassy materials in thermal histories.[16] On the basis of the pioneering work of Tool,[7−9] the kinetics of structural recovery in the glassy state depend on both the temperature and the instantaneous structure of the glass. In the KAHR formula, the characteristic relaxation time τ evolves during structural recovery and can be expressed as a function of temperature (T) and departure from equilibrium (δ), as in the following equation:[13]

$$\tau(T,\delta) = \tau_0 \exp(-\theta_T(T - T_r)) \exp(-(1 - x)\theta_T\delta/\Delta\alpha) \tag{2}$$

where x is the nonlinearity parameter first introduced by Moynihan,[11,12] θ is a form of activation energy and has units of ($1/T$), T_r is the reference temperature, τ_0 is the relaxation time at the reference temperature,[15] and $\Delta\alpha = \alpha_l - \alpha_g$ is the difference between the coefficient of thermal expansion in the liquid state (α_l) and the glassy state (α_g). In an analogy to linear viscoelasticity but with the response being $\delta(t)$ and stimulation being temperature history, Bolzmann superposition is assumed to be applicable but on a reduced time scale.[10] Furthermore, the relaxation behavior of glass forming systems is nonexponential in nature, as evidenced by the memory effect, and can be represented either through a spectrum of relaxation times (sum of exponentials) or using the stretched exponential Kohlrausch–Williams–Watts (KWW) formalism as introduced by Moynihan.[11] Weaving these ideas together, a model to describe the glass transition and structural recovery in terms of δ can be expressed in the following form

$$\delta(z) = -\Delta\alpha_T \int_0^z \exp\left(-\left(\frac{z - z'}{\tau_0}\right)^{\beta}\right) \frac{dT}{dz'}\, dz' \tag{3a}$$

$$z = \int_0^t \frac{d\xi}{a_T a_\delta} \tag{3b}$$

where τ_0 is the prefactor in eq 2; β is the nonexponentiality parameter, and a_T and a_δ are temperature and structure shift factors, respectively, and can be obtained from eq 2.

In the present study, we extended this model to isothermal relative humidity histories by simply replacing T, T_r, θ_T, and $\Delta\alpha_T$ with RH, RH_r, θ_{RH}, and $\Delta\alpha_{RH}$ in eqs 2 and 3. θ_{RH} is a dimensionless parameter because there is no dimension for relative humidity. $\Delta\alpha_{RH}$ is the difference of hygrothermal (RH) expansion rate between the equilibrium and nonequilibrium glassy states.

Prior Literature. Small molecules such as water, carbon dioxide, and other organic solvents have similar effects on polymers.[17–24,28,29,31] In the 1970s and 1980s, several authors observed a peculiar sorption mode of small molecules into polymers. This type of sorption starts with an initial stage that is Fickian. This is followed by a linear increase of mass with time and is clearly non-Fickian.[17–21,25] Berens et al.[17–19] studied the absorption and desorption behavior of poly(vinyl chloride) and poly(styrene) powders subjected to organic vapors. Their results suggested that the absorption and desorption of organic vapors induced structural relaxation in the polymers. The structural relaxation on the other hand affected the sorption of the organic vapors, which resulted in deviations from Fick's law. Berens et al.'s results were consistent with observations from studies of water in epoxy glasses.[20,21] Those studies involved absorption–desorption–absorption cycles. The water uptake rate was higher in the second absorption than in the first absorption at the initial stage, which suggested that after desorption the material is in a high (free) volume state. However, as the time interval between desorption and absorption increased, the volume increment for the second absorption above the first absorption decreased. This result implies that structural relaxation occurs in the sorption–desorption experiments. Also, an extra enthalpy in addition to the excess enthalpy of a glassy polymer due to absorption and desorption of a solvent was evidenced in the results of Berens and Hodge on poly(vinyl chloride), and that may be relevant to the results presented later in this paper, though they did not have a clear interpretation at the time.[23]

Some authors have suggested that the effect of water or small molecules on the polymeric system could be attributed to chemical or mechanical damage caused by the water or another small molecule.[21,22] Nonetheless, many results also show that no permanent damage is introduced by the ingress of water or small molecules. The results of Zhou and Lucas,[26] for example, show that the T_g of an epoxy system after absorption and desorption cycles of water could be fully recovered to the values of the dry sample. In their experiments, the measurements of T_g were performed with DSC and corroborated with TMA. Similar results were also obtained by Sun et al.[24] In their experiments the shape of the endothermal peak for a desorbed PET sample during a DSC scan was fully recovered to that of the original dry sample.

Studies also have been done to investigate the impact of small molecules on structural and mechanical properties of polymers, even though few of those studies focused on the kinetics of the property evolution.[27–29,31–34] Wang et al.[27] observed a minimum in the T_g of polystyrene as the sample was subjected to carbon dioxide, the pressure of which was increased over a range of 0.1–105 MPa. Results from both ultrasonic measurements of Young's modulus and static measurements of the creep compliance were reported. Fleming and Koros performed a series of measurements on the mass sorption/desorption and volume change for both polycarbonate and silicone rubber.[28] Their results on polycarbonate agreed well with those from Wissinger and Paulaitis, which indicated that this polymer undergoes a glass transition as the pressure of carbon dioxide goes from low to high pressure.[29,30] Mechanical tests for the effect of water on PVAc by Knauss et al.[31] suggested that the material response to the absorption of water was similar to that of increasing temperature, and a similar result was shown by Alcoutlabi et al.[32] for carbon dioxide uptake. In addition, Han and McKenna[35] measured volume recovery of epoxy resins in an experiment with symmetrical up and down relative humidity jumps. Their results showed an asymmetry of approach that was similar to that observed in temperature jumps.

Although all of the above results imply small molecule induced structural recovery, direct measurements of volume recovery analogous to Kovacs' extensive thermal experiments on PVAc, except for the preliminary results from Han and McKenna,[35] have not been reported. In addition, a direct comparison of the responses after temperature and relative humidity jumps to the same final state has not been previously reported.

In the following sections, we describe the experimental methods used to perform structural recovery experiments in RH-jump conditions and present results for intrinsic isopiestics, asymmetry of approach, and memory effects. This is followed by a presentation of results from using the extended TNM–KAHR model to describe the structural recovery in RH-jump conditions. In addition, the results for the RH-jump experiments are compared

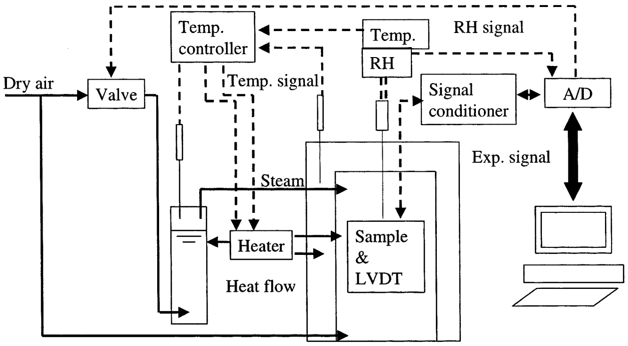

Figure 5. Illustration of the experimental system for isothermal RH-jump and isopiestic T-jump experiments.

with those for temperature jumps (T-jumps) to the same final conditions. A discussion of the significance of the results is then presented, followed by a conclusion section.

II. Experimental Methods

Environmental Chamber. A double-layered environmental chamber was built. Temperature and relative humidity were controlled independently. The experimental system is illustrated in Figure 5. Temperature control was performed using an Omega temperature controller (CN77000 series). Relative humidity control was based on a PID[36] program written in Pascal. As illustrated in Figure 5, one stream of dry cold air was directed to the system at a constant flow rate. The second air stream, regulated by a solenoid valve (Aalborg GFC series), passed through a steam generator before entering the environmental chamber. The degree of valve opening was regulated by an analog signal from the relative humidity feedback loop. The dry and wet air were mixed by tube fans in the chamber. The relative humidity was measured using a relative humidity sensor (Vaisala HMP233) placed near the sample. With this setting, the system was capable of performing isothermal relative humidity down and up jumps for a range of rates. The variation of temperature during the segment of the experiment in which relative humidity varied (RH-jump) was about ±0.3 °C, and it was about ±0.1 °C during the isopiestic aging segment. The variation for RH was within ±0.5%. Examples of relative humidity ramp and isopiestic segment are shown in Figure 6. The humidify and heat up segments form the initial stage. Between the initial stage and the down jump, the sample was stabilized for 1 h above T_g to erase previous histories. The subsequent RH down jump and also up jump are almost linear as a function of time, and the system temperature is constant during jumps, as shown in Figure 6a. In addition, a second down jump has a rate identical to that of the first jump.

Epoxy Network. The sample used in the experiments was a thin film made from an epoxy-terminated diglycidyl ether of bisphenol A (DGEBA, DER332, Dow Chemical) cured with an amine-terminated poly(propylene oxide) (T403, Huntsman). The preparation of the sample followed the protocol of Lee and McKenna.[37,38] First, a mixture of the epoxy and amine in the stoichiometric ratio was degassed for 1 h at room temperature. Then, the mixture was cast onto a smooth brass mold and fully cured at 100 °C between two brass plates under a pressure of 2 atm for 24 h. The pressure prevents bubbles from forming due to residual air in the sample. Then, the sample was slowly cooled to room temperature overnight. The T_g of the sample after cure was approximately 72 °C, determined from DSC (differential scanning calorimetry) measurement at a heating rate of 10 °C/min after cooling from 100 °C to ambient temperature at 10 °C/min. Even though the sample was relatively stable in the dry state, when the sample was subjected to the water sorption−desorption, aging, and drying cycles, its T_g steadily increased up to 76 °C. Therefore, all the reported measurements were performed after several cycles of sorption−desorption and aging until the data were reproducible, that is, the T_g had stabilized. (Surprisingly, the Lee and McKenna[37,38] work in dry conditions exhibited no change in T_g during aging. Nor did the work of Alcoutlabi et al.[31] in CO_2 plasticizing conditions and at the same temperatures. This is something that may be of interest in future research and suggests hygrothermally induced changes in the epoxy network that saturate over relatively short times.) The thickness of the sample was approximately 40 μm, such that the diffusion time for water was less than 2 min,[35] which was far less than the experimental time.

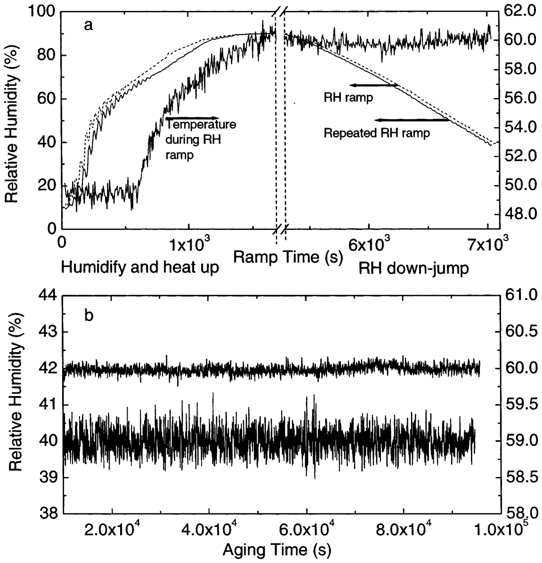

Figure 6. System response showing RH and T variability (a) in a relative humidity ramp and (b) at constant relative humidity.

Volume Measurements. The measurements of volume change were performed by determining the length change of the sample with an LVDT. The volume thus was calculated, assuming material isotropy. However, the material under study is a viscoelastic material. The weight of the sample, LVDT core, and gripping system exerted a uniaxial stress on the sample (approximately 0.1 MPa) and in the same dimension as the change of length to be attributed to a volume change. Since the samples were stabilized above the glass transition either at high relative humidity or at high temperature, the creep of the samples caused by this weight reached the limiting rubbery modulus or compliance value before the relevant jumps. Assuming time−temperature and time−concentration superposition[3] are valid, then the creep should not intervene in subsequent volume measurements at lower temperature and relative humidity. Minor effects due to entropic elasticity could slightly affect the results, but these were ignored. Experiments in which the measurements were carried out using a mass of the LVDT core and grip system half that of our normal system gave volume recovery results that were the same within the experimental uncertainty.

Structural Recovery Experiments. The experimental protocols used were similar to those of Kovacs shown in Figures 2a, 3a, and 4a. However, in those figures the abscissa "temperature" is now replaced with RH in our experiments.

(1) RH Down Ramp To Determine RH$_g$. The sample was first equilibrated at 90% RH for 1 h to erase the impact of the prior hygrothermal history. At such high relative humidity, the glass transition temperature is below the experimental temperatures (55, 60, and 65 °C), which was confirmed by our volume measurements. The RH was then reduced to 30% at the rate of 1.5%/min isothermally, and the length change of the sample was measured during the change of RH. We report the time abscissa as $t-t_i$, which is the time from the end of the humidity jump (ramp).

(2) Intrinsic Isopiestics (Refer to Figure 2a). The sample was first equilibrated at 90% for 1 h, and then the RH was decreased to the aging RH of 30%, 40%, 50%, and 60% at 1.5%/

Table 1. Glass Transition Relative Humidity (RH_g) and Hygrothermal Expansion Coefficients (α_{RH})

	55 °C	60 °C	65 °C
RH_g	$64 \pm 1\%$	$65 \pm 1\%$	$60 \pm 1\%$
$\alpha_{RH(l)}$	$(3.14 \pm 0.02) \times 10^{-4}$/%RH	$(3.86 \pm 0.02) \times 10^{-4}$/%RH	$(4.06 \pm 0.04) \times 10^{-4}$/%RH
$\alpha_{RH(g)}$	$(1.77 \pm 0.02) \times 10^{-4}$/%RH	$(2.09 \pm 0.02) \times 10^{-4}$/%RH	$(1.97 \pm 0.04) \times 10^{-4}$/%RH
$\Delta\alpha_{RH(g)}$	$(1.37 \pm 0.02) \times 10^{-4}$/%RH	$(1.77 \pm 0.02) \times 10^{-4}$/%RH	$(2.09 \pm 0.04) \times 10^{-4}$/%RH

Table 2. Curve Fitting Parameters for the TNM−KAHR Model by Fitting Intrinsic Isopiestic Curves (Method 1)

	RH-jump at 60 °C	RH-jump at 65 °C
x	0.07 ± 0.02	0.05 ± 0.02
β	0.23 ± 0.01	0.26 ± 0.01
θ_{RH}	0.06 ± 0.01	0.08 ± 0.01
τ_{ref} (s)	100	100
$\Delta\alpha_{RH}$ (/%RH)	$(1.77 \pm 0.02) \times 10^{-4}$	$(2.09 \pm 0.04) \times 10^{-4}$
RH_{ref}	$65 \pm 1\%$	$60 \pm 1\%$

min at the relevant test temperature isothermally. After reaching the aging RH, the structural recovery of the sample was measured. We report the time abscissa as $t-t_i$, which is the time from the end of the humidity jump (ramp).

(3) Asymmetry of Approach (Refer to Figure 3a). RH up jumps and RH down jumps of the same magnitude were performed for this experiment. For the RH down jump, the sample was first equilibrated at 90% RH for 1 h to eliminate the previous history. Then the RH was reduced to 65%, and the sample was annealed for 50 h to reach equilibrium. The RH was reduced again to 50%, where the structural recovery was measured. For the RH up jump, the sample was first equilibrated at 90% RH for 1 h to eliminate the previous history. Then the RH was reduced to 35%, and the sample was annealed for 100 h to reach equilibrium (as detected from volume measurement). Then the RH was increased to 50% RH to measure the structural recovery. We report the time abscissa as $t-t_i$, which is the time from the end of the humidity jump (ramp).

(4) Memory (Refer to Figure 4a). The sample was first equilibrated at 90% RH for 1 h eliminate the previous history. Then the RH was reduced to 30% or 40%, and the sample was aged for 5 h. With 5 h of aging, the sample did not reach equilibrium at either RH. Finally, the RH was raised to 50% and the measurement of the structural recovery was carried out. We report the time abscissa as $t-t_i$, which is the time from the end of the humidity jump (ramp).

(5) Comparison of Structural Recovery after the RH-Jump and the *T*-Jump. The effect of change of relative humidity was compared with the effect of change of temperature for the same final state as defined by the relative humidity and temperature. For the RH-jump, the RH was increased or decreased (at a rate of 1.5%/min) while the temperature was maintained at the relevant final temperature. For the temperature jump, the temperature was increased or decreased (at a rate of 0.5 °C/min) while the relative humidity was maintained at the final relative humidity. By choosing those rates of changes, the time scales for the temperature jumps and for relative humidity jumps are almost the same. We report the time abscissa as $t-t_i$, which is the time from the end of the humidity jump (ramp) or the temperature jump (ramp).

III. Method of Analysis

We have used the TNM−KAHR model to describe the material behaviors. $\Delta\alpha_T$ was measured from temperature down ramp experiments, and $\Delta\alpha_{RH}$ was obtained from relative humidity down ramp experiments. The values are listed in Tables 2 and 3. For the reference relaxation time in eq 2, 100 s was used for the transition region[15] The activation energy θ, the nonlinearity parameter x, and the nonexponentiality parameter β were obtained through curve fitting the experimental data with a previously written program.[39] Two methods of curve fitting were practiced in this study:

(1) A set of intrinsic isopiestic curves was fitted simultaneously to give the model parameters for the overall best fit. Then the model parameters were used to calculate asymmetry of approach and memory effect.[40]

(2) A set of asymmetry of approach curves was fitted simultaneously to obtain the model parameters for the overall best fit. The model parameters were used to calculate memory effect and intrinsic isopiestics.[16] For the temperature jumps, only this method was used.

A common practice for such calculations assumes a perfect jump of either temperature or relative humidity. In the modeling, since the rate of change was far less than a jump, we instead calculated the ramps using a step size of 0.2 °C during temperature jumps and one of 0.5% during relative humidity jumps. The time interval during structural relaxation was 5 s in the calculations. However, only the data from the structural recovery portions of the curves were used in the curve fits themselves.

On the basis of the model parameters obtained from the asymmetry of approach curves or modeling method 2, a quantitative comparison between RH-jump and T-jump results was performed by using the concept of the isothermal volume sensitivity (S). This concept was originally proposed by Struik[41] and elaborated by McKenna and Kovacs,[42] and it can be expressed in terms of the TNM−KAHR model parameters as

$$-\frac{d \ln \tau}{d\delta} = S = (1 - x)\theta/\Delta\alpha \tag{4}$$

where x and θ are the same parameters as in eq 2. The higher the value of S, the more sensitive is the rate of structural recovery to the current structure.

IV. Results

Volume Change during Isothermal Relative Humidity Down Ramp. Figure 7 exhibits the volume change during isothermal relative humidity down ramps at three temperatures: (a) 55, (b) 60, and (c) 65 °C. The volume is normalized over the initial volume for the sample at 55 °C and 90% at equilibrium. The figure shows that all three curves exhibit a clear transition behavior similar to that observed in temperature down ramp experiments. In addition, temperature does have an effect on the value of RH_g where the transition takes place. At 65 °C, the sample has the lowest RH_g (60%). However, at 55 and 60 °C, the difference between RH_g values (64% and 65%) is within the experimental error. In addition, $\Delta\alpha_{RH}$, which is the difference of the hygrothermal expansion rate between the rubbery and glassy states, increases as the temperature increases. The values of the RH_g, α_{RH} in the glassy and rubbery states, and $\Delta\alpha_{RH}$ are listed in Table 1.

Intrinsic Isopiestics. Figure 8 shows the results for intrinsic isopiestic experiments for different aging relative humidities and at two experimental temperatures: (a) 60 and (b) 65 °C. The samples used at the two different testing temperatures were from different sample preparation batches. For each temperature, the

Table 3. Curve Fitting Parameters for the TNM−KAHR Model by Fitting Asymmetry of Approach Curves (Method 2)

	RH-jump at 60 °C	RH-jump at 65 °C	T-jump at 50%
x	0.34 ± 0.02	0.17 ± 0.02	0.17 ± 0.02
β	0.26 ± 0.01	0.26 ± 0.01	0.32 ± 0.01
θ_{RH}, θ_T (1/K)	0.16 ± 0.01	0.16 ± 0.01	0.46 ± 0.01
τ_{ref} (s)	100	100	100
$\Delta\alpha_{\mathrm{RH}}$ (/%RH), $\Delta\alpha_T$ (1/K)	$(1.77 \pm 0.02) \times 10^{-4}$	$(2.09 \pm 0.04) \times 10^{-4}$	$(3.00 \pm 0.02) \times 10^{-4}$
$\mathrm{RH}_{\mathrm{ref}}$, T_{ref} (K)	65 ± 1%	60 ± 1%	338.2 ± 0.5
S (volume sensitivity)	597 ± 41	635 ± 43	1273 ± 42

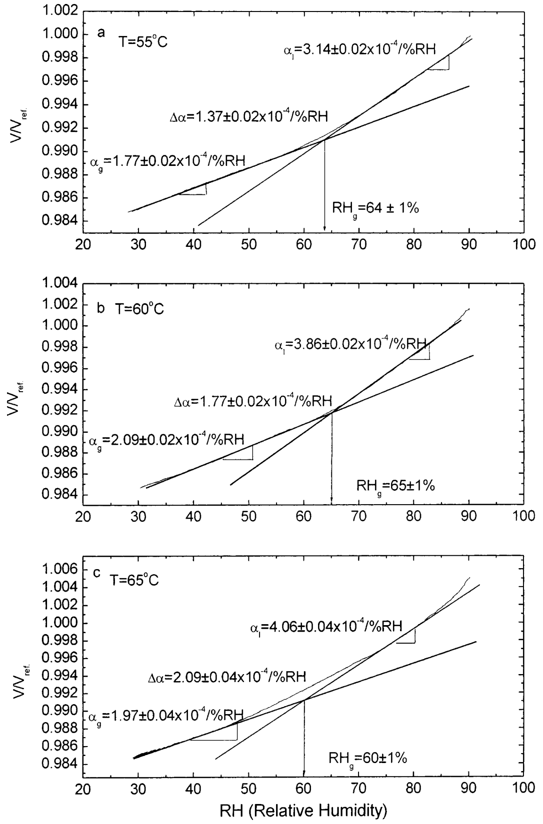

Figure 7. Volume change during relative humidity down ramps at three different temperatures: (a) 55 °C, (b) 60 °C, and (c) 65 °C. The reference volume is the volume at 90% RH and 55 °C.

results of the intrinsic isopiestics, memory effect, and asymmetry of approach experiments are from the same sample.

Following the isopiestic curves in Figure 8, the time for the sample to reach equilibrium increases as relative humidity decreases. These results are quite similar to those for intrinsic isotherms. In fact, the Kovacs data could be considered as 0% RH intrinsic isotherms. For the isopiestics at low relative humidity, which did not reach equilibrium within the experimental time, their equilibrium volumes are estimated by linear extrapolation from the equilibrium volume at high relative humidity. Clearly, the structural recovery in intrinsic isopiestic conditions depends on relative humidity just as the intrinsic isotherm depends on temperature.

Asymmetry of approach. Figure 9 presents the results from the asymmetry of approach experiment. As seen in the figure, the volume response from a RH up jump and the volume response from a RH down jump of the same magnitude approach the equilibrium volume asymmetrically. This is again analogous to what is observed in T-jump experiments. These results imply that the structural recovery after a relative humidity change depends on the current structure and bears the characteristic of nonlinearity. This is similar to the asymmetry of approach after temperature changes illustrated in Figure 3b.

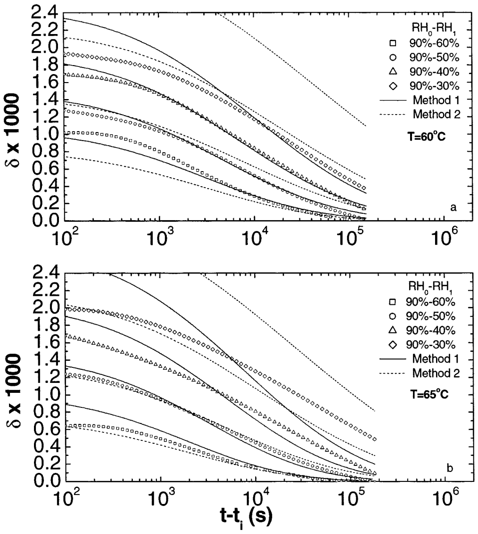

Figure 8. (a) Intrinsic isopiestics at 60 °C. (b) Intrinsic isopiestics at 65 °C. The solid lines are the TNM−KAHR model curve fitting (method 1); dashed lines are the model predictions based on the model parameters obtained from curve fitting the asymmetry of approach data (method 2).

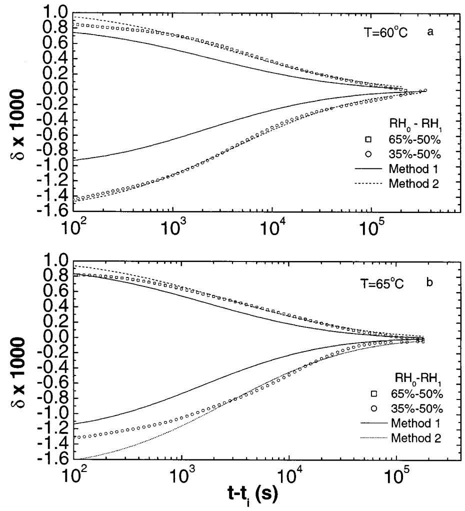

Figure 9. (a) Asymmetry of approach results at 60 °C. (b) Asymmetry of approach results at 65 °C. Solid lines are TNM−KAHR model calculation based on the model parameter obtained from curve fitting intrinsic isopiestics (method 1); dashed lines are the model curve fits to the data (method 2). The samples were equilibrated by aging for 50 h at 65% RH and for 100 h at 35% RH at both temperatures.

Memory Experiment. Figure 10 shows the results of the memory experiments. Monotonic maximums are observed for both experimental temperatures. These

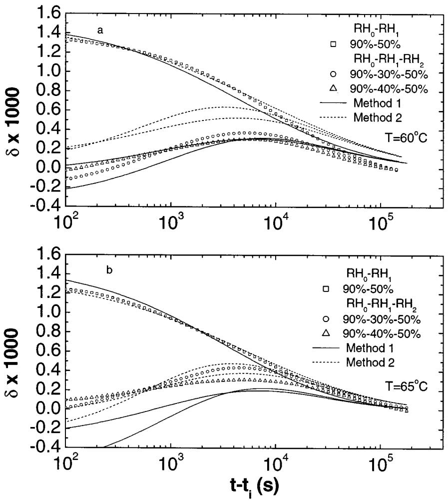

Figure 10. (a) Memory experiments at 60 °C. (b) Memory experiment at 65 °C. Solid lines are the TNM−KAHR model calculation based on the model parameters obtained from curve fitting intrinsic isopiestics (method 1); dashed lines are the model calculations based on the model parameter obtained from curve fitting asymmetry of approach (method 2). The samples were allowed to partially recover at 30% RH and 40% RH by aging for 5 h for both temperatures.

results imply a distribution of relaxation times or other nonexponential relaxation in the structural recovery kinetics after relative humidity changes. These behaviors are similar to the memory effect in thermal experiments.

TNM−KAHR Model. The results for the structural recovery in the RH-jump experiments are similar to those observed by Kovacs *T*-jump experiments. Therefore, the hypothesis "the change of relative humidity has a similar effect to temperature changes on structural recovery and physical aging" is qualitatively correct. On the basis of these experimental results, the TNM−KAHR model was extended to describe the structural recovery in the relative humidity-jump experiment by curve fitting the experimental data using the method developed previously.[39] The model parameters from the curve fitting are listed in Tables 1 and 2 for curve fitting methods 1 and 2, respectively. The results of the model calculations are plotted together with the experimental data in Figures 8−10.

We compared the model calculations with the experimental results. If the model parameters from the asymmetry of approach experiment are applied, the calculated δ values (dashed lines) are higher than the experimental data for the memory experiment and the intrinsic isopiestics. If the model parameters are determined from the intrinsic isopiestics, the calculated δ values are lower than the experimental data for the memory experiments and the asymmetry of approach experiments. This result implies that the model parameters are history dependent for its application in RH-jump experiments. Similar results have been found in *T*-jump conditions and represent a known problem of the TNM−KAHR model.[16]

On the basis of the results of RH-jump experiments, it is clear that our hypothesis that the change of relative humidity has an effect similar to that of temperature change on the structural recovery is qualitatively correct. To test whether the hypothesis is quantitatively correct, we have to compare the kinetics of structural recovery after RH-jumps with those after *T*-jumps for the same final state as defined by relative humidity and temperature. The comparisons are presented in the following section.

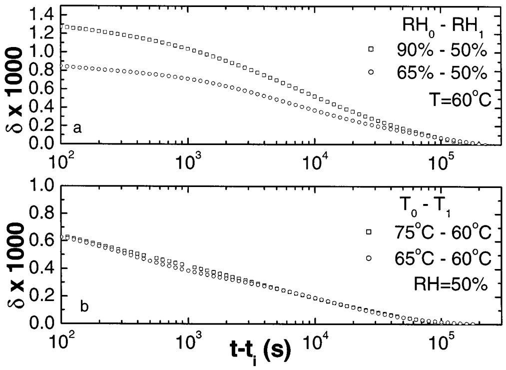

Figure 11. (a) Intrinsic isopiestics for different magnitude relative humidity jumps. (b) Intrinsic isotherms for different magnitude temperature jumps.

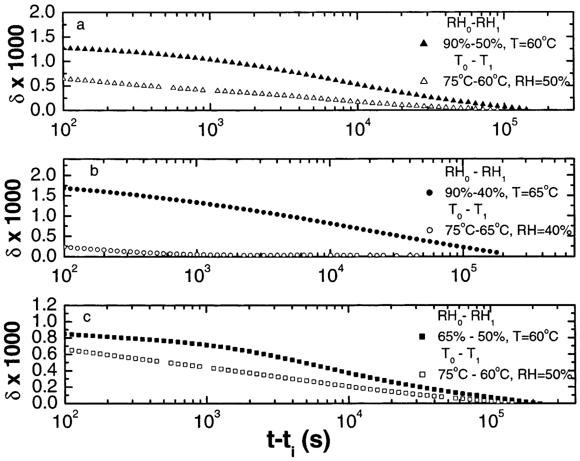

Figure 12. (a) Comparison between intrinsic isotherms and isopiestics at the same final state: 60 °C and 50%. (b) Comparison between intrinsic isotherms and intrinsic isopiestics at the same final state: 65 °C and 40%. (c) Comparison between intrinsic isotherms and intrinsic isopiestics of the same magnitude jumps at the same final state: 60 °C and 50%.

Relative Humidity Change versus Temperature Change. Referring to Figure 1, each state on the equilibrium surface is solely determined by temperature and relative humidity. However, the path the system follows as it approaches equilibrium in the glassy state depends on its previous temperature and relative humidity history. Figure 11a exhibits a comparison of two isopiestics after different magnitudes of RH-jump. Figure 11b shows a comparison of two isotherms after different magnitudes of *T*-jump. From both parts of the figure, regardless of the magnitudes, the curves join together before they reach equilibrium. These results are consistent with Kovacs' results.[6,13] However, it is interesting that the merging of the curves is much closer to equilibrium ($\delta = 0$) and at longer times for the RH-jump than for the *T*-jump experiments.

Figure 12 presents a comparison between isotherms and isopiestics for the same final state as defined by the relative humidity and temperature. Parts a and b show the structural recoveries for different magnitude jumps. Figure 12c shows the structural recovery for an RH-jump and a *T*-jump in which the departures from equilibrium at 1 s after the jumps are the same. In contrast to the curves in Figure 11, the isotherms reach

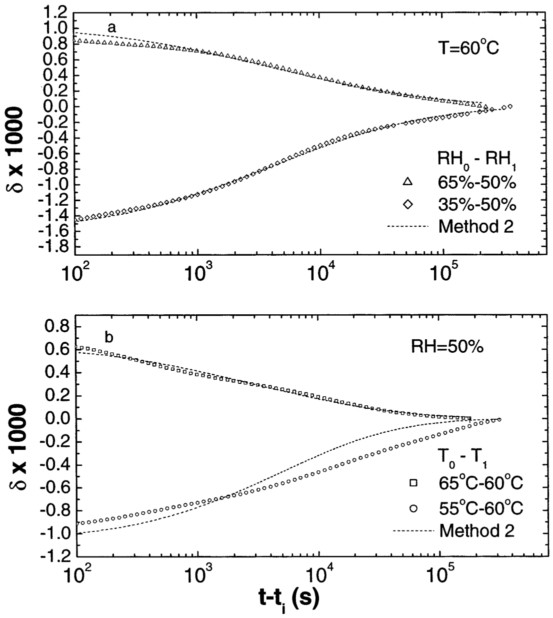

Figure 13. (a) Asymmetry of approach for RH-jump at the final state: 60 °C and 50%. (b) Asymmetry of approach for T-jump at the final state: 60 °C and 50%. The dashed lines are the fitting curves by the TNM−KAHR model. The sample was stabilized for 50 h for the conditions 65% RH and 60 °C; 65 °C and 50% RH, and stabilized for 100 h for the conditions 35% RH and 60 °C; 55 °C and 50% RH.

equilibrium earlier than do the isopiestics. In Figure 12c, even though the initial values of δ are the same, the isotherm is very different from the isopiestic. This indicates very different structural recovery kinetics for the RH-jump and T-jump conditions. In fact, it is surprising that the epoxy in the RH-jump experiments, in which the excess volume is greater than that in the T-jump experiments, seems to exhibit the lower molecular mobility. This is discussed subsequently.

As another comparison of the responses in the T-jump and RH-jump behaviors at the same final conditions, we used the TNM−KAHR model to curve fit asymmetry of approach data in T-jump and RH-jump conditions and compared the model parameters. The fitting curves are shown in Figure 13, and the model parameters are listed in Table 3. The differences between T-jump and RH-jump can then be expressed in terms of the nonexponentiality parameter β and the volume sensitivity S (see eq 4), which includes the contributions from θ and x. The values of β and S after the T-jump are 0.32 ± 0.01 and 1273 ± 42, respectively, and these are larger than the parameters of 0.26 ± 0.01 and 597 ± 42 obtained after the RH-jump experiments.

V. Discussion

A series of RH-jump experiments similar to Kovacs' T-jump experiments were performed on an epoxy network. The structural recovery responses after RH-jump conditions are quite similar to those for T-jump conditions in terms of intrinsic isotherm, asymmetry of approach, and memory effect. This result suggests the original hypothesis that motivated this work, viz., that traversing the glass transition concentration (RH) from above the glass transition to below results in a change in distance from the transition that is similar in nature to a temperature jump. However, when comparing the structural responses between RH-jumps and T-jumps to the same final state, the structural recovery kinetics of the RH-jump are significantly different from those for the T-jump experiment.

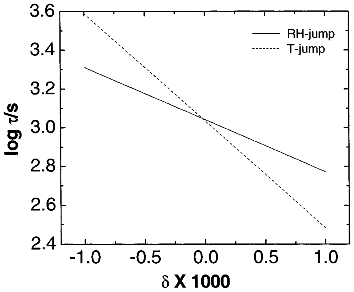

Figure 14. Retardation time as a function of departure from equilibrium (δ) calculated on the basis of eq 2 for RH-jumps and T-jumps to the same final state: 60 °C and 50% RH (Asymmetry of approach experiment). The errors due to the standard deviations of model parameters are negligible on this graph.

The larger volume sensitivity of the response after the T-jump than that after the RH-jump is consistent with the differences between temperature and relative humidity jumps (refer to Figures 10 and 11). Since the relaxation in the RH-jump experiment is less sensitive to its current structure than it is under T-jump conditions, its relaxation approaches equilibrium more slowly than it does after the T-jump. A plot of the structural recovery retardation time τ (eq 2) versus the departure from equilibrium δ for asymmetry of approach conditions in the RH-jump and T-jump conditions is shown in Figure 14. The value of τ after the T-jump is considerably smaller than that after the RH-jump when δ has a large positive value, that is, there is a large excess of volume. Similarly, when δ has a large negative value, viz., a deficit in volume, the value of τ is lower for the RH-jump experiment. These results are quite similar to the relaxation times obtained in physical aging measurements on the same material subject to CO_2-jumps and T-jumps, as reported by Alcoutlabi et al.[32]

We consider the results just described to be anomalous and to require an understanding of glassy structure that does not currently exist. In the work of Alcoutlabi et al.[32] a tentative explanation was proposed on the basis of the thought that kinetics in glass forming systems are governed by an energy landscape that is determined by the heterogeneous nature of glass-forming liquids.[43−54] In the conventional case, the landscape is populated differently as temperature decreases and only certain potential wells come into play, with the deepest wells becoming more populated and leading to a large slowing down of the kinetics as T_g is approached. One could imagine a similar scenario as plasticizer content is varied in the material. However, plasticizer content could well be changing the energy landscape in the isothermal condition as RH_g (or the concentration glass transition) is changed. Can it be that the energy landscape of the nonequilibrium system that results from the RH-jump is dramatically different from that that results from the T-jump? Another possibility is that the energy landscape is the same and that the parts of the landscape that are populated when moving from the RH-jump to the T-jump condition are different. Here we suggest that measures of heterogeneity of the dynamics in the T-jump and RH-jump conditions could provide further insight into the apparently anomalous results obtained in this work. Our observations of a slightly changed distribution of retardation times (due to heterogeneity) as reflected in the KWW β parameter are not robust enough to make a conclusion on their basis.

Finally, it is also worth considering the different nature of the glass formed by changing moisture content versus that formed by changing temperature. There are several possible scenarios. First, the plasticizing environment may be more heterogeneous even above the glass transition due to, for example, water clustering or a mixture of bound and unbound water in the sample, as has been argued in the literature.[55] The result of this could be that removal of the moisture results in a glassy structure that reflects this heterogeneity and is therefore different from that formed by the change in temperature. The structural recovery that is measured would then reflect a "normal" component as well as a redistribution of this heterogeneity toward the equilibrium state during the recovery. This speculation may also be related to the above discussion of different energy landscapes that reflect the heterogeneity. However, we also remind the reader that there are also reports in the literature for water in similar epoxy networks to that studied here that do not show a partitioning of the water into bound and unbound states.[56] It may also be that the space between molecules of the epoxy glass collapses differently when a water (plasticizer) molecule is removed than when the temperature changes. In any event, further research is required to explain the observation that a glass having higher excess volume (from the RH-jump) exhibits lower molecular mobility than does the lower excess volume glass (from the *T*-jump).

VI. Summary and Conclusions

To study the effects of moisture content on the physical aging responses of glassy polymers, we built a programmable RH experimental system and measured the volume recovery after relative humidity jumps. A series of hygrothermal experiments, which in principle are similar to Kovacs' thermal experiments, were performed. We have demonstrated that the RH experiments exhibit similar structural recovery behavior to that observed in *T*-jump experiments, viz., intrinsic isopiestics, asymmetry of approach, and memory. Although the RH-jump and *T*-jump experiments gave qualitatively similar results, quantitative comparison of the intrinsic isopiestics with intrinsic isotherms and asymmetry of approach of RH-jump with *T*-jump for the same final states shows that the kinetics are different for the two different types of jump. The differences are further confirmed by the measurements of volume sensitivity *S* and nonexponential parameter β obtained from curving fitting with the TNM−KAHR model. We found that an extended TNM−KAHR model qualitatively described the structural relaxation due to change of relative humidity. Errors in the predicted behavior are similar in nature to those obtained in *T*-jump experiments. This work demonstrates that the hypothesis "the change of relative humidity has similar effects to temperature changes on the physical aging response of glassy polymers" is qualitatively correct. Quantitatively, however, the kinetics of structural recovery in RH-jump and *T*-jump histories are anomalously different in that the RH-jump experiment results in longer structural recovery times even though the excess volume in these experiments is greater than that in the *T*-jump case. Also we expect that changes of concentration in other plasticized polymeric systems will lead to similar phenomena.

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Note Added after ASAP Posting

This article was inadvertently posted without corrections on March 13, 2003. A revised, corrected version was posted on 3/14/2003.

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