M. L. *J. Am. Chem. Soc.* **1942**, *64*, 1712. (f) Huggins, M. L. *Physical Chemistry of High Polymers*; Wiley: New York, 1958.

(7) Ohta, T.; Oono, Y. *Phys. Lett. A* **1982**, *89A*, 460.

(8) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley-Interscience: New York, 1987.

(9) Cherayil, B. J.; Douglas, J. F.; Freed, K. J. *J. Chem. Phys.* **1985**, *83*, 5293, and references therein.

(10) For a recent self-consistent field approach to phase separation in a polymer–solvent mixture that incorporates three-body effects, see, for instance Muthukumar, M. *J. Chem. Phys.* **1986**, *85*, 4722.

(11) Edwards, S. F. *Proc. Phys. Soc., London* **1966**, *88*, 265; *J. Phys. A: Math. Gen.* **1975**, *A10*, 1670.

(12) (a) Schäfer, L.; Witten, T. A. *J. Chem. Phys.* **1977**, *66*, 224. (b) des Cloizeaux, J. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 281.

(13) Freed, K. F. *J. Chem. Phys.* **1983**, *79*, 6357.

(14) In the units that define H/k_BT of eq 2.1, distances $\mathbf{r}(\tau)$ have dimensions of (length)$^{1/2}$. They are related to ordinary Euclidean distances through scale transformations that are discussed at length in: Kosmas, M. K.; Freed, K. F. *J. Chem. Phys.* **1978**, *69*, 3647.

(15) Cherayil, B. J.; Bawendi, M.; Miyake, A.; Freed, K. F. *Macromolecules* **1986**, *19*, 2770.

(16) There are nonuniversal contributions to the free energy of (2.11) as discussed in: Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *Macromolecules* **1987**, *20*, 1345. These terms appear linearly in the concentrations ϕ_A and ϕ_B and so do not contribute to free energy differences, so thay may be absorbed into the zero of free energy.

(17) (a) Freed, K. F. *J. Phys. A: Math. Gen.* **1985**, *18*, 871. (b) Bawendi, M. G.; Freed, K. F.; Mohanty, U. *J. Chem. Phys.* **1986**, *84*, 7036. (c) Bawendi, M. G.; Freed, K. F. *J. Chem. Phys.* **1988**, *88*, 2741. (d) Freed, K. F.; Pesci, A. I. *J. Chem. Phys.* **1987**, *87*, 7342. (e) Nemirovsky, A. M.; Bawendi, M. G.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 7272.

(18) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, 1979.

(19) (a) Ohta, T.; Oono, Y.; Freed, K. F. *J. Phys. A: Math. Gen.* **1982**, *A15*, 1931. (b) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 1854.

(20) (a) Hefford, R. J. *Polymer* **1984**, *25*, 979. (b) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*; Wiley-Interscience: New York, 1975. (c) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1984**, *17*, 548. (d) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1986**, *19*, 1411. (e) Shiomi, T.; Kohno, K.; Yoneda, K.; Tomita, T.; Miya, M.; Imai, K. *Macromolecules* **1985**, *18*, 414. (f) Ould Kaddour, L.; Strazielle, C. *Polymer* **1987**, *28*, 459.

(21) (a) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833. (b) Koningsveld, R.; Chermin, H. A. G.; Gordon, M. *Proc. R. Soc. London A* **1970**, *319*, 331. (c) McMaster, L. P. *Macromolecules* **1973**, *6*, 760. (d) Patterson, D.; Robard, A. *Macromolecules* **1978**, *11*, 690. (e) Sanchez, I. C. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic: New York, 1978; Chapter 3. (f) Hamada, F.; Shiomi, T.; Fujisawa, K.; Nakajimia, A. *Macromolecules* **1980**, *13*, 729. (g) See also ref 17.

(22) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 1854; **1985**, *18*, 201.

(23) Einaga, Y.; Tong, Z.; Fujita, H. *Macromolecules* **1987**, *20*, 2027.

(24) (a) Cherayil, B. J.; Freed, K. F. *J. Chem. Phys.* **1988**, *88*, 7851. (b) Reference 24a provides a general crossover analysis in the three excluded interactions that would enable the lifting of an approximation used here in deriving (2.12), (2.15), and (2.17), where as explained in the section after (2.12) the excluded volume interactions are replaced to order ϵ by virial coefficients. A more accurate approach is now possible based on ref 24a, but is is unnecessary here as the corrections appear to be most relevant only in the scaling limit of fully developed excluded volume, which our computations do not explicitly consider.

(25) Callen, H. B. *Thermodynamics*; Wiley: New York, 1960.

(26) Broseta, D.; Leibler, L.; Joanny, J.-F. *Macromolecules* **1987**, *20*, 1935.

(27) Greer, A. S. *Acc. Chem. Res.* **1978**, *11*, 427.

(28) Greer, S. C.; Moldover, M. R. *Annu. Rev. Phys. Chem.* **1981**, *32*, 233.

(29) Ohta, T.; Nakanishi, A. *J. Phys. A: Math. Gen.* **1983**, *16*, 4155.

Multiple-Temperature Steps: A Further Test of an Aging Theory for Polymer Glasses

Richard E. Robertson*

Department of Materials Science and Engineering and Macromolecular Research Center,
The University of Michigan, Ann Arbor, Michigan 48109-2136

Robert Simha[†]

Department of Macromolecular Science, Case Western Reserve University,
Cleveland, Ohio 44106

John G. Curro[‡]

Sandia National Laboratories, Albuquerque, New Mexico 87185.

Received August 21, 1987; Revised Manuscript Received May 9, 1988

ABSTRACT: A recent theory for the aging kinetics of polymer glasses has been further tested by comparing its predictions of volume recovery with the experimental results of Kovacs on poly(vinyl acetate) when subjected to two sequential temperature steps. Kovac's results present an important test because the recovering volume goes through a maximum before approaching equilibrium. With the same parameters used previously, the computed curves properly describe the essence of the experimental data: the general height, location, and ranking of the various maxima. A more quantitative fit to the data is obtained, however, by augmenting the free volume theory with an additional activation energy to account more accurately for the purely thermal effects.

Introduction

Liquids near the glass transition can exhibit unusual behavior when subjected to a sequence of steps in temperature or pressure. Properties like volume and enthalpy may pass at constant temperature and pressure through extrema. If, for example, the temperature of a liquid at equilibrium at the temperature T_0 is suddenly stepped to T_1 and held there for a relatively short time and then stepped to a third temperature T_2 somewhere between T_0 and T_1 and held at this temperature, the observed volume is likely to pass through either a minimum or a maximum before evolving toward a final, equilibrium value. A

[†] Supported by NSF Grant DMR-84-08341, Polymers Program.

[‡] Supported by U.S. DOE DE-AC04-76 DP00789.

0024-9297/88/2221-3216$01.50/0 © 1988 American Chemical Society

maximum occurs when the first step is downward in temperature, and a minimum occurs when the first step is upward. This behavior is often called the "memory effect."

Striking examples of the memory effect were observed in the volume recovery experiments of Kovacs.[1,2] Kovacs found volume maxima for polystyrene[1] and poly(vinyl acetate)[2] from a sequence of temperature steps that began with a downward step. Similar changes in volume have been observed by others in these polymers[3] and in the amorphous part of crystalline polyethylene.[4] Analogous behavior was observed recently in the dielectric loss of polystyrene blends.[5] Memory effects are well-known also with inorganic glasses, from both steps in temperature[6] and steps in pressure.[7]

This unusual behavior during the recovery of equilibrium is not easily explained. It cannot be explained at all by any hypothesis that assumes a simple molecular process that approaches equilibrium at a rate that is proportional to the deviation from equilibrium, which would then be describable by a single-exponential decay. More complex explanations have been required, and these have generally taken one of two forms: the assumption of two or more basic processes, whether molecular or not, that give rise to more than one exponential decay or the assumption of a single basic process, again molecular or not, that responds with nonexponential decay.

The multiplicity of processes, each with an exponential decay, has been the more common explanation.[8-10] Models assuming but a pair of processes, for example, with the two decay or retardation times differing by about a factor of 10, have fitted well the response data from inorganic glasses.[8] Goldstein,[11] among others, has warned, however, that the ability to fit data with a distribution of retardation times does not mean that a multiplicity of mechanisms must be involved. The Kohlrausch–Williams–Watts or stretched exponential function,[12] for example, used in a form where it decays more slowly than an exponential, is sufficient to explain memory effects,[13] though a distribution of such functions allows an even better fit to the data.[14]

Because the exponentials compose a set of independent functions, any monotonic function such as the Kohlrausch–Williams–Watts function can be expanded in terms of them.[15] That is, irrespective of its nature (as long as it is not pathological), any monotonic nonexponential can be expressed as a series of exponentials, thus giving what will look exactly like a multiplicity of retardation mechanisms. It is very difficult, therefore, to distinguish between an actual multiplicity of exponential processes and a single nonexponential process. As a third approach, Douglas has suggested that under certain conditions the behavior can be described by using the superposition principle with a variable relaxation time.[16] This approach seems to be equivalent to a distribution of relaxation times or a nonexponential function, however.

Not all explanations of the memory effect have assumed an explicit or implicit multiplicity of retardation times. Curro, Lagasse, and Simha,[17] for example, have been able to simulate the memory effect with the diffusion of free volume along free volume gradients.

The purpose of the present work is to examine Kovacs' double-temperature step data for poly(vinyl acetate) in terms of the molecular-based theory described previously and referred to in what follows as the RSC theory.[18-20] (The RSC theory was first described in ref 18 and summarized and extended to pressure effects in ref 19. A modification of the original theory is discussed in ref 20.) The theory assumes a multiplicity of retardation times. These are suggested to arise naturally from the totality of segmental rearrangements occuring in a multiplicity of environments. The macroscopic behavior is assumed to be the sum of segmental rearrangements. The multiplicity of environments is suggested to be a consequence of the variation in structure in the liquid associated with thermal fluctuations. Because of the small size of the regions in which segmental rearrangements typically occur, the fluctuations can be large, thus producing a large variation in structure. The variation in structure, insofar as it affects the kinetics of segmental rearrangements, is assumed to be equivalent to a variation in free volume. The free volume function used is that derived from the Simha–Somcynsky model for the equation of state for polymer liquids. The (excess) free volume is identified with the hole fraction occurring in this model.

Table I
Parameters for Volume Recovery Kinetics of Poly(vinyl acetate)

$p^* = 9380$ bar[a]	Simha–Somcynsky characteristic parameters
$V^* = 814.1$ mm^3/g[a]	
$T^* = 9419$ K[a]	
$c_1 = 12.81$[b]	time–temperature shift parameters
$c_2 = 28.74$ K[b]	
$C_1 = 11.24$[c]	
$C_2 = 45.96$ K[c]	
$T_g = 308$ K	glass transition temperature
$\tau_g = 1$ h (3600 s)	nominal relaxation time at T_g
$\tau_b = 36\,000$ s[c]	relaxation time of sub-T_g motion at T_g
$N_s = 26$	number of monomer segments in free volume transition region
$z = 13$	size ratio for region controlling free volume changes
$R = 0.0022$	translation factor between macroscopic and microscopic processes

[a] McKinney, J. E.; Simha, R. *Macromolecules* **1974**, *7*, 894. [b] Plazek, D. J. *Polym. J.* **1980**, *12*, 43. [c] Robertson, R. E. *Macromolecules* **1985**, *18*, 953.

Computation

The general mathematical formulation of the RSC theory was originally described in ref 18 and summarized in ref 19. The specific mathematical formulation and parameters used in the present computations for poly(vinyl acetate) were those derived in ref 20. The latter paper was concerned mainly with the segmental mobility in the equilibrium liquid below the glass transition. The recovery rate, expressed as the reciprocal of the relaxation rate, was suggested there to be

$$\tau^{-1} = (\tau_g a_T)^{-1} + (\tau_b b_T)^{-1} \qquad (1)$$

where

$$\log a_T = -c_1 + c_1 c_2 / [c_2 + (f - f_g) T^* / f^*] \qquad (2)$$

$$\log b_T = -C_1 + C_1 C_2 / [C_2 + (f - f_g) T^* / f^*] \qquad (3)$$

f is the free volume, f_g is the free volume at the glass transition, and f^* is a constant that relates the change in free volume in the liquid with change in temperature. Other parameters in eq 2 and 3 are constants and are defined in Table I, where values for these and the rest of the quantities used in the computation are given also.

For many purposes, only the first term in eq 1 need be used. The entire expression was suggested[20] to improve the fit to Kovac's volume recovery data for poly(vinyl acetate) when using a particular set of time–temperature shift parameters derived by Plazek.[21] The suggestion arose from the excellent fit with these parameters to Kovacs' volume recovery data at the glass transition temperature

Table II
Double-Temperature-Step Experiments

experiment	T_0, K	T_1, K	t_1, 10^5 s	T_2, K
1	313			303
2	313	283	5.75	303
3	313	288	5.0	303
4	313	298	3.25	303

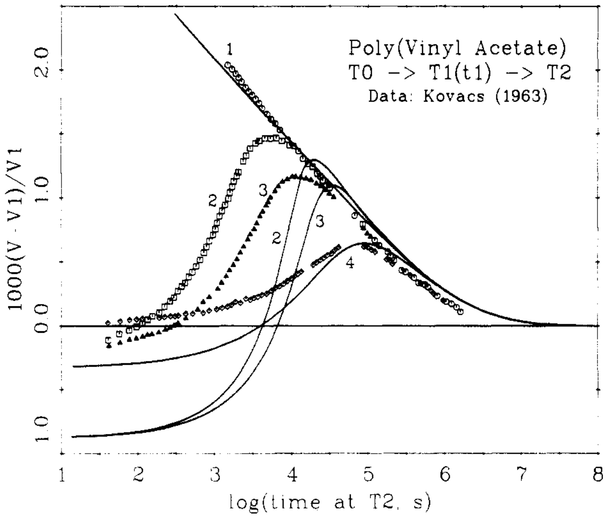

Figure 1. Volume recovery computed by using the RSC theory of poly(vinyl acetate) at 30 °C following a previous history described in Table II. The data are from Kovacs.[2]

and above and from the much worse fit at lower temperatures. The normal time–temperature shift parameter was modified in eq 1 by adding a term representing sub-T_g motions, which were believed to be affecting low-temperature relaxations. This term, however, is not exhibited until long times have passed at low temperatures, which does not occur in the present simulation at the low first temperature to which the system is stepped.

Results

The temperatures and times of the experiments that were simulated are given in Table II. The results of the computation are shown in Figure 1 with the experimental data of Kovacs.[2] The abscissa is the elapsed time since the last temperature step, namely, the step to 303 K. As indicated in Table II, experiment 1 involves only a single-temperature step, from T_0 to T_2. The other three experiments involve double steps, with t_1 being the time spent at T_1. The main difference between the real and the simulated experiments is the time required to change temperature. The computer simulation executes an instantaneous temperature change. This difference probably has little effect on the comparison, however.

The computed curves in Figure 1 are seen to represent the essential features of the data. The general magnitudes of the maxima are well represented, as is the ordering of the curves. Moreover, all of the computed curves are seen to converge at long times, as occurs experimentally.

Discussion

Though the computed curves in Figure 1 represent the essential features of the data, they clearly fail to coincide with the experimental data. A minor discrepancy is the suggestion from the computation that the curves from the double-step experiments can rise above that of the single-step experiment and then converge with the single-step curve at long times from above. This behavior has not been seen experimentally; rather, the experimental double-step volumes seem always to converge with the single-step volume at long times from below.

The major discrepancy between theory and experiment in Figure 1 is caused by the magnitudes of the volumes at the beginning of recovery at T_2. The computed volumes have fallen too far during the residence at T_1. As is seen in Figure 1, this is a more serious problem with the lower temperatures T_1. That is, the discrepancy is worse with experiments 2 and 3 than with experiment 1. The problem had not been noticed in the previous work with the single-temperature steps, where the temperature was never below 30 °C. This too rapid fall in volume at T_1 then results in the two major problems apparent in Figure 1: the times at which the maxima occur after the step to T_2 are delayed, and the heights of the maxima are reduced.

Although it might seem as if the use of the "softened" time–temperature shift expression for glassy poly(vinyl acetate), eq 1, either caused or at least exacerbated the rapid fall computed for the volumes at T_1 this was not the case. As mentioned, the softening of the time–temperature shift expression becomes effective only after very long times, but the stay at the temperature T_1 that has resulted in the fall in volume indicated by the initial values in Figure 1 was comparatively short.

A likely reason for the excessively high rate of recovery predicted at low temperatures is that the individual effects of thermal agitation and structure on the rate have not been properly accounted for. In particular, the theory has not slowed the kinetics in proportion to the dimunition in thermal agitation at lower temperatures. The RSC theory is basically, but not exclusively, a structure or free volume theory. The theory with eq 1 seems to be correct in the liquid, when the system is in equilibrium, and seems to be nearly correct for small deviations from equilibrium. For large deviations from equilibrium, however, the deficiency of the theory in not accounting sufficiently for purely thermal effects under conditions where the structure is nominaly constant becomes manifestly apparent. Thus, a different form for the theory is needed.

By analogy with other molecular processes, if the structure were to remain constant, the recovery rate would be expected to have an Arrhenius form, such as

$$\tau^{-1} = A \exp[-H^*(\theta)/RT] \qquad (4)$$

where H^* is the activation energy for the particular structure denoted by θ. But the structure of the recovering glass does not remain constant, meaning that H^* changes with time. The changing structure will be assumed to be describable approximately by the single parameter θ, the fictive temperature. The fictive temperature is the temperature of the equilibrium structure that the actual structure would be most similar to if it were brought instantaneously to that same temperature. This definition is more easily understood by reference to a plot of volume vs temperature, as in Figure 2. The lines parallel to the glass line represent "instantaneous" changes in temperature. Thus, the fictive temperature is the point of intersection of the equilibrium volume line and a line drawn parallel with the glass line and through the volume–temperature point having the same volume as the average volume of the actual glass. For the glass at temperature T_A that has the volume V_A (point A in Figure 2), for example, the fictive temperature is θ_A. When the system is in equilibrium at the temperature T, then $\theta = T$.

A straightforward approach for finding $H^*(\theta)$ is to begin with the equilibrium liquid where $\theta = T$. The right-hand sides of eq 1 and 4 are equal to one another. Setting these equal and taking the natural logarithm of both sides give

$$\ln [(\tau_g a_T)^{-1} + (\tau_b b_T)^{-1}] = \ln A - H^*(T)/RT \qquad (5)$$

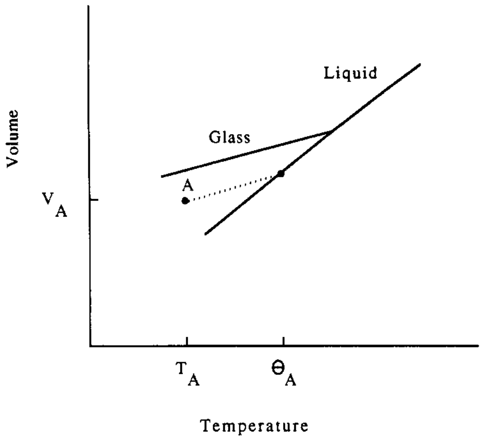

Figure 2. Diagram showing the procedure for determining the fictive temperature, θ.

At the glass transition temperature T_g, eq 5 can be written with eq 2 and 3, where $f = f_g$, as

$$\ln(\tau_g^{-1} + \tau_b^{-1}) = \ln A - H_g^*/RT_g \qquad (6)$$

H_g^* is the activation enthalpy at the glass transition. Equation 6 is an equation for A if H_g^* can be estimated or otherwise obtained. The equation divides the rate at the glass transition temperature given on the left into the activation enthalpy and a front factor. Combining eq 5 and 6, the activation enthalpy for the equilibrium liquid at the temperature T is then

$$H^*(T) = RT[\ln(\tau_g^{-1} + \tau_b^{-1}) - \ln[(\tau_g a_T)^{-1} + (\tau_b b_T)^{-1}] + H_g^*RT_g] \qquad (7)$$

The structural dependence of H^* in this equation is expressed by the temperature T. Away from equilibrium, this is no longer satisfactory, and the structure must be described differently, such as by the fictive temperature θ. If the recovery rates are intrinsically Arrhenius, as described by eq 4, i.e., Arrhenius for constant structure, and A is independent of temperature, then the activation enthalpy for a nonequilibrium structure θ is estimated to be

$$H^*(\theta) = R\theta[\ln(\tau_g^{-1} + \tau_b^{-1}) - \ln[(\tau_g a_T)^{-1} + (\tau_b b_T)^{-1}] + H_g^*/RT_g] \qquad (8)$$

where the description of structure by temperature has been replaced by a description by fictive temperature. The replacement would also be made for any explicit dependence on temperature of a_T and b_T as well, but that has not been necessary here because the structural (free volume) dependence has already been assumed in eq 2 and 3. Note that the common method of taking the derivative of the natural logarithm of eq 1 with respect to $1/T$, with the shift parameters expressed in terms of temperature, does not give the activation enthalpy, because the implicit temperature-dependent change in structure is not excluded.

Use of eq 4 with eq 8 and the value for A in eq 6 then gives

$$\ln \tau^{-1} = (\theta/T)\ln[(\tau_g a_T)^{-1} + (\tau_b b_T)^{-1}] + (1 - \theta/T)[\ln(\tau_g^{-1} + \tau_b^{-1}) + H_g^*/RT_g] \qquad (9)$$

The form of this equation is similar to one used previously.[22] Note that eq 9 reverts to eq 1 at equilibrium.

A comparison between theory and experiment with H_g^* = 50 kJ/mol is shown in Figure 3. The fit is seen to be considerably improved over that in Figure 1. No other changes in the calculations were made, and the values of the parameters N_s, z, and R that had previously been used to fit Kovac's single-step data have been retained. The fit is improved slightly if these parameters are optimized for eq 9 instead of eq 1, but this has not been done, so the effect of replacing eq 1 by eq 9 may be seen in the absence of any other changes.

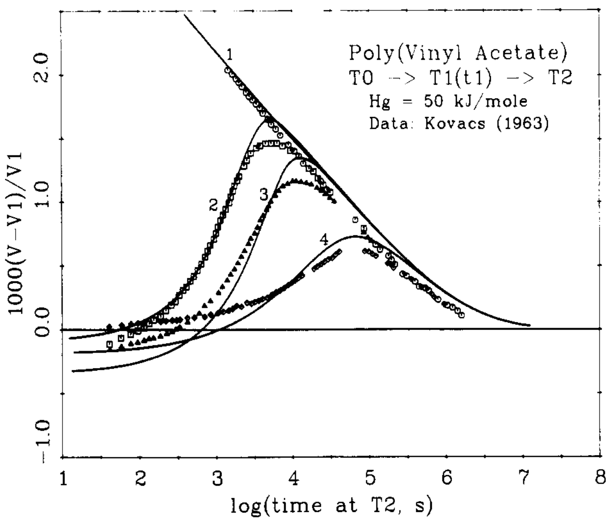

Figure 3. Computed volume recovery of poly(vinyl acetate) at 30 °C following a previous history described in Table II. The computation used the RSC theory augmented by an additional Arrhenius term to obtain better separation between structural and thermal influences on the recovery kinetics. The additional activation enthalpy assumed was 50 kJ/mol. The data are from Kovacs.[2]

It should be noted that the explicit thermal dependence in eq 9 does not establish a thermal dependence for the kietics of aging; rather, it augments that already existing. A thermal effect is predicted below the glass transition because of the behavior of the extended Simha–Somcynsky theory. In the extended form of the theory, used to describe the glass, the measured volume is used as the needed subsidiary relation instead of the minimization of the Helmholtz free energy. The thermal effect appears as a decreasing free volume with decreasing temperature, resulting in an increasing activation enthalpy, even for constant fictive temperature (constant nominal structure). The rate of change of the activation enthalpy with temperature at constant fictive temperature, evaluated at the glass transition temperature, for instance, is found from eq 8 to be

$$\left(\frac{\partial H^*(\theta)}{\partial T}\right)_\theta\Bigg|_{T_g} = -2.303\frac{R\theta}{(1 + \tau_g/\tau_b)} \times \left(\frac{c_1}{c_2} + \frac{\tau_g C_1}{\tau_b C_2}\right)\frac{T^*}{f^*}\left(\frac{\partial f}{\partial T}\right)_\theta = -0.44 \text{ kJ/(mol·K)} \qquad (10)$$

which is independent of the value assumed for H_g^*. Along the equilibrium liquid line, $(T^*/f^*)(\partial f/\partial T) = 1$; along a glass line of poly(vinyl acetate) for constant fictive temperature, $(T^*/f^*)(\partial f/\partial T)_\theta = 0.175$, not 0. Hence, the thermal effect represented by H_g^* merely augments the effect already contained in the original RSC theory.

A further exhibition of double-temperature-step behavior as predicted by the theory using eq 9 with H_g^* = 50 kJ/mol is shown in Figures 4–6. The double-temperature steps in these figures are from 40 to 10 to 30 °C, from 40 to 25 to 30 °C, and from 25 to 35 to 30 °C, respectively. The first step was downward in Figures 4 and

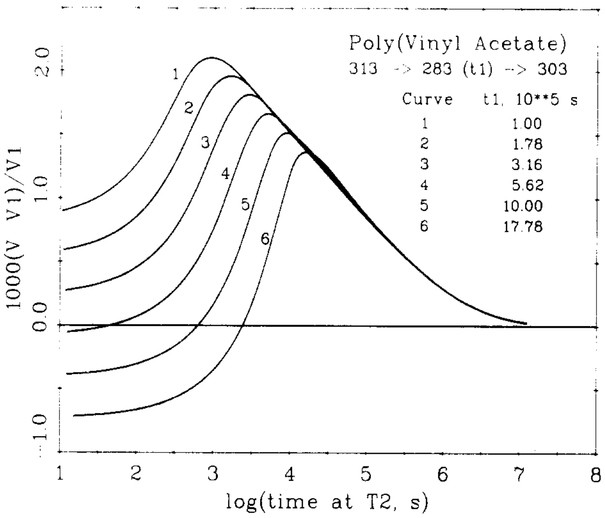

Figure 4. Computed volume recovery of poly(vinyl acetate) at 30 °C (303 K) following a previous step from 40 to 10 °C with various waiting times (t_1) at 10 °C before stepping to 30 °C. All steps were made instantaneously.

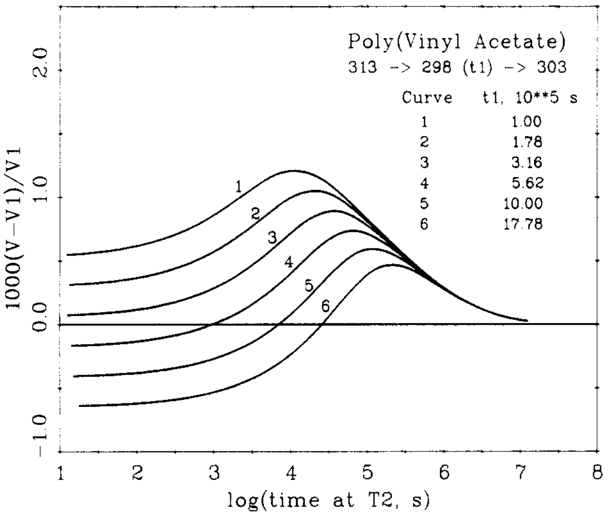

Figure 5. Computed volume recovery of poly(vinyl acetate) at 30 °C (303 K) following a previous step from 40 to 25 °C with various waiting times (t_1) at 25 °C before stepping to 30 °C. All steps were made instantaneously.

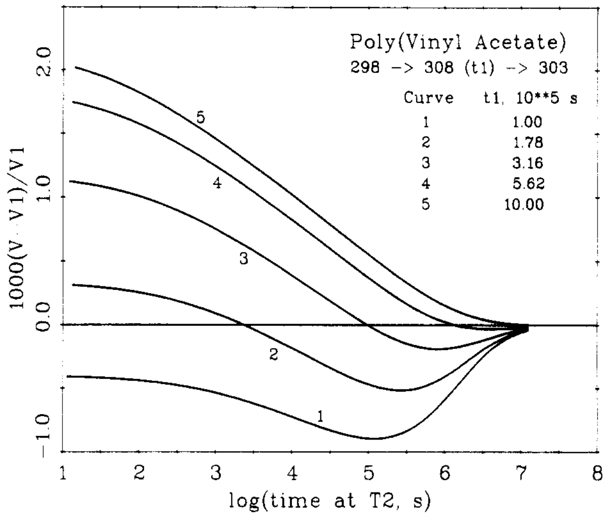

Figure 6. Computed volume recovery of poly(vinyl acetate) at 30 °C (303 K) following a previous step from 25 to 35 °C with various waiting times (t_1) at 35 °C before stepping to 30 °C. All steps were made instantaneously.

5 and upward in Figure 6. Only the volume evolution during the final temperature, 30 °C, is shown. In each simulation, the system was assumed to be in equilibrium at the beginning temperature and was maintained at the second temperature for the times t_1 indicated before stepping to the third temperature, which for all was 30 °C.

Except for very short or very long times at the first temperatures, T_1, all of the simulated experiments exhibited extrema. Also, a volume minimum occurs at the final temperature if the first step is upward, and a volume minimum occurs if the first step is downward. The largest transient deviations from the most direct path between the initial and final volumes at T_2 are seen in Figures 4–6 to occur when the time t_1 at T_1 was in a relatively narrow range of (2–5 × 10^5 s. This behavior is relatively independent of the temperature T_1: T_1 was 25 °C below the glass transition in Figure 4 and equal to the glass transition temperature (35 °C) in Figure 6. Another characteristic apparent in Figure 4, though not in Figures 5 and 6, is the overshoot that appears also in Figures 1 and 3. Although it may only be an artifact of the numerical calculation, the overshoot has become increasingly prominent for the longer waiting times at 10 °C (283 K).

Registry No. Poly(vinyl acetate), 9003-20-7.

References and Notes

(1) Kovacs, A. J. *J. Polym. Sci.* **1958**, *30*, 131.
(2) Kovacs, A. J. *Fortschr. Hochpolym.-Forsch.* **1963**, *3*, 394.
(3) (a) Hozumi, S.; Wakabayashi, T.; Sugihara, K. *Polym. J. (Tokyo)* **1970**, *1*, 632. (b) Hozumi, S. *Polym. J. (Tokyo)* **1971**, *2*, 756. (c) Adachi, K.; Kotaka, T. *Polym. J. (Tokyo)* **1982**, *12*, 959.
(4) Davis, G. T.; Eby, R. K. *J. Appl. Phys.* **1973**, *44*, 4274.
(5) Pathmanathan, K.; Johari, G. P.; Faivre, J. P.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1587.
(6) (a) Kruithof, A. M. *Verres Refract.* **1955**, *9*, 311. (b) Ritland, H. N. *J. Am. Ceram. Soc.* **1956**, *39*, 403. (c) Spinner, S.; Napolitano, A. *J. Res. Natl. Bur. Stand., Sect. A* **1966**, *70A*, 147.
(7) Corsaro, R. D. *J. Am. Ceram. Soc.* **1976**, *59*, 115.
(8) (a) Macedo, P. B.; Napolitano, A. *J. Res. Natl. Bur. Stand., Sect. A* **1967**, *71A*, 231. (b) Napolitano, A.; Macedo, P. B. *J. Res. Natl. Bur. Stand., Sect. A* **1968**, *72A*, 425. (c) Boesch, L.; Napolitano, A.; Macedo, P. B. *J. Am. Ceram. Soc.* **1970**, *53*, 148. (d) Narayanaswamy, O. S. *J. Am. Ceram. Soc.* **1971**, *54*, 491.
(9) Scherer, G. W. *J. Am. Ceram. Soc.* **1984**, *67*, 504.
(10) Kovacs, A. J. *Ann. N.Y. Acad. Sci.* **1981**, *371*, 38.
(11) Goldstein, M. In *Modern Aspects of the Vitreous State* Mackenzie, J. D., Ed.; Butterworth: London, 1964; Vol 3, pp 90–125.
(12) (a) Kolrausch, R. *Pogg. Ann. Physik* **1854**, *91*, 56, 179. (b) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.
(13) Moynihan, C. T.; Macedo, P. B.; Montrose, C. J.; Gupta, P. K.; DeBolt, M. A.; Dill, J. F.; Dom, B. E.; Drake, P. W.; Easteal, A. J.; Elterman, P. B.; Moeller, R. P.; Sasabe, H.; Wilder, J. A. *Ann. N.Y. Acad. Sci.* **1976**, *279*, 15.
(14) (a) Chow, T. S. *Polym. Eng. Sci.* **1984**, *24*, 1079. (b) Chow, T. S. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 699. (c) Chow, T. S. *Macromolecules* **1984**, *17*, 2336.
(15) Bernstein, S. *Acta math.* **1928**, *52*, 1.
(16) Douglas, R. W. In *Amorphous Materials*; Douglas, R. W., Ellis, B., Eds.; Wiley-Interscience: London, 1972; pp 3–22.
(17) Curro, J. G.; Lagasse, R. R.; Simha, R. *Macromolecules* **1982**, *15*, 1621.
(18) Robertson, R. E.; Simha, R.; Curro, J. G. *Macromolecules* **1984**, *17*, 911.
(19) Robertson, R. E.; Simha, R.; Curro, J. G. *Macromolecules* **1985**, *18*, 2239.
(20) Robertson, R. E. *Macromolecules* **1985**, *18*, 953.
(21) Plazek, D. J. *Polym. J. (Tokyo)* **1980**, *12*, 43.
(22) Robertson, R. E. *J. Appl. Phys.* **1978**, *49*, 5048.