Macromolecules **1998,** *31,* 2611−2615

Physical Aging in Poly(vinyl acetate). 2. Relative Rates of Volume and Enthalpy Relaxation

J. M. G. Cowie,* S. Harris,† and I. J. McEwen

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, Scotland

Received March 4, 1997; Revised Manuscript Received September 29, 1997

ABSTRACT: The isothermal volume contractions obtained on physically aging a sample of poly(vinyl acetate) at three temperatures below the glass transition were measured dilatometrically. These were compared with enthalpy aging data for the same polymer sample on the basis of characteristic relaxation times by fitting both types of relaxation to the Kolrausch−Williams−Watt (KWW) expression. It was found that the ratios of enthalpy and volume relaxation times depend on the temperature and that there is no simple correspondence between them. Further comparison of the isothermal aging using a time-dependent characteristic relaxation time indicated that conclusions on rates of aging must be considered within the context of the model chosen for data analysis. The possibility of predicting the rate of volume aging from enthalpy data was explored using an expression derived from the equation of state of Simha and Somcynsky, but the correlation between the actual behavior and that predicted was disappointing. An order parameter description of relaxation is discussed with reference to the equation of state.

Introduction

As a polymer is cooled through its glass transition (T_g) the molecular mobility which maintains it in conformational equilibrium can no longer occur on the time scale of cooling and the material becomes a thermodynamically unstable glass. In this state, physical and mechanical properties change with time as the glass attempts to achieve equilibrium by slow changes in molecular configurations. This structural relaxation underlies the accompanying changes in thermodynamic properties, such as volume and enthalpy, and in mechanical responses, such as creep or stress relaxation, whose time-dependent behavior is the experimental expression of physical aging in glasses.

Full knowledge of the time dependence of material properties is desirable if optimum material performance is required, and one of the more accessible of those properties reflecting physical aging is the enthalpy, which can be conveniently monitored using differential scanning calorimetry. Testing for the time dependence of one property and thereby predicting the future equilibrium behavior of another are only possible if the relaxation time scales for both are the same, or at least are related in some transparent manner. Some while ago now Roe[1] recognized that different properties do not age at rates which differ simply by a constant factor and pointed out it is likely that the effects of structure on different properties are dissimilar. Given this, one is forced to conclude that only when the effective equilibrium structure has been reached will all the material properties exhibit time independence. The different sensitivities of different properties will thus result in apparently different rates of physical aging dependent on the property being monitored. Indeed it appears that even in equilibrium (above T_g) certain dynamic variables, all nominally responding to the same local segmental motion (e.g. light scattering, longitudinal compliance, mechanical shear compliance and electric compliance) can show differences in some polymers.[2] It is always desirable then to examine aging effects from different standpoints and so in this paper we present data on the isothermal volume contraction of poly(vinyl acetate) (PVAc) and compare these with enthalpy relaxation measurements previously made on the same sample.[3]

The literature contains few reports on the relative time scales for the relaxation of these two properties in polymer glasses. Sasabe and Moynihan[4] have compared volume and enthalpy relaxation in PVAc by applying the Narayanaswamy[5] model to heat capacity vs temperature curves and to specific volume vs temperature data. For their one temperature considered these workers concluded that the characteristic time for enthalpy relaxation was a factor of 2 greater than that for volume relaxation. A similar situation was found by Perez and co-workers[6] for poly(methyl methacrylate). The opposite effect, enthalpy readjusting more quickly than volume, is reported for polystyrene by Adachi and Kotaka,[7] who measured the times to reach a maximum in recovered enthalpy and volume in double-step temperature jump experiments. The effect of aging on mechnical response has also been examined; for example, Roe and Millman[8] have observed that the creep behavior of polystyrene continued to change after the enthalpy had apparently reached a constant value. McKenna's group,[9,10] comparing rates of volume and mechanical change in an epoxy glass, suggest that the relative time scales for stress relaxation and volume recovery depend on the aging temperature and that mechanical relaxation may actually be completed before volume equilibration.

Whether these results represent real or apparent contradictions is unclear. There is always an uncertainty where analyses are based on different models, and in any case there is no a priori reason different polymer structures should exhibit the same relative responses in their material properties. Previously[11] we published a limited comparison at a single temperature of the measured enthalpy recovery for PVAc with the volume relaxation data of Kovacs[12] for this polymer within the framework of Simha−Jain theory.[13] In this

---

[†] Present address: Hughes Microelectronics Europa Ltd., Glenrothes, Fife KY7 5PY, Scotland.

S0024-9297(97)00287-8 CCC: $15.00

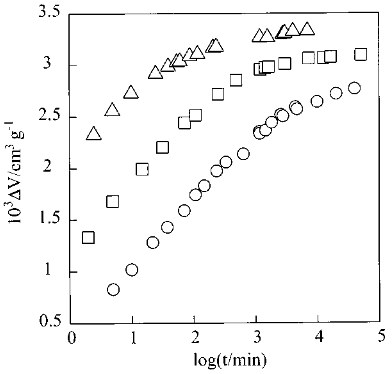

Figure 1. Volume contractions for PVAc at 303 (circles), 305 (squares), and 308 K (triangles). For clarity, the 305 and 308 K data are displaced upward 0.3 and 1.0 ordinate units, respectively.

study we have aimed to be as direct as we can in making comparisons between these two relaxing quantities by analyzing data from the same polymer sample and also by extending the aging time and temperature range examined. We present the effects of physical aging on the relaxation modulus of this sample in another paper.[14]

Experimental Section

The sample of PVAc has been described previously[3] and has a T_g of 315 K. Volume relaxation measurements were made at three aging temperatures $T_a = (T_g - 7\text{ K})$, $(T_g - 10\text{ K})$, and $(T_g - 12\text{ K})$ using a mercury dilatometer similar in design to that of Richardson and Saville.[15] The capillary was calibrated by measuring the variation in length of a mercury column moved along the length of the tubing. The radius was established to be 15.04×10^{-3} cm with a standard deviation of 0.02×10^{-3} cm.

The PVAc sample (2.6206 g) was formed into a cylindrical plug by heating the pellets supplied at 373 K under vacuum for 2 weeks. This was then loaded into the dilatometer bulb, and, before introduction of the mercury, the sample was further outgassed in the dilatometer, while being heated at 333 K until a pressure of 10^{-4} Torr was achieved (~24 h). The volume of mercury used was ca. twice the volume of the polymer sample.

Prior to making volume contraction measurements, the dilatometer was held at 353 K for 10 min to erase the polymer's previous thermal history. The sample was then quenched to the desired aging temperature by rapidly transferring the dilatometer assembly to a water bath fitted with a Jalabo Paratherm II electronic thermostat controlled to ±0.02 K. A cathetometer was used to follow the height of the mercury column, and volume contractions ($\Delta V(t)$) are estimated to be ca. $\pm 0.005 \times 10^{-3}$ cm^3 g^{-1}.

The time required for the PVAc to equilibrate thermally at T_a after the quench was estimated in a separate experiment where a thermocouple was mounted in the center of the sample. A period of 2.5 min after inserting the dilatometer into the thermostat bath was found appropriate to define t_0, i.e., the onset of purely isothermal sample contraction readings at all three aging temperatures. The values of ΔV presented in Figure 1 are the measured contractions in volume from this time.

Results and Discussion

Figure 1 shows the volume contractions for aging times in the range 5 min $< t <$ 50 days, where at two of the aging temperatures, 305 and 308 K, the sample appears to have achieved its equilibrium volume, $\Delta V(t) = \Delta V(\infty)$, within the experimental time scale. The enthalpy recovered during isothermal aging at the same three values of aging temperature, $\Delta H(t)$, was published in the previous paper of this series,[3] and these data are shown along with the corresponding volume recovery in Figures 2–4 as the normalized relaxation process

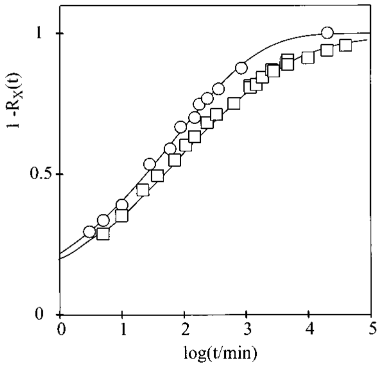

Figure 2. Normalized volume (squares) and enthalpy (circles) changes at 303 K. Lines through data as described in text.

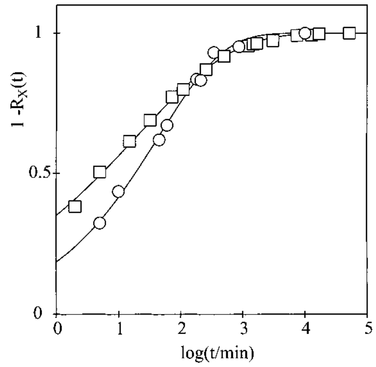

Figure 3. Normalized volume (squares) and enthalpy (circles) changes at 305 K. Lines through data as described in text.

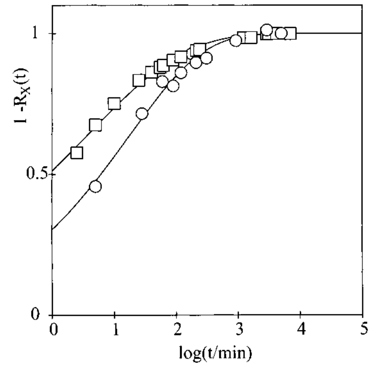

Figure 4. Normalized volume (squares) and enthalpy (circles) changes at 308 K. Lines through data as described in text.

$$R_X(t) = 1 - \frac{\Delta X(t)}{\Delta X(\infty)} \qquad (1)$$

where X is either volume V or enthalpy H. Both enthalpy and volume relaxation data are adequately described by the empirical Kolrausch–Williams–Watt (KWW) expression

$$\Delta X(t) = \Delta X(\infty)\{1 - \exp[-(t/\tau_X)^{\beta_X}]\} \qquad (2)$$

in which the parameter τ_X represents the characteristic relaxation time. The data were fitted to eq 2, using nonlinear techniques which employ the Levenberg–Marquardt algorithm,[16] and these lines are also shown

Table 1. KWW Parameters for Volume and Enthalpy[a] Aging of PVAc

T/K	$10^3\Delta V(\infty)$/ (cm^3 g^{-1})	log (τ_V/min)	β_V	$\Delta H(\infty)$/ (J g^{-1})	log (τ_H/min)	β_H
308	2.3	0.5_4	0.2_7	1.9	1.2	0.4_5
305	2.8	1.3	0.2_9	2.5	1.7	0.4_2
303	2.9[b]	2.3	0.2_6	3.0	1.9	0.3_3

[a] From ref 3. [b] Extrapolated value from fit of KWW function to the data.

Table 2. Average KWW Relaxation Times for Aging of PVAc

T/K	log($\langle\tau_V\rangle$/min)	log($\langle\tau_H\rangle$/min)	$\langle\tau_H\rangle/\langle\tau_V\rangle$	τ_H/τ_V
308	1.7	1.6	0.72	4.5
305	2.3	2.1	0.68	2.5
303	3.6	2.7	0.13	0.40

on the figures. The values of the KWW parameters τ_X and β_X for both the enthalpy and volume relaxations are collected in Table 1.

Simple visual comparisons of the data reveal that the relative extents of volume and enthalpy loss depend quite markedly on the aging temperature. At 303 K (T_g − 12 K) the rates of the volume and enthalpy relaxation processes are not dissimilar, with the former marginally lagging behind the latter. However, at the two temperatures successively closer to T_g this is no longer the case, and now volume has relaxed to a greater extent than enthalpy at similar times. Here (see Table 2), the ratio of the KWW characteristic times τ_H/τ_V at 305 K is 2.5, close to the ratio of the mean equilibrium relaxation times found by Sasabe and Moynihan[4] at 304.3 K. It must be cautioned, however, that the phenomenological Narayanaswamy model employed by these workers allows τ within the "stretched exponential" formalism of eq 2 to depend explicitly on the instantaneous glass structure through the fictive temperature of the glass, a refinement which we have found neither to be necessary here nor previously[3] to obtain a satisfactory description of the data. The KWW equation also describes situations where there is a spectrum of relaxation times which is then characterized by the parameter β, small values of β imply a broad distribution, and vice versa. An average relaxation time $\langle\tau_X\rangle$ for the distribution may be obtained from the expression

$$\langle\tau_X\rangle = \tau_X\Gamma(1 + {\beta_X}^{-1}) \tag{3}$$

where Γ is the gamma function. The average relaxation times from eq 3 corresponding to the data in Table 1 are shown in Table 2, where now a somewhat different picture emerges.

Both ratios τ_H/τ_V and $\langle\tau_H\rangle/\langle\tau_V\rangle$ vary such that the implied relative rate of enthalpic aging compared with that of volume aging decreases with temperature. Interpolation of the values of the former ratio suggests that enthalpy and volume aging will occur at the same rate at 303.5 K. Moreover at 304.5 K this interpolation indicates the enthalpic relaxation rate is exactly a factor of 2 greater than that of volume, a remarkable, but surely coincidental, agreement with Sasabe and Moynihans' results.[4] The ratio $\langle\tau_H\rangle/\langle\tau_V\rangle$, on the other hand, predicts that parity of enthalpic and volume aging rates will eventually occur close to the glass transition—a quite reasonable state of affairs. The two characteristic time ratios are of course nonequivalent since, in contrast to τ_X, the distribution average $\langle\tau_X\rangle$ depends explicitly on the value of β_X. The values obtained for β_V are significantly less on average than those for β_H, indicating that the spectrum of relaxation times corresponding to eq 2 is broader for volume relaxation than for enthalpy relaxation.

It is clear that a comparison of relative aging rates made on the basis of a *single* model parameter must be viewed with a modicum of caution. Although each model has its own shortcomings, the physical situation to which it is applied is necessarily best described using *all* of its parameters. Sasabe and Moynihan[4] additionally chose to set their Naranaswamy model parameters for volume behavior, other than of course τ_V, equal to the corresponding parameters determined from their heat capacity measurements for the enthalpy behavior. Nevertheless a direct comparison of their volume and enthalpy data on the basis of relative fictive temperatures implies that enthalpy relaxes the more slowly which, from inspection of Figure 3, is also the case here where our enthalpy certainly "lags" behind the volume.

Following Kovacs[17] a more unequivocal, "single parameter" correlation between the enthalpy and volume data of Figures 2−4 can be obtained by recalling that, for any relaxing quantity X, the following holds

$$\frac{\mathrm{d}\ln X}{\mathrm{d}t} = \frac{1}{X}\frac{\mathrm{d}X}{\mathrm{d}t} \tag{4}$$

Further, if the rate of change of X depends on the instantaneous value of X through a time-dependent relaxation parameter $\tau(t)$, i.e.

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \frac{-1}{\tau_X(t)}X \tag{5}$$

then it is readily shown that

$$\frac{\mathrm{d}\log X}{\mathrm{d}\log(t)} = \frac{-1}{\tau_X(t)} \tag{6}$$

so the slope of a plot of log X vs log(time) will reveal the time evolution of the relaxation parameter $\tau_X(t)$. This approach[18] was applied to the data of Figures 2−4 by reproducing the KWW lines, which for our present purposes we accept as adequate continuous descriptions of the enthalpy and the volume data, with

$$R_X(t) = 10^U \tag{7}$$

where U is a fourth degree polynomial from which the derivatives forming the left hand side of eq 6 may be obtained analytically from the coefficients. $\tau_X(t)$ can then be evaluated for both the normalized enthalpy and volume relaxations for the range 0.5 < log(t/min) < 4.5 within which the relaxation was studied experimentally.

Rather than show how $\tau_H(t)$ and $\tau_V(t)$ vary with the aging time, it is perhaps more pertinant to relate these parameters to some instantaneous state of the glass. To this end then, plots of $\tau_V(t)$ against $V(t) - V(\infty)$, the distance of the system from its equilibrium configurational state as determined by the relaxing volume, are drawn in Figure 5, where the rapidly increasing values of the relaxation times, characteristic of the self-retarding nature of the process, are evident as the glass approaches equilibrium. Since, from Figures 2−4, at any particular instant during structural relaxation the relative amount of enthalpy relaxed is in general not the same as the relative amount of volume relaxed, we have compared $\tau_H(t)$ with $\tau_V(t)$ by plotting this former

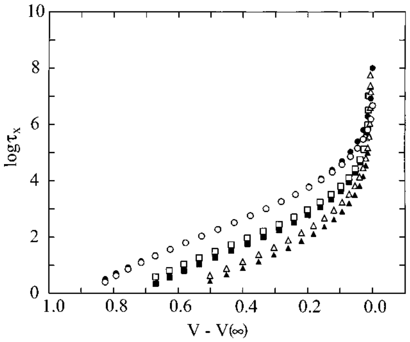

Figure 5. Log τ_X for volume relaxation ($X = V$, open symbols) and enthalpy relaxation ($X = H$, filled symbols) as a function of the distance of the system from volume equilibrium: circles, 303 K; squares, 305 K; triangles, 308 K.

parameter against $V(t) - V(\infty)$ also. The pairs of curves for each aging temperature in Figure 5 thus illustrate the relative rates of enthalpy and volume aging at the same condition of a one time evolving macroscopic thermodynamic variable, $V(t)$.

At 303 K the enthalpy and volume relaxation parameters $\tau_H(t)$ and $\tau_V(t)$ show an almost identical dependence on the instantaneous volume of the system for the major part of the aging process, so the rate of enthalpy change is equal to the rate of volume change at these same values of $V(t)$. (The same coincidence of aging rates will be found if $\tau_H(t)$ and $\tau_V(t)$ are plotted alternatively against $H(t) - H(\infty)$.) This state of affairs does not pertain, however, at the other two temperatures; $\tau_V(t)$ indicates volume relaxation times are longer than those of enthalpy relaxation. For example when $V(t) - V(\infty)$ is ~0.4, enthalpy is relaxing ~1.8 times faster than volume at 308 K, a distinctly different conclusion from that obtained when the KWW-derived characteristic times were employed as the basis of comparison as described earlier.

This difference is not too difficult to rationalize; the characteristic times τ_X of eq 2 are the inflection points of the function on a log(time) scale, the actual slopes of the function are more influenced by the value of the exponent β_X which describes the distribution of relaxation times. As noted above, it appears from the present data that the volume and enthalpy recovery processes respond to quite different distributions, giving rise to different instantaneous rates. So the question, *"is the enthalpy relaxing faster than volume during structural relaxation?"*, requires caution when answered since the model used and the parameters compared may lead to quite different answers. A parallel comparison to that in Figure 5 but with time as the abscissa, i.e. the instantaneous relaxing structure, shows a picture similar to that using instantaneous volume. This is effectively what is shown in Figure 6, which follows from the Simha–Jain theory now described.

Simha and Jain[13] utilized their scaled equation of state to transform time dependent volumes $V(t)$ into time-dependent free volume fractions $h(t)$ from which isothermal configurational enthalpies $H(t)$ are obtained. The scaled equation of state is derived from the mean field theory of Simha and Somcynsky[19] in which the polymer is confined to cells on a regular lattice in conjunction with empty cells or holes. An expression for the theoretical configurational enthalpy can be derived from the theory

$$H = P^*V^*\{(y/2)x^{-2}[1.011x^{-2} - 2.409] + 3\tilde{T}/2\} \qquad (8)$$

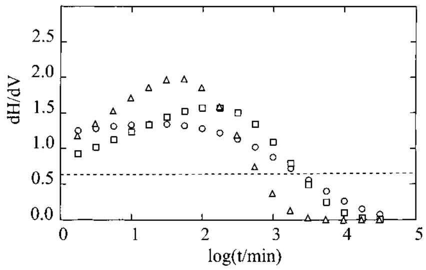

Figure 6. The ratio of dH/dt:dV/dt at 303 (circles), 305 (squares), and 308 K (triangles). The dashed line is the predicted behavior of this ratio as described in the text at the same three temperatures (not resolvable on this scale).

where P^* and V^* are the characteristic pressure and volume scaling parameters and $y = 1 - h$. Here h is the hole fraction or free volume fraction, representing a characteristic structure factor. The reduced temperature is $\tilde{T}$, and $x = (y\tilde{V})^{-2}$ with $\tilde{V} = V/V^*$ being the reduced volume. When eq 8 was used previously to predict the expected volume relaxation at 303 K from experimental enthalpy data for $t_a \leq 360$ min, this was found[11] to relax rather faster than the Kovacs' volume as interpolated at this temperature from Lagasse and Curro's empirical equation.[20]

Implicit in comparisons of volume and enthalpy recovery is an assumption that both samples have at least experienced the same thermal history during the down-jump to the aging temperature. Since the two techniques utilize very different sample sizes, this can never be achieved and the effect of nonideal down-jumping have recently been addressed by Struik,[21] who suggests that the effect of nonideal cooling may persist for considerable times after thermal equilibration. The form of the correction does not appear to be straightforward, and our data remain uncorrected for any effect. Accepting this caveat, we are in a position to make a direct comparison, in the sense that the data all refer to the same polymer sample, of volume changes predicted from enthalpy data with the experimental volume changes. However, the absolute changes in volume obtained from eq 8 are extremely small, and a more sensitive basis for comparison is the rate of aging. For this, eq 8 can be used to establish a link between the time derivatives of volume and isothermal configurational enthalpy using the chain rule

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{\partial H}{\partial y}\frac{\mathrm{d}y}{\mathrm{d}t} + \frac{\partial H}{\mathrm{d}\tilde{V}}\frac{\partial \tilde{V}}{\mathrm{d}t} \qquad (9)$$

The partial derivatives may be obtained using the equation of state, and, after some mathematics, the following relation between the rates of the volume and enthalpy change is obtained

$$\frac{\mathrm{d}H}{\mathrm{d}t} = P^*\frac{\mathrm{d}V}{\mathrm{d}t}f(y,\tilde{V}) \qquad (10)$$

The function $f(y,V)$, though somewhat complex, may be evaluated using the literature scaling parameters for PVAc.[13]

Equation 10 was tested against experiment, assuming again that the KWW lines provide an adequate continuous description of the data in Figures 2–4, by evaluating the ratios of dV/dt to dH/dt at set intervals for all three temperatures, as shown in Figure 6. According to eq 10 these should fall on the line $P^*f(y,V)$, which is also drawn on the figure, but it is quite apparent that they fail so to do.

One must conclude then from this comparison that sensible prediction of the rates of isothermal volume change from independent enthalpy data are outside the scope of the Simha−Jain theory. The proposed correlating function $f(y,V)$ exhibits an almost linear trend with log t and only a very minor temperature response, quite contrary to what is obtained from experiment. The promising, if modest, agreement obtained earlier[11] was perhaps fortuitous, being obtained at 303 K where near coincidence of enthalpy and volume relaxations is found to occur, as shown by the data in Figure 2 or Figure 5. The deviation of the experimentally derived behavior of the relative rates in Figure 6 from the Simha−Jain line is at its most marked at $T_g - 7$ K but becomes marginally better at $T_g - 12$ K. It is a matter of speculation whether this trend indicates that at lower temperatures there is general coincidence of the volume and enthalpy aging rates. Temperatures far below T_g are normally experimentally inconvenient for aging measurements on sensible time scales, but are also those of most practical applications for polymers.

The inability to correlate enthalpy and volume by the above approach is disappointing, and it may be that a "structural simplicity" within the equation of state approach is responsible. A connection between the rates of physical aging as observed through any pair of physical properties has been proposed[4,22] if the structural state of a glass is quantified in terms of a set of N so-called order parameters Z_i. The microscopic significance of these order parameters in liquids or glasses escapes precise definition at present, but the set could include such things as the number of holes or the number of flexed bonds. This means for any property X

$$X = X(T, P, Z_1, Z_2, ... Z_N) \tag{11}$$

Isothermal isobaric changes in properties such as the volume and the enthalpy are then related to the rates of change of the order parameters toward their particular equilibrium values; i.e., generally one can write

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \sum_{i=1}^{N} \frac{\partial X}{\partial Z_i} \frac{\mathrm{d}Z_i}{\mathrm{d}t} \tag{12}$$

In our case eq 12 is written twice, once for $X = H$ and once for $X = V$. This equation links the thermodynamics of structural relaxation, the partial derivatives, and structural relaxation kinetics where each of the N order parameters changes with time according to its own characteristic τ_i.

If, in the simplest possible case, physical aging is due to changes in a single order parameter Z_1, then the ratio of enthalpy and volume relaxation rates plotted in Figure 6 is given by the relative dependences of enthalpy and volume on that order parameter, i.e., on the ratio $\partial H/\partial Z{:}\partial V/\partial Z$. This is essentially what emerges from the Simha−Jain calculations in which h, the hole fraction, is the single order parameter, and in fact the dashed line in Figure 6 gives the value of this ratio. Values for the hole fraction for PVAc are presented in ref 8, and by recasting the enthalpy and volume changes also given there as normalized variables, it is possible to make first order estimates of $\partial H/\partial h$ and $\partial V/\partial h$; we calculate both to be ~600, making their ratio of the order of unity in fair agreement with Figure 6.

Leaving aside all other deficiencies in the equation of state theory, it is clear that physical aging in PVAc cannot be described by only a single order parameter since, to express the behavior shown in Figure 6, more than one term is required in the summation of eq 12. We must infer then that any comparisons between the aging rates of different physical properties of a polymer glass must perforce remain within the experimental discipline of kinetics until more extensive, multiparameter, microscopic descriptions of glass behavior are available. The wisdom of employing a common kinetic model for analysis and comparison is also demonstrated by this study.

Acknowledgment. The authors are indebted to Dr. R. Ferguson for helpful discussions, and S.H. gratefully acknowledges support from the SERC during the course of this study.

References and Notes

(1) Roe, J. R. *J. Appl. Phys.* **1977**, *48*, 4084.
(2) Ngai, K. L.; Mashimo, S.; Fytas, G. *Macromolecules* **1988**, *21*, 3030.
(3) Cowie, J. M. G.; Harris, S.; McEwen, I. J. *J. Polym. Sci., Part B: Polym.* Phys. **1997**, *35*, 1107.
(4) Sasabe, H.; Moynihan, C. T. *J. Polym. Sci., Polymer Phys. Ed.* **1978**, *16*, 1447.
(5) Narayanaswamy, O. S. *J. Am. Ceram. Soc.* **1971**, *54*, 491.
(6) Perez, J.; Cavaille, J. Y.; Calleja, R. D.; Ribelles, J. L. G.; Pradas, M. M.; Greus, A. R. *Makromol. Chem.* **1991**, *192*, 2141.
(7) Adachi, K.; Kotaka, T. *Polym. J.* **1982**, *14*, 959.
(8) Roe, J. R.; Millman, G. M. *Polym. Eng. Sci.* **1983**, *23*, 318.
(9) McKenna, G. B. *Comput. Mater. Sci.* **1995**, *4*, 349.
(10) McKenna, G. B.; Leterrier, Y.; Schultheisz, C. R. *Polym. Eng. Sci.* **1995**, *35*, 403.
(11) Cowie, J. M. G.; Elliot, S.; Ferguson, R.; Simha, R. *Polym. Commun.* **1987**, *28*, 298.
(12) Kovacs, A. J. *Adv. Polym. Sci.* **1963**, *3*, 394.
(13) Jain, S. C.; Simha, R. *Macromolecules* **1982**, *15*, 1522.
(14) Cowie, J. M. G.; Ferguson, R.; Harris, S.; McEwen, I. J. *Polymer*, in press..
(15) Richardson, M. J.; Saville, N. G. *Polymer* **1977**, *18*, 413.
(16) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling. W. T. *Numerical Recipes: The Art of Scientific Programming*; Cambridge University Press: Cambridge, U.K., 1986.
(17) Kovacs, A. L. *Fortschr. Hochpolym.-Forsch.* **1964**, *3*, 394.
(18) Equations 5 and 2 are related: if $1/\tau_X(t)$ decreases with time according to an inverse fractional power law, then integration of eq 5 leads to the KWW expression.
(19) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 342.
(20) Lagasse, R. R.; Curro, J. G. *Macromolecules* **1982**, *15*, 1559.
(21) Struik, L. C. E. *Polymer* **1997**, *38*, 4677.
(22) Gupta, P. K.; Moynihan, C. T. *J. Chem. Phys.* **1976**, *65*, 4136.

MA970287T