Enthalpy Relaxation in Polymer Glasses: Evaluation and Interpretation of the Tool–Narayanaswamy Parameter x for Poly(vinyl chloride)

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Received April 1, 1991; Revised Manuscript Received July 3, 1991

ABSTRACT: The enthalpy relaxation of poly(vinyl chloride) (PVC) in the glass-transition region has been investigated by differential scanning calorimetry (DSC), and the peak-shift method has been used to evaluate the Narayanaswamy parameter x, which controls the relative contributions of temperature and structure to the retardation times. The value of $x = 0.27 \pm 0.05$ which results from the present study is rather larger than the value of 0.11 found previously by Hodge for the same sample. Nevertheless, both values are considered to be small in comparison with those quoted for many other polymer glasses, which is consistent with its classification as a "fragile" system on the basis of Angell's concept of "strong" and "fragile" liquids.

Introduction

Structural relaxation in glasses has long been of interest from both practical and theoretical viewpoints. The diversity of glass-forming systems available, both organic and inorganic, and the range of potential applications for such glasses fuel the need for a basic understanding of glass behavior.

One approach to this is a treatment of the structural recovery of glasses at temperatures close to the glass-transition temperature, T_g. The basis of many such studies is the equation usually attributed to Tool[1] and Narayanaswamy:[2]

$$\tau_i = A_i \exp\left\{\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right\} \qquad (1)$$

This equation separates the dependence of the retardation times τ_i on the actual temperature T from their dependence on the fictive temperature T_f. The apparent activation energy for structural recovery is given by Δh^*, while the relative contributions of temperature and structure to the retardation times are governed by the parameter x, where $0 \le x \le 1$, known variously as the Narayanaswamy, structure, or nonlinearity parameter. By determining the values of x for a range of different systems, it is hoped that some physical significance could be attributed to this parameter, which could thereby provide a basis of comparison between different glass systems.

One suggestion made recently by Ingram et al.[3] is that x measures the degree of *continuity* of behavior between the molten and the glassy states. Thus, a large x value indicates that activation energies above and below T_g are similar, and that glass properties depend mainly on the actual or instantaneous temperature. On the other hand, a low x value indicates the importance of fictive temperature, and a glass whose structure is strongly influenced by thermal history, quench rate, etc.

Several groups of workers[4-11] have carried out evaluations of x and Δh^* using curve-fitting techniques in conjunction with experimental data obtained by differential scanning calorimetry (DSC), on a variety of inorganic and organic glasses. Among the latter class, Hodge has studied a range of polymers, for which values of x ranged from 0.11 for poly(vinyl chloride) (PVC) to 0.43 for a polydisperse polystyrene.[7]

An alternative method of evaluating x has, however, been proposed and is considered to offer several advantages;[12] this is the peak-shift method developed by Hutchinson et al.[13-17] from the original KAHR model.[13] It has previously been used to obtain a value of $x = 0.46 \pm 0.02$ for polystyrene[12] (cf. Hodge's value of 0.43 above) and also to investigate the variation of x with the AgI content in AgI–Ag_2O–MoO_3 glasses.[3] The purpose of the present study is to determine x for PVC using the peak-shift method and to compare this with the value of 0.11 quoted by Hodge, which appears to be exceptionally low.

Theory of Structural Recovery

The peak-shift method examines the response of the glass to a series of three-step thermal cycles.[12] The following development refers to data which would be obtained by DSC, but the approach may also be applied to dilatometric measurements.

The thermal cycling involves: (i) cooling from the equilibrium melt (T_0) at a constant rate q_1 to a temperature T_1 (below T_g); (ii) annealing at T_1, during which the enthalpy is reduced by an amount $\bar{\delta}_H$; and (iii) reheating through the glass-transition region at a constant rate q_2, during which the heat capacity passes through a maximum at a temperature T_p. The latter temperature is dependent on the whole thermal history of the sample, and therefore the experimental parameters which define the behavior of the sample are q_1, q_2, $\bar{\delta}_H$, and T_1. The dependences of the peak temperatures T_p on each of these experimental variables are used to define the peak shifts, which are determined from experiments in which three of the variables are held constant while the other one is altered. For the purposes of the evaluation of x, these shifts must be evaluated under conditions in which the glass is well-stabilized (implying long annealing times and/or very slow cooling rates), and these are defined below (Note that the shift $\hat{s}(T_1)$ is not included here. In fact, it can be shown[13] that, for these cycles, $\hat{s}(T_1) = 0$ and cannot therefore lead to an evaluation of x):

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$$\hat{s}(\bar{D}) = \Delta C_p \left\{\frac{\partial T_p}{\partial \bar{\delta}_H}\right\}_{q_1,T_1,q_2} \tag{2}$$

$$\hat{s}(Q_1) = \theta \left\{\frac{\partial T_p}{\partial \ln |q_1|}\right\}_{T_1,\bar{\delta}_H,q_2} \tag{3}$$

$$\hat{s}(Q_2) = \theta \left\{\frac{\partial T_p}{\partial \ln q_2}\right\}_{q_1,T_1,\bar{\delta}_H} \tag{4}$$

in which ΔC_p is the difference between the specific heat capacities of the glass and of the liquid, and θ is a material constant defining the temperature dependence of the retardation times. It can be shown[16] that these shifts are interrelated by a simple expression:

$$F(x) = -\hat{s}(Q_1) = \hat{s}(Q_2) - 1 = \hat{s}(\bar{D}) \tag{5}$$

which can be seen to afford three independent approaches to the evaluation of x. The relationship between $F(x)$ and x has been theoretically determined,[15] and x may therefore be found directly from the resulting master curve, reproduced in Figure 1.

In contrast to the above requirement for well-annealed glasses in the evaluation of x by the peak-shift method, conditions may exist under which the glass is *not* well-stabilized. Most commonly this occurs when no annealing has been allowed to take place between cooling and reheating a sample, and hence $\bar{\delta}_H = 0$. This particular experimental condition is referred to as an intrinsic cycle, and gives rise to a so-called "upper peak" on reheating,[18] in contrast to the well-stabilized glass which exhibits a "main peak". Equivalent peak shifts s_u may be defined for upper peaks in terms of the dependence of the upper peak temperature T_u on the experimental variables as follows:

$$s_u(\bar{D}) = 0 \tag{6}$$

$$s_u(Q_1) = \theta \left\{\frac{\partial T_u}{\partial \ln |q_1|}\right\}_{T_1,\bar{\delta}_H,q_2} \tag{7}$$

$$s_u(Q_2) = \theta \left\{\frac{\partial T_u}{\partial \ln q_2}\right\}_{q_1,T_1,\bar{\delta}_H} \tag{8}$$

and may be shown to be related by a subset of the expression in eq 5:

$$s_u(Q_1) + s_u(Q_2) = 1 \tag{9}$$

This relationship provides a means of evaluating θ, since eq 7 and 8 can be combined with eq 9 to give

$$\theta^{-1} = \left\{\frac{\partial T_u}{\partial \ln |q_1|}\right\}_{T_1,\bar{\delta}_H,q_2} + \left\{\frac{\partial T_u}{\partial \ln q_2}\right\}_{q_1,T_1,\bar{\delta}_H} \tag{10}$$

Another method for the evaluation of θ is through the use of intrinsic cycles ($\bar{\delta}_H = 0$) in which the ratio ρ of the cooling rate to the heating rate is kept constant. Here, the appropriate relationship can be shown to be[12]

$$\theta^{-1} = \left\{\frac{\partial T_u}{\partial \ln q_2}\right\}_{\rho,\bar{\delta}_H=0} \tag{11}$$

In addition, the evaluation of θ can be achieved by a third method, which uses the dependence of the fictive temperature on the cooling rate. The fictive temperatures for a series of intrinsic cycles, involving a range of cooling rates and, ideally, a single heating rate, may be determined either graphically or algebraically using approaches due to Moynihan[19] and Richardson,[20] respectively. From this dependence, Δh^* may be evaluated and hence θ may be obtained using the approximate relationship[12]

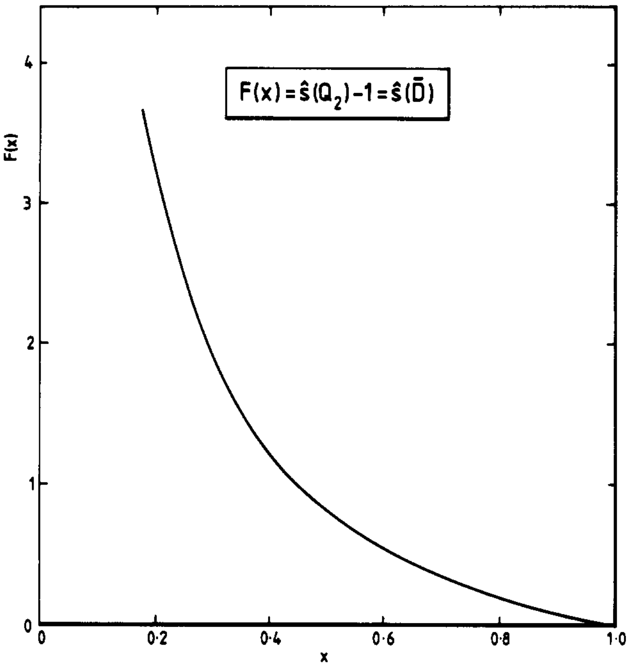

Figure 1. Master curve for the dependence of $F(x)$ on x.

$$\theta = \frac{\Delta h^*}{R T_g^{\,2}} \tag{12}$$

where T_g is a temperature within the transition interval.

Experimental Section

The sample of PVC was kindly supplied by Hodge from a batch originally obtained from B.F. Goodrich, Geon 103EP-F76, Lot 05603-10. It was a white, free-flowing powder and was identical to the sample used by Hodge in his earlier work.[5]

Differential scanning calorimetry was carried out using a Perkin-Elmer DSC-4 equipped with a TADS interface and computer. It was also fitted with a liquid nitrogen controlled cooling accessory. The samples (15.0 ± 0.1 mg) were encapsulated in standard aluminum pans. Baseline calibration was carried out daily. Heating rate calibrations were performed as required using indium (onset of melting 156.6 °C).

Values of ΔC_p were determined using Perkin-Elmer software, following calibration with a sapphire standard. For all the peak-shift measurements, the samples were pretreated as follows: the glass was heated from 20 to 120 °C at 20 or 40 K min^{-1} and then immediately allowed to cool at 10 K min^{-1}. It was removed from the DSC at 60 °C and transferred to a copper tube in a thermostated bath for annealing.

Results of the DSC Investigation

Evaluation of ΔC_p. This was carried out on both annealed and unannealed samples. The samples were heated through the range 20–120 °C at 10 K min^{-1}; between heating scans the sample was cooled at 10 K min^{-1}.

It should be noted that no melting endotherm was ever observed in the DSC scans, in contrast to the observations of Lehr[21] and Hodge[22] using an identical sample. This is due to our limiting the maximum temperature in any heating scan to the lowest value that would allow an unambiguous definition of the equilibrium line, usually some 10° or so above the "step change" at the glass transition. Repeat scans following cooling of the sample to below T_g were sufficiently reproducible to confirm that

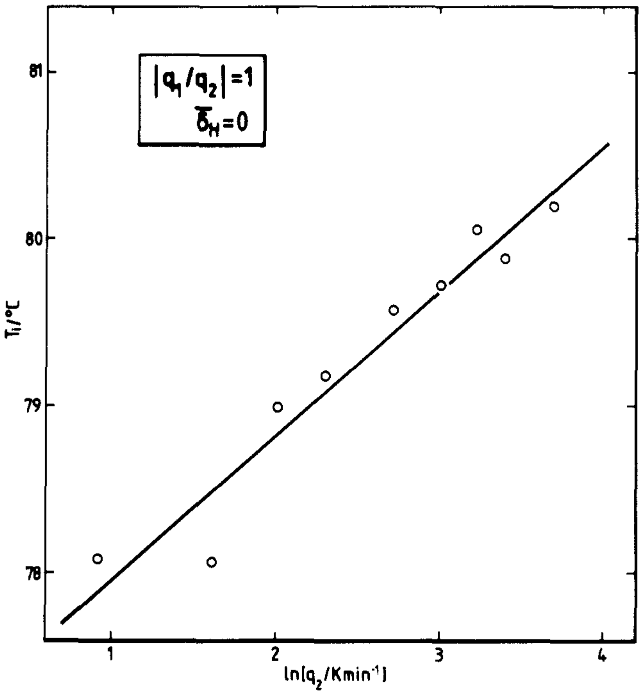

Figure 2. Dependence of peak onset temperature T_i on ln (heating rate) for intrinsic cycles with ratio ρ (cooling rate to heating rate) of unity.

no significant crystallization had taken place at the higher temperatures.

The average value of ΔC_p obtained from 14 determinations using five samples was 0.335 ± 0.015 J g^{-1} K^{-1}. This is in good agreement with the value quoted for the same sample by Lehr et al.[21] of 0.347 ± 0.004 J g^{-1} K^{-1} and with values obtained by other workers[23-25] on other samples of PVC.

Evaluation of θ. The value of θ was determined by two of the three methods described above, namely the intrinsic cycle and fictive temperature methods.

(i) Intrinsic Cycles with $\rho = 1$. The glass was cooled and heated at rates between 2.5 and 40 K min^{-1}, keeping the ratio of the cooling rate to heating rate constant at 1 and always having zero annealing time at the lower temperature T_1 of 20 °C. The value of θ was obtained as the reciprocal gradient of the graph of T_i (onset temperature) against ln q_2 (Figure 2). The onset temperature was used since the peak was not well enough defined to determine the peak temperature T_u accurately. In fact, there was no evidence of a peak at all in these intrinsic cycles, but only a "step change" in ΔC_p in the transition region. This appears to be a characteristic feature of the response of PVC as is shown, for example, by the early results of Illers[23] and is discussed below in terms of the values of the material parameters in the Narayanaswamy equation.

A procedure has previously been proposed[26] for correcting the data for thermal lag in the sample. This procedure is based upon the invariance of the shape of the upper peak in the intrinsic cycles with constant ratio ρ. Since no upper peak was evident here, this correction could not be applied. However, the width (on the temperature scale) of the ΔC_p step at the transition appeared to be relatively unchanged with increasing heating rate, and hence corrections for thermal lag in the sample were not considered to be necessary.

The value of θ found by this method was 1.21 ± 0.04 K^{-1}, in which the error estimate was obtained by repeating the experiments to include three complete sets of data under nominally identical conditions.

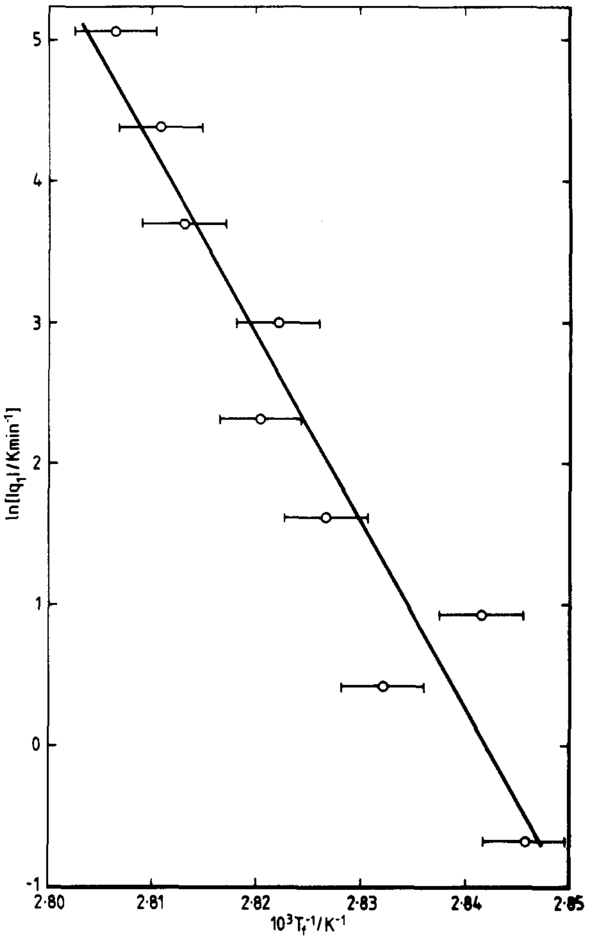

Figure 3. Relationship between ln (cooling rate) and reciprocal fictive temperature, T_f. Heating rate was 10 K min^{-1} in all cases.

(ii) The Fictive Temperature Method. The sample was cooled at rates between 320 and 0.5 K min^{-1} and reheated at a single rate of 10 K min^{-1}. No annealing was allowed between the cooling and heating stages of these cycles. The peak areas between selected temperature limits were measured using a planimeter, the asymptotic glassy and equilibrium liquid lines were established, and the fictive temperatures were calculated algebraically according to the procedure outlined by Richardson and Savill.[20] From a plot of ln $|q_1|$ as a function of the reciprocal of T_f, Δh^* was obtained as the gradient (see Figure 3), and θ was then calculated by substitution into eq 12, using T_g = 353 K.

It was estimated that the error in the determination of T_f was approximately 0.5 K, and the length of the error bars in Figure 3 has been shown accordingly. Because the whole range of T_f covered is only about 5 K, these uncertainties are significant and give rise to a significant uncertainty in the slope, a problem noted also by Hodge and Berens in their studies of the same PVC sample (see, in particular, Figure 12 in ref 6). The value of $\Delta h^* R^{-1}$ = 135 kK, obtained from a least-squares fit to the data in Figure 3, is therefore estimated to be within ±10% (the equivalent value of Δh^* is then in the range 1010–1235 kJ mol^{-1}), and from this we obtain a value of θ = 1.1 ± 0.1 K^{-1}. This is consistent with the value obtained for θ above by the intrinsic cycle method.

Evaluation of $\delta(Q_2)$. The shift of the peak temperature as a function of the heating rate was obtained as follows. Each sample was cooled from the equilibrium melt at 10 K min^{-1} to 60 °C and then annealed for 96 h in a thermostated oil bath at this temperature. The

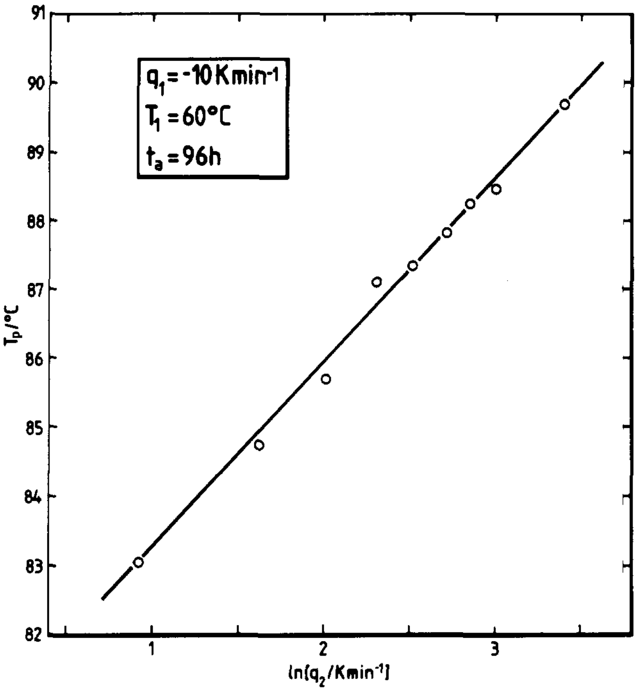

Figure 4. Dependence of peak temperature, T_p, on ln (heating rate) for cycles with cooling rate = −10 K min^{-1}, lower temperature = 60 °C, and annealing time 96 h.

Table I
Values of $\hat{s}(Q_2)$ Obtained Using m_{q_2} from Figure 4 and θ from (a) Intrinsic Cycles and (b) Fictive Temperature

	m_{q_2}/K	θ/K^{-1}	$\hat{s}(Q_2)$
a	2.71	1.21 ± 0.04	3.28 ± 0.11
b	2.71	1.1 ± 0.1	2.98 ± 0.27

samples were removed from the bath, cooled to 20 °C, and then reheated in the DSC at rates between 2.5 and 30 K min^{-1} over the range 20–120 °C, and the peak temperatures were found as a function of the heating rate. The results are plotted in Figure 4 in the form of T_p versus ln q_2. Note that, since it was not possible to determine a correction factor for thermal lag in the sample in the usual way, the data in Figure 4 are uncorrected. From the clearly linear relationship between T_p and ln q_2, the gradient m_{q_2} was determined and combined with the values of θ found above to yield the values of $\hat{s}(Q_2)$ given in Table I.

Evaluation of $\hat{s}(\bar{D})$. The variation of peak temperature with enthalpy loss on annealing was determined in the following fashion. Samples were cooled from the equilibrium melt at 10 K min^{-1} to 60 °C and annealed for periods ranging from 2.4 h to 960 h at this temperature. After each annealing period the sample was cooled to 20 °C and then reheated at 10 K min^{-1} between 20 and 120 °C, each cycle being followed immediately by an intrinsic cycle (i.e. one for which the annealing period t_a = 0). The peak temperatures for the annealed samples were found and plotted as a function of log t_a. No correction for thermal lag was necessary, since all samples were heated at the same rate. The linear relationship between T_p and log t_a is shown in Figure 5. The enthalpy loss on annealing, $\bar{\delta}_H$, is calculated from the difference between the areas under the annealed and corresponding intrinsic cycles, and a plot of T_p as a function of $\bar{\delta}_H$ is shown in Figure 6.

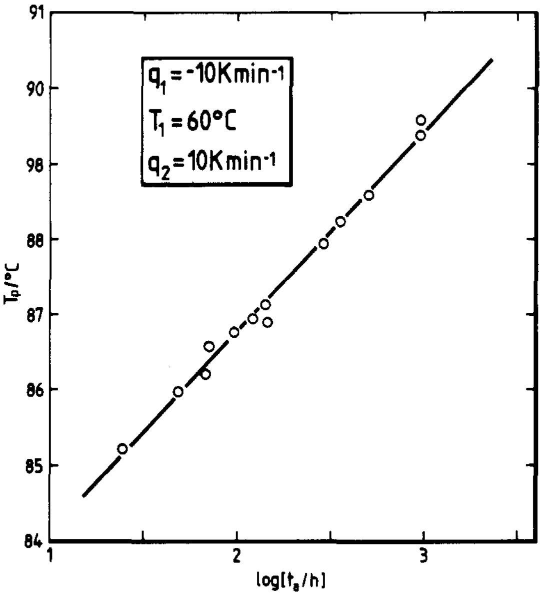

Figure 5. Dependence of peak temperature, T_p, on log (annealing time) for cycles with cooling rate = −10 K min^{-1}, lower temperature T_l = 60 °C, and heating rate = 10 K min^{-1}.

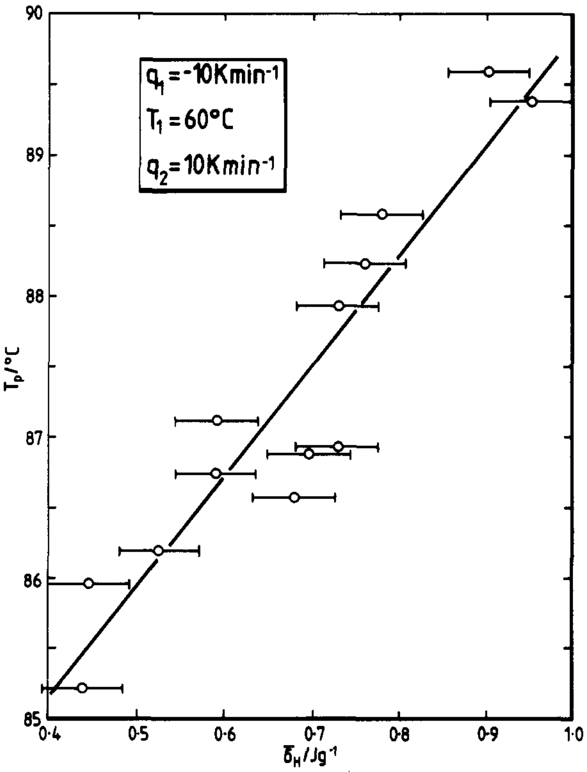

Figure 6. Dependence of peak temperature, T_p, on enthalpy loss during annealing at T_l = 60 °C, for cycles with cooling rate = −10 K min^{-1} and heating rate = 10 K min^{-1}.

Once again, it can be seen that the data are subject to some experimental error. Here the error arises from the need to superpose annealed and unannealed heating traces in order to determine the area difference; inevitably there is a certain mismatch in the two curves which will cause an uncertainty in the value of $\bar{\delta}_H$. It is estimated that this error is approximately ±0.04 J g^{-1} as indicated by the length of the error bars in Figure 6. The gradient m_H of the least-squares fit to the data is combined with the value of ΔC_p obtained earlier to give the values of $\hat{s}(\bar{D})$ shown below.

m_H/g K J^{-1}	ΔC_p/J g^{-1} K^{-1}	$\hat{s}(\bar{D})$
7.80	0.335 ± 0.015	2.61 ± 0.36

Discussion

On the basis of the data presented in the Results section above, the value of x may be estimated independently

Table II
Values of x Determined through $\hat{s}(Q_2)$ and $\hat{s}(\bar{D})$

$\hat{s}(Q_2)$	$F(x)$	x
3.28 ± 0.11[a]	2.28 ± 0.11	0.27 ± 0.01
2.98 ± 0.27[b]	1.98 ± 0.27	0.29 ± 0.03

$\hat{s}(\bar{D})$	$F(x)$	x
2.61 ± 0.36	2.61 ± 0.36	0.24 ± 0.03

[a] From intrinsic cycles. [b] From fictive temperature.

through both of the shifts $\hat{s}(Q_2)$ and $\hat{s}(\bar{D})$. This is done by reading off from the master curve in Figure 1 the value of x corresponding to the appropriate value of $F(x)$ (see eq 5). The results are presented in Table II.

From these data we derive an average value of $x = 0.27 \pm 0.05$. This is considerably higher than the value found by Hodge ($x = 0.11$), but is still significantly lower than earlier reported values quoted for polystyrene ($x = 0.46$ from Hutchinson and Ruddy[12] and $x = 0.43$ from Hodge[7]). The reason for the difference between our value of x and that quoted by Hodge for the same polymer is not clear. It should be noted, however, that there are several practical difficulties associated with making measurements on PVC.

(1) **$\hat{s}(Q_2)$.** The main problem here is associated with the measurement of θ, which is required in the evaluation of $\hat{s}(Q_2)$ (see eq 4). In the first of the methods available (intrinsic cycles), upper peaks should supposedly appear in the DSC heating trace; indeed, it has been shown theoretically (see ref 14, Appendix A) that the heating scan must show at least one peak. However, in none of these intrinsic cycles was a peak noticeable. This is believed to be the result of a very broad distribution of retardation times, equivalent to a rather small value of β in the KWW stretched exponential formulation,[27] which has been shown[18] to lead to upper peaks of very small magnitude. In the present case, the DSC is unable to resolve these very small peaks, and the heating scan appears simply as a sigmoidal curve. The problem is not only that this does not permit the usual temperature corrections for thermal lag in the sample[26] to be made but also that the peak shifts have to be estimated from peak-onset temperatures, T_i, rather than actual upper peak temperatures, T_u.

In the second of the methods available (fictive temperature) for the evaluation of θ, the determination of T_f is subject to quite large experimental errors, as is discussed earlier, which are combined with only a limited range of T_f over the whole range of cooling rates used. This results in part from the extremely high value of activation enthalpy Δh^* for PVC (and consequently a high value for θ), which has been noted before by Hodge[8] to correlate with low values of β, i.e. with a broad distribution, in agreement with our observations immediately above. For comparison, the range of values of Δh^* for PVC found here, from 1010 to 1235 kJ mol^{-1}, are nearly twice the activation enthalpy for polystyrene of 578 kJ mol^{-1} found in earlier work.[12]

2. **$\hat{s}(\bar{D})$.** In contrast to the determination of x through $\hat{s}(Q_2)$, the main problem in the evaluation of $\hat{s}(\bar{D})$ lies not in ΔC_p, for which we find a value subject to only small experimental error and in good agreement with other reported values, but in the dependence of the peak temperature, T_p, on the enthalpy loss, $\bar{\delta}_H$, on annealing. This is because the enthalpy losses are very small—less than 1 J g^{-1} after annealing for 1000 h compared with over 3 J g^{-1} for the same annealing period for polystyrene[12]—and the experimental error in the measurement of $\bar{\delta}_H$ becomes proportionately larger. Thus, although there is a good linear relationship between T_p and log (annealing time) (see Figure 5), the slope m_H derived from the graph of T_p versus $\bar{\delta}_H$ (Figure 6) is subject to considerable error (nearly 15%).

In spite of these problems, it is difficult to reconcile the differences, particularly with respect to Δh^* (or θ), between the present results and those of Hodge[8] for the same PVC sample. The uncertainty in Hodge's values of T_f (±0.5 K) leads, through the method of Moynihan et al.,[19] to a value of θ which would lie in the approximate range from 1.7 to 1.8 K^{-1}. Our value, in the approximate range 1.1–1.2 K^{-1}, is clearly very much lower than his, but has the advantage that it is derived from two independent methods of measurement.

Furthermore, it is interesting to note that even if we were to use the largest value for θ from Hodge's data (1.8 K^{-1}) in conjunction with our value for m_{q_2} (=2.71 K), this would give $\hat{s}(Q_2) = 4.88$ and hence $F(x) = 3.88$. From the master curve in Figure 1 this would yield a value of $x = 0.17$, still considerably larger than Hodge's quoted value of 0.11. In fact, a consideration of Figure 1 will show immediately that it is difficult to envisage how a value of x as low as 0.11 could be achieved; the master curve becomes extremely steep in this region of low x. Indeed, it is this very fact that transforms the rather large uncertainties in $F(x)$ in Table II into acceptable uncertainties in x. The analysis appears to be in a way *self-correcting*. Small values of x, which seem to correlate[8] with small values of β and hence with large values of Δh^*, would imply large uncertainties in the evaluation of θ by the fictive temperature method. However, the correspondingly large uncertainties in $\hat{s}(Q_2)$, and hence in $F(x)$, are significantly reduced because of the shape (steepness) of the master curve in this range of values of x.

A possible explanation for how a value of x as low as 0.11 may be derived from the data could lie in the master curve (Figure 1). This master curve was found theoretically using a number of distributions, both discrete and continuous, but not for a distribution as extraordinarily wide as is the case for PVC. Although we believe that the master curve is essentially independent of distribution,[15–17] this has not been verified theoretically for very low values of β, for which it is harder to achieve the limiting conditions required for the peak-shift method. On the other hand, the reasonable linear relationships between T_p and ln q_2 in Figure 4 and between T_p and log t_a in Figure 5 suggest that such limiting conditions have indeed been achieved in our experiments on PVC.

Nevertheless, in spite of these unresolved differences in the actual values of the material parameters, the main conclusion to this work is that PVC does have a very low x value, and in that respect our results are in qualitative agreement with those of Hodge and Berens.[6] The value of x given here (ca. 0.27) suggests that the thermal behavior of PVC resembles that of polycarbonate (BPAPC), where Hodge[8] had earlier found an x value of 0.22.

Using Angell's concept of "strong" and "fragile" liquids,[28] one can argue that PVC is a very fragile system. Close to T_g the processes of viscous flow will involve a high degree of *cooperativity*, and this in turn is indicated by the large values of θ and Δh^* which are obtained from the measurements. This sample of PVC is approximately 50% syndiotactic,[29] and perhaps 10–15% crystalline.[21] One could speculate that higher x values reported for polystyrene [0.43 (Hodge[8]), 0.46 (Hutchinson and Ruddy[12]), and in the range 0.40–0.48 (Privalko et al.[30])] refer to essentially atactic polymers. As yet, however, the existence of a general correlation among strength and fragility, tacticity, and x has yet to be established.

Acknowledgment. We thank I. M. Hodge (Kodak, Rochester, NY) for sending the sample of PVC and for helpful discussions. We are also indebted to the Science and Engineering Research Council (U.K.) for financial support.

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Registry No. Geon 103EP-F76, 9002-86-2.