

## Effects of Annealing and Prior History on Enthalpy Relaxation in Glassy Polymers. 3. Experimental and Modeling Studies of Polystyrene

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**ABSTRACT:** The relaxation component of the heat capacity at constant heating rate ( $10 \text{ K min}^{-1}$ ) of a polydisperse polystyrene as a function of previous cooling rate, annealing time, and annealing temperature is accurately predicted by an adaptation of an algorithm due to Moynihan using parameter values determined from an analysis of the glass transition kinetics of a single thermal history. For this material, the annealing behavior below  $T_g$  is determined by the same kinetic parameters that describe the glass transition phenomenon. A similar analysis of published data for a monodisperse polystyrene indicates that the monodisperse material has a broader distribution of relaxation times and is more nonlinear. The parameter optimization method used appears to be sufficiently sensitive to permit routine characterization of the enthalpy relaxation of amorphous materials.

### Introduction

Annealing of polymers below the glass transition temperature range results in a decrease in enthalpy, which is recovered during reheating to above the transition range. This recovery is manifested as an endothermic peak or inflection in the heat capacity at temperatures ranging from well below<sup>1-7</sup> to the upper edge<sup>8-10</sup> of the glass transition range. A review of experimental aspects of this phenomenon has been given by Petrie.<sup>10</sup> Sufficient data have now been published to permit several generalizations to be made: (1) The decrease in enthalpy during annealing,  $\Delta H$ , and the temperature at which the heat capacity maximum occurs,  $T_{\max}$ , are both increasing linear functions of annealing temperature  $T_e$  when  $T_e$  is more than ca. 30 K below  $T_g$ . When  $T_e$  is about 20 K below  $T_g$ ,  $\Delta H$  passes through a maximum and then decreases with increasing  $T_e$ . (2)  $\Delta H$  and  $T_{\max}$  are linear functions of  $\log t_e$  ( $t_e$  = annealing time) when  $t_e$  is sufficiently short that the annealed glass is still far from equilibrium. At long  $t_e$ ,  $\Delta H$  becomes constant as the annealed glass approaches equilibrium. (3) Both  $\Delta H$  and the value of  $C_p$  at  $T_{\max}$ ,  $C_{p\max}$ , increase with heating rate  $Q_H$ .  $T_{\max}$  increases approximately linearly with  $\log Q_H$ .

Kovacs et al.<sup>11</sup> and Hodge and Berens<sup>12</sup> have demonstrated that sub- $T_g$  peaks result from the nonexponentiality and nonlinearity of the glass transition kinetics. Hodge and Berens also demonstrated that all of the experimental observations listed above are reproduced by applying the successful treatment of glass transition kinetics described by Moynihan and co-workers<sup>13</sup> to thermal histories, which included annealing. In addition, a good description of  $T_{\max}$  and  $C_{p\max}$  as a function of  $T_e$  and  $t_e$  for poly(vinyl chloride) (PVC) was obtained.<sup>12</sup>

Although the validity of applying Moynihan's formulation to annealing effects is well supported by the reproduction of the general trends listed above, its reproduction of the data for PVC is not a good quantitative test of its accuracy for several reasons. First, the amount of

"crystallinity" in the PVC (as measured by the area of the broad endotherms well above  $T_g$ ) was not closely controlled, and in view of suggestions that crystallinity may immobilize chain segments in the amorphous phase at the interface,<sup>14-16</sup> the possibility exists that the distribution of relaxation times (or nonexponentiality) differed from one sample to another. Also, it is known that the breadth of the glass transition increases with crystallinity in several polymers,<sup>15</sup> and since this breadth is determined by a number of factors in addition to the distribution width (e.g., activation energy and nonlinearity), it is possible that other aspects of the glass transitions were affected as well. Second, the PVC powder was quenched into liquid nitrogen in order to accelerate the annealing process, so that the cooling rate through  $T_g$  could only be estimated. Finally, the extraction of parameters from the experimental data was performed by a subjective judgment of goodness of fit.

The work described here was motivated by the need to test the application of Moynihan's formulation to annealing more rigorously. For this purpose a completely amorphous polymer, atactic polystyrene (PS), was chosen and all cooling, annealing, and reheating were performed in the DSC instrument under controlled conditions. Model parameters were obtained from experimental data for a single thermal history by the optimization procedure described below, and the model was tested by comparing predictions for other thermal histories with experimental data. Since it was not our purpose to compare the merits of the Moynihan approach with any other description (e.g., that of Kovacs et al.<sup>11</sup>), other formulations were not tested.

### The Model

For convenience, we give a brief account of Moynihan's treatment and how annealing is introduced. A full description is given elsewhere.<sup>12</sup> Enthalpy relaxation is calculated from Boltzmann superposition of responses to the total thermal history by considering cooling and

heating as a series of small temperature steps (1 K) and isothermal holds. For convenience, the enthalpy is assumed to decay according to the nonexponential function

$$\phi(t) = \exp[-(t/\tau_0)^\beta] \quad (1)$$

where  $\beta$  determines the degree of nonexponentiality ( $0 < \beta \leq 1$ ) and  $\tau_0$  is a characteristic relaxation time that depends on both temperature and enthalpy. The latter is defined in terms of the fictive temperature,  $T_f$ , defined as the temperature at which the observed enthalpy would be the equilibrium value. The expression used for  $\tau_0$  is<sup>17</sup>

$$\tau_0 = A \exp \left[ \frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f} \right] \quad (2)$$

where  $A$ ,  $x$ , and  $\Delta h^*$  are parameters assumed to be independent of  $T$  and  $T_f$ , and  $R$  is the ideal gas constant. The parameter  $\Delta h^*$  determines how the frozen-in fictive temperature of the glass,  $T_f'$ , varies with cooling rate  $Q_C$ :

$$\frac{\partial \ln Q_C}{\partial (1/T_f')} = -\Delta h^*/R \quad (3)$$

Thus,  $\Delta h^*$  can be determined directly from experimental data. The parameter  $A$ , together with  $\Delta h^*$ , largely determines the value of  $T_f'$  for a given  $Q_C$ . The parameter  $x$  is a direct measure of nonlinearity, i.e., the relative importance of  $T$  and  $T_f$  in determining the average relaxation time.

Adaptation of this treatment to include the effects of annealing involves inserting a holding time of  $t_e$  at  $T = T_e$  during cooling. The time  $t_e$  is divided into ten subintervals to allow for the nonlinearity of enthalpy relaxation during annealing. A normalized heat capacity  $C_p^N$ , defined as  $dT_f'/dT$ , has the values  $C_p^N(\text{glass}) = 0$  and  $C_p^N(\text{liquid}) = 1.0$ . The method for normalizing the experimental data is described below.

### Experimental Section

A single sample (20.1 mg) of Aldrich Secondary Standard polystyrene (lot 03) was dried at 130 °C for 2 h before being sealed in the DSC pan. The material is specified by the supplier as having  $M_w = 3.21 \times 10^5$  and  $M_n = 8.46 \times 10^4$ . The sample was kept in the DSC instrument between runs, in an attempt to reduce experimental scatter due to differences in heat transfer effects. Measurements were performed on a Perkin-Elmer DSC-2 fitted with a Scanning Auto Zero module. Base line curvature was corrected at the only heating rate used, 10 K min<sup>-1</sup>.

To monitor possible decomposition, a total of five rate cooling and reheating scans was run between the annealing experiments. For these, a cooling rate of -40 K min<sup>-1</sup> from 420 to 300 K was followed immediately by reheating at 10 K min<sup>-1</sup> over the same temperature range. For convenience, this thermal history will be referred to as -40/+10, with appropriate changes for other cooling rates. As a further test of reproducibility, three separate scans following 1-h anneals at 360 K were also run during the course of the experiments. In addition to serving as monitors of decomposition, these repeat experiments also provided a measure of experimental uncertainty which was used for evaluating the uncertainty in the model parameters obtained from the optimization procedure. Another sample of ca. 10 mg was also subjected to -40/+10 scans, to test for systematic thermal lag effects.

The experimental data were normalized by expressing the difference between the observed heat capacity  $C_p$  and the glassy heat capacity  $C_{pg}$  (linearly extrapolated into the transition region) as a fraction of the difference between the liquid heat capacity  $C_{pe}$  (similarly extrapolated) and  $C_{pg}$ . The temperature dependence of  $C_{pe}$  was always linear from 390 to 420 K, and extrapolation of  $C_{pe}$  into the transition region was not subject to significant uncertainty. In determining  $C_{pg}$ , however, care was taken to ensure that only the lowest temperature range (300 to ca. 330 K) was used. If a wider range was used, the slight exotherm just below the glass transition region caused a significant change in the slope

of  $C_{pg}$ . This significantly affected only those data at the lower end of the glass transition, and most of the transition range, particularly the overshoot, is much less affected. In the five scans used to monitor decomposition, for example, the random scatter in the maximum of the overshoot,  $C_{pmax}$ , was much larger than the uncertainties introduced by the choice of  $C_{pg}$ .

To determine  $T_f'$  as a function of  $Q_C$ , scans at 10 K min<sup>-1</sup> were recorded following cooling rates of -20, -10, and -5 K min<sup>-1</sup>, in addition to the five -40/+10 runs. For each scan the normalized data were integrated up to temperatures at which the normalized heat capacity was unity, when  $T_f' = T$  and the integral is a linear function of  $T$  with unit slope. The temperature intercept of this linear function defines  $T_f'$ .

Annealing was performed during the cooling cycle to match the thermal history used in the calculations. Two sets of annealing experiments were performed. In the first, the annealing time was kept constant at 1 h and the annealing temperature was varied from 350 to 370 K in 5 K intervals. In the second set, the annealing temperature was held at 350 K and annealing performed for 4, 16, and 66 h. For both sets of experiments the cooling rate before and after annealing was 40 K min<sup>-1</sup> and the reheating rate was 10 K min<sup>-1</sup>. Cooling commenced at 420 K and stopped at 300 K, and reheating data were recorded over the same temperature range.

### Optimization Procedure

Model parameters were obtained from the experimental data by a computer search using the Marquardt algorithm given by Kuester and Mize.<sup>18</sup> Predicted values of the normalized heat capacity,  $\hat{C}_p(T)$ , were obtained from the trial parameters, and the least-squares objective function,  $\psi$ , was defined as  $\psi = \sum_T [C_p(T) - \hat{C}_p(T)]^2$ , where  $C_p(T)$  is the measured normalized heat capacity. The Marquardt algorithm minimizes  $\psi$  and allows for constraints on the search space for each parameter. For the present application  $x$  and  $\beta$  were constrained to lie between 0 and 1, the upper and lower bounds on  $A$  were input manually, and  $\Delta h^*$  was input as a constant. The optimum value of  $\Delta h^*$  was determined graphically from the minimum in  $\psi$  with respect to  $\Delta h^*$ . It was not possible to optimize all four parameters with the Marquardt program because  $A$ ,  $\Delta h^*$ , and  $x$  are highly correlated. Although the best  $\Delta h^*$  might have been found by nesting two search routines, this was not attempted because of practical considerations of computer time.

### Data Analysis

Optimum values of  $A$ ,  $\Delta h^*$ ,  $x$ , and  $\beta$  were obtained for each of the five -40/+10 runs and for a data set constructed from an average of the five normalized  $C_p$  values at each temperature. The averaged data set was assumed to represent the population of -40/+10 data sets, and the optimum set of parameters for it was used to predict the normalized  $C_p$  curves for other thermal histories.

Uncertainties in the best-fit parameters arise from two sources: (a) experimental scatter in the five runs and (b) uncertainties due to possible imperfect convergence of the Marquardt search. The parameter uncertainties due to experimental scatter were evaluated by comparing the optimum standard deviations for each of the five data sets with the deviation for the averaged data set,  $\sigma_{av}$ . The value of  $\sigma_{av}$  was assumed to represent the population and provided a basis for identifying any of the individual data sets as being unrepresentative of the population. An  $F$  test was used for this purpose. A data set was accepted as representative at the 95% confidence level if its standard deviation  $\sigma$  conformed to the  $F$  test inequality appropriate for the number of data points and degrees of freedom:

$$1/1.37 = 0.73 \leq (\sigma/\sigma_{av})^2 \leq 1.37 \quad (4)$$

The variation in parameters for the best fits to the rep-

Table I  
Best-Fit Parameters

| parameter         | average            | uncertainties due to  |                     |                        |
|-------------------|--------------------|-----------------------|---------------------|------------------------|
|                   |                    | exptl scatter         | fitting procedure   | total uncertainty      |
| $\Delta h^*/R, K$ | $8.25 \times 10^4$ | $\pm 2.5 \times 10^3$ | $\pm 5 \times 10^2$ | $\pm 2.55 \times 10^3$ |
| $\ln A (s)$       | -216.4             | $\pm 8$               | $\pm 1$             | 8.1                    |
| $x$               | 0.4255             | $\pm 0.017$           | $\pm 0.035$         | $\pm 0.038$            |
| $\beta$           | 0.6767             | $\pm 0.036$           | $\pm 0.023$         | $\pm 0.043$            |

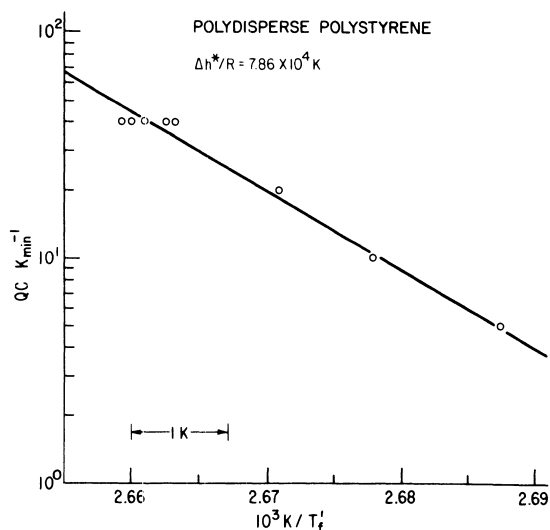


Figure 1. Experimental variation of  $1/T_f'$  (see text for definition) with  $Q_C$ . Line is linear least-squares best fit and gives a value for  $\Delta h^*/R$  of  $7.86 \times 10^4 K$ .

representative data sets was assumed to reflect the experimental scatter.

Uncertainties associated with convergence of the Marquardt algorithm were estimated from a sensitivity analysis of the averaged data set. This was done by changing each parameter one at a time, with the other three held at their optimum values, and comparing the resulting standard deviation with  $\sigma_{av}$ . The maximum change in each parameter for which the inequality (4) remained valid was assumed to be the uncertainty associated with the fitting procedure. The total uncertainty was estimated as the square root of the sum of squares of the two sources of uncertainty for each parameter. This procedure gives a conservative estimate of the uncertainties in each of the optimum parameters, in the sense that if two or more of the parameters are held at their extreme values the best fit is unacceptably poor.

## Results

From the variations in  $C_{pmax}$  for the five  $-40/+10$  runs and the three 1-h anneals at 360 K, the random experimental uncertainty in the normalized heat capacity is estimated as  $\pm 5\%$ . The results of  $-40/+10$  scans with the 10-mg sample also agreed within this uncertainty, indicating no systematic thermal lag effects for this history. A plot of  $\log Q_C$  vs.  $1/T_f'$  is shown in Figure 1. Data for all five  $-40/+10$  runs are included. The linear least-squares estimate of  $\Delta h^*/R$  is  $7.9 \times 10^4 K$ , with an estimated uncertainty of  $\pm 1.0 \times 10^4 K$ .

In the statistical analysis of experimental uncertainty two of the  $-40/+10$  runs were found to be unrepresentative and were rejected. The remaining three were used to estimate the uncertainties in the parameters. The optimum parameters and their uncertainties are given in Table I, and the optimum fit to the averaged  $-40/+10$  data set is shown in Figure 2. The predicted curves for the  $-20/+10$ ,  $-10/+10$ , and  $-5/+10$  runs are compared with experimental points in Figure 3. A similar comparison

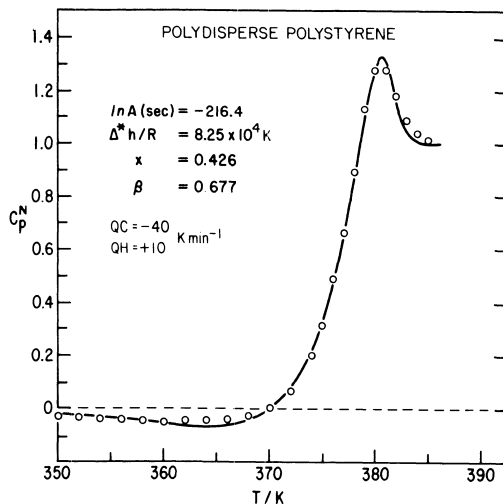


Figure 2. Optimum fit (line) to experimental  $C_p^N$  data (points) obtained by averaging five  $-40/+10$  runs. The optimum value of  $\Delta h^*/R$  agrees within uncertainty with the value obtained from Figure 1. Uncertainties in the parameters are given in Table I.

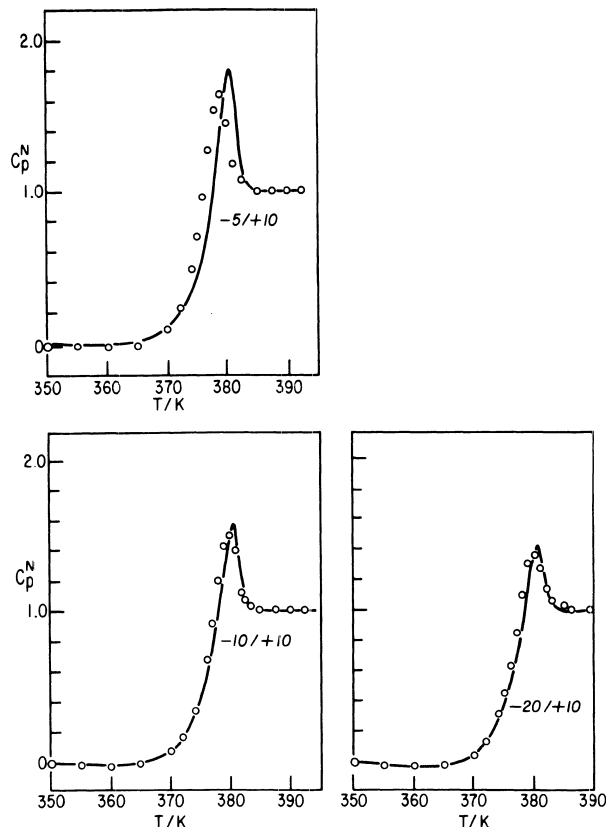


Figure 3. Predicted temperature dependence of  $C_p^N$  (lines) with cooling rate, using parameters determined from fit shown in Figure 2. Experimental data are shown as points.

is shown in Figure 4 for 1-h anneals at the indicated annealing temperatures. The data for the 360 K anneal are an average of the three experiments referred to above. Predicted curves and experimental points for anneals at

