Communications to the Editor

Calculation of the Effects of Annealing on Sub-T_g Endotherms

In recent years endothermic heat capacity peaks below T_g have been observed in several polymers, including poly(vinyl chloride),[1,2] polystyrene,[3,4] and poly(methyl methacrylate).[5] Several features are shared by these endotherms:

(1) They increased in magnitude ($C_{p\,\max}$) and shift to higher temperatures ($T_{\max}$) with increasing annealing time (t_e) and annealing temperature (T_e). At long t_e and/or high T_e they merge with the glass transition and become the well-known endothermic overshoot.[6]

(2) The time t_e required to produce a given peak height decreases with increasing T_e.

(3) $T_{\max}$ is proportional to T_e at constant t_e[3] and approximately proportional to log (t_e) at constant T_e.

(4) For equal annealing conditions, $C_{p\,\max}$ increases with increased rate of quenching through T_g.

We report here data for PVC which exemplify some of these trends and outline a model which reproduces all of them. The model is similar to that of Kovacs et al.[7] but uses a single nonexponential decay function (two parameters) rather than a discrete number of exponential functions.

It is well established that the glass transition, as observed experimentally, is a kinetic phenomenon and that the kinetics are both nonexponential and nonlinear. Several descriptions have been advanced, of which those by Kovacs et al.,[7] Wunderlich et al.,[8,9] and De Bolt et al.[10] are representative. In modeling the effects of annealing we have adopted the approach of De Bolt et al.,[10] in which cooling and heating are treated as a sequence of temperature jumps, followed by isothermal holds whose duration is determined by the cooling and heating rates. The structural relaxation is described by a four-parameter model, which gives a good account of the endothermic overshoot as a function of relative cooling and reheating rates.[10,11] Annealing is modeled by replacing the isothermal hold time at T_e (during cooling) with t_e.

Briefly, the calculation proceeds as follows. After each temperature jump, the enthalpy is assumed to relax according to the empirical function

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

where β ($0 < \beta \leq 1$) is a measure of nonexponentiality. The enthalpy is expressed in terms of the fictive temperature T_f, defined as the temperature at which the observed enthalpy would be an equilibrium one.[10] The value of T_f after n temperature steps is given by

$$T_{fn} = T_0 + \sum_{j=1}^{n} \Delta T_j \{1 - \exp[-(\sum_{k=j}^{n} \Delta T_k / Q_k \tau_{0,k})^{\beta}]\} \qquad (2)$$

where T_0 is a starting temperature well above T_g, Q_k is the cooling or heating rate, and $\tau_{0,k}$ is determined by both the temperature T_k and fictive temperature $T_{f,k-1}$ according to the relation

$$\tau_{0,k} = A \exp\left(\frac{x \Delta h^*}{R T_k}\right) + \frac{(1-x) \Delta h^*}{R T_{f,k-1}} \qquad (3)$$

Table I

T_e, °C	t_e, h	$C_{p\,\max}$ obsd	$C_{p\,\max}$ calcd	$T_{\max}$, °C obsd	$T_{\max}$, °C calcd
23 °C (x = 0.325)	7	0.13	0.05	55	47
	150	0.19	0.18	59	60
40 °C (x = 0.365)	6	0.13	0.12	62	61
	24	0.27	0.23	68	67
	50	0.34	0.32	70	70
60 °C (x = 0.480)	1	0.21	0.25	78	75
	7	0.66	0.63	84	81
	24	1.10	1.2	86	85
	50	1.55	1.64	87	88

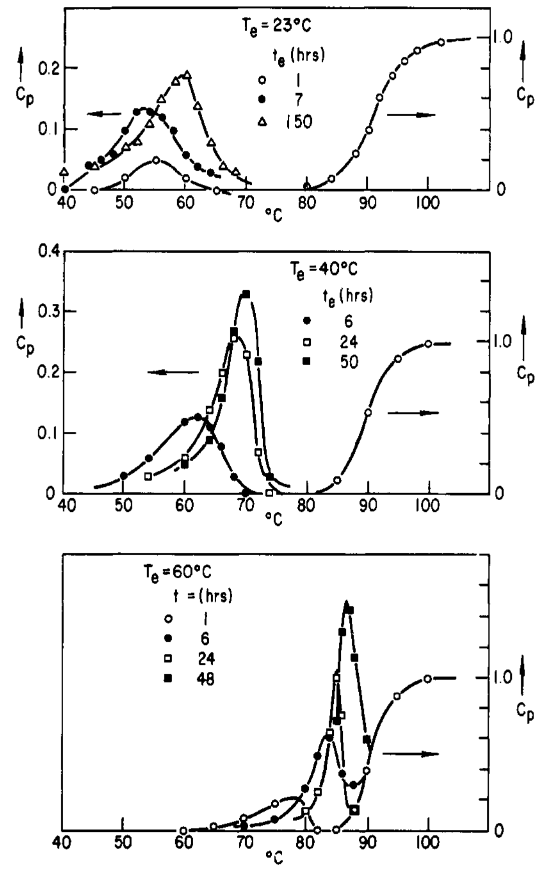

Figure 1. Experimentally observed normalized heat capacity data for PVC after annealing for the indicated times and temperatures. To emphasize the sub-T_g endotherms their scales have been expanded. Data are normalized to give a rubber C_p of 1.0 and glass C_p of 0.0.

where A and Δh^* determine T_g, and Δh^* determines the rate at which T_g changes with quench rate.[10] Equations 2 and 3 are calculated with a straightforward computer program. The heat capacity at temperature T_k, C_{pk}, is defined as

$$C_{pk} = \frac{T_{f,k} - T_{f,k-1}}{T_k - T_{k-1}} \qquad (4)$$

Thus, C_{pk} depends on the total response to all previous thermal history (see ref 10 for details).

Annealing at T_e is introduced by replacing the term $\Delta T_e / Q_e$ in eq 2 with the annealing time, t_e, during cooling.

Experimental data for a commercial PVC resin (Geon 103EP, BFGoodrich Co.) were obtained with a Perkin-Elmer DSC-2 at a heating rate of 20 °C min^{-1} from room

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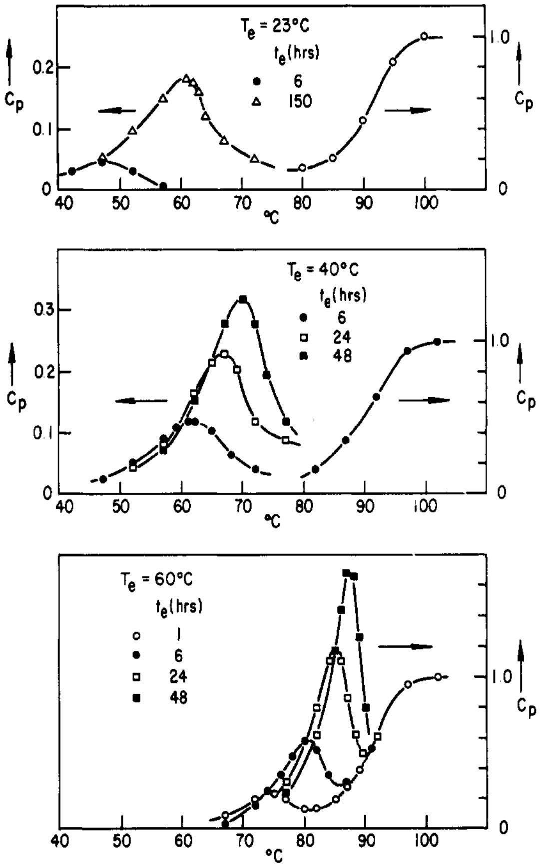

Figure 2. Model calculations of the normalized heat capacity for the combinations of T_e and t_e given in Figure 1. Parameters are ln $A = -274.0$, $\Delta H/R = 10^5$ K, and $\beta = 0.28$. The values of x are 0.325 at 23 °C, 0.365 at 40 °C, and 0.48 at 60 °C.

temperature after the following thermal history: holding at 120 °C for 30 min, plunging into liquid nitrogen (estimated cooling rate 10^3 K min^{-1}), heating to T_e and holding there for t_e, and cooling to room temperature. Annealing times varied from 1 to 48 h at room temperature, 40 °C, and 60 °C. The data are shown in Figure 1. To facilitate comparison with the predictions of eq 4, experimental heat capacity data were normalized to the dimensionless quantity $C_p{}^N$ defined by the expression

$$C_p{}^N(T) = \frac{C_p(T) - C_{pg}(T)}{C_{pe}(T) - C_{pg}(T)} \tag{5}$$

where C_{pg} is the glassy heat capacity well below the relaxation temperature range (linearly extrapolated into the transition range), and C_{pe} is the liquid (or rubber) heat capacity (similarly extrapolated). Thus, $C_p{}^N = 0.0$ in the glassy state and $C_p{}^N = 1.0$ in the rubbery state.

The calculated normalized heat capacities for the same combinations of T_e and t_e are shown in Figure 2. The thermal history used for the calculations was cooling from above T_g at 10^3 K min^{-1} to T_e, annealing for t_e, cooling to room temperature (300 K) at 10^3 K min^{-1}, and heating at 20 K min^{-1}. This approximation to the experimental history is considered adequate for testing the validity of the model.

The effects of varying t_e are reproduced by the model with a single set of values for the four parameters (A, ΔH, β, and x). However, reproduction of the effects of varying T_e requires that x increase with T_e. More recent work, to be detailed later,[12] indicates that this is due to neglect of the self-retarding kinetics during annealing, i.e., the simplification that during annealing $\tau_{0,e}$ is independent of time. Also, the parameter Δh^* was fixed by the quench rate dependence of T_g (estimated from preliminary data) and A fixed by the value of T_g. Thus only two parameters, β and x, were varied in fitting the model to the sub-T_g peaks. With the chosen values of Δh^* and A, the estimated uncertainties in β and x are ±0.01. Other values of Δh^* were not tried.

Acknowledgment. This research was supported in part by National Science Foundation Grant No. CPE-7920740 under the Industry/University Cooperative Research Program. It is a pleasure to acknowledge useful discussions with Professor H. Hopfenberg of North Carolina State University and the experimental assistance of F. W. Kunig. We thank the BFGoodrich Co. for permission to publish this paper.

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Received March 16, 1981

Anionic Polymerization of Methacrylates. Novel Functional Polymers and Copolymers

We report here, in preliminary form, methods we have developed for the synthesis of block and random methacrylate polymers and copolymers with well-defined compositions, many bearing functional groups incorporated either through the use of special initiators or by reaction of the living polymethacrylate anion with electrophiles.

Beginning in the 1950s, the pioneering work of Szwarc, Bywater, and Morton on the anionic polymerization of styrene and dienes introduced the concept of "living" polymers and demonstrated their great potential for the preparation of well-defined block copolymers and terminal-functional polymers. Subsequently, in the early 1960s, extensive interest in the anionic initiation of methacrylate polymerization began to develop. These studies dealt mainly with mechanisms, kinetics, and polymer configuration. In contrast to the polymerization of styrene and dienes, the anionic polymerization of methacrylates proceeds predictably only with careful selection of solvent, temperature, and initiator. In our synthetic work, we have investigated some of these aspects and have extensively applied nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), and high-performance liquid chromatography to the characterization of our polymers.

We began by reinvestigating the work of Braun and co-workers.[1] Their prime interest was in the effect of solvent composition, temperature, and initiator counterion on the *configuration* of poly(methyl methacrylate)

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