

water is less mobile than in liquid water. The relatively large activation energies indicate that there is more cooperative character to the motion. A somewhat similar relaxation has been observed for water adsorbed on silica gel.<sup>15</sup>

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## Effects of Annealing and Prior History on Enthalpy Relaxation in Glassy Polymers. 1. Experimental Study on Poly(vinyl chloride)

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**ABSTRACT:** Endothermic peaks below  $T_g$  have been observed by differential scanning calorimetry (DSC) in samples of poly(vinyl chloride) (PVC) which were given a variety of thermal, mechanical, and vapor treatments and subsequently aged for varied times ( $t_a$ ) at several temperatures ( $T_a$ ). The peaks increase in magnitude and shift to higher temperature with increased  $t_a$  and  $T_a$  and appear as the well-known " $T_g$  overshoot" as  $T_a$  approaches  $T_g$ . The magnitude, but not the position, of the peaks is strongly dependent upon the treatment given the sample before aging. The peaks are enhanced by an increased rate of thermal quenching, by tensile or compressive mechanical stressing, and by prior exposure to a swelling vapor (e.g., methyl chloride). Development of the peaks upon aging is suppressed by the presence of a soluble vapor ( $\text{CH}_3\text{Cl}$  or  $\text{CO}_2$ ) during aging. The DSC observations may be qualitatively explained as a consequence of the slow approach toward equilibrium of a system with a broad distribution of relaxation times.

## Introduction

Differential scanning calorimetry (DSC) has revealed enthalpy relaxations occurring near or below  $T_g$  in glassy polymers aged after a wide variety of thermal, mechanical, and solvent or vapor treatments. Illers<sup>1</sup> and Gray and Gilbert<sup>2</sup> observed sub- $T_g$  endothermic peaks in annealed PVC samples which had been rapidly quenched and found that the magnitude and temperature of the peaks increased with increasing annealing time and/or temperature between the quench and the DSC scan. Foltz and McKinney<sup>3</sup> and Petrie<sup>4</sup> demonstrated that the magnitude of the DSC endothermic peak at  $T_g$  (" $T_g$  overshoot") provided a quantitative measure of the enthalpy relaxation which had occurred during prior annealing at temperatures somewhat below  $T_g$ . In a recent study of aging in ABS and SAN, Wysgoski<sup>5</sup> found no endothermic peaks in samples scanned immediately after a rapid quench, whereas aging at room temperature led to a slow development of small, broad endotherms well below  $T_g$ ; with increasing aging temperature, the endotherms became more pronounced and occurred at higher temperatures, appearing as the familiar  $T_g$  overshoot for aging temperatures within about 20 °C of  $T_g$ .

DSC endotherms showing similar dependences upon annealing time and temperature have been observed by Weitz and Wunderlich<sup>6</sup> and others<sup>7-9</sup> in polymers vitrified by cooling through  $T_g$  under high hydrostatic pressure. Application of mechanical stress to polymers in the glassy state, through either compression<sup>10</sup> or tensile drawing,<sup>11</sup>

also results in endothermic maxima below or near  $T_g$ . Matsuoka<sup>12</sup> has suggested that dilation under tensile stress increases the enthalpy of the glass, reducing the relaxation time and therefore increasing the rate of enthalpy relaxation during annealing.

Compared with these studies of enthalpy relaxations induced by thermal and mechanical treatments, reports dealing with vapor or solvent effects on glassy state relaxations are less extensive or explicit but nonetheless suggestive of closely related effects. Chan and Paul<sup>13</sup> found that exposure of annealed polycarbonate to high  $\text{CO}_2$  pressure reduced the magnitude of the DSC endotherm and suggested that sorption of  $\text{CO}_2$  dilated the polymer, increasing its enthalpy relative to the annealed state. Shultz and Young,<sup>14</sup> in studying polystyrene and PMMA samples freeze-dried from naphthalene solutions, observed sub- $T_g$  endothermal maxima which intensified and moved to higher temperature with increasing annealing time or temperature. Their observations were attributed to a broad distribution of relaxation times in the very "open" glass structure produced by the rapid quench and matrix sublimation. Berens and Hopfenberg<sup>15,16</sup> found that prior exposure to a swelling vapor enhances the sorptive capacity of glassy PVC and polystyrene and suggested this effect may be due to an increase of frozen-in free volume; although DSC data were not included in their study, it seemed likely, in view of the other calorimetric findings, that the vapor-swelling process might also produce an enhancement of enthalpy relaxation effects.

The present study was undertaken to confirm the anticipated effects of vapor treatments upon enthalpy relaxations and to directly compare these effects with those of varied thermal and mechanical treatments for a given polymer and similar annealing conditions. The results seem to reveal a common explanation for the effects of the widely diverse treatments. The enthalpy relaxations in all cases closely follow the predictions of a nonlinear, non-exponential relaxation model<sup>20,21</sup> as detailed in part 2.<sup>22</sup>

## Experimental Section

**Materials.** The polymer used in all experiments reported here was a commercial, suspension-polymerized PVC (Geon 103EP, BFGoodrich Chemical Group), obtained as a free-flowing white powder. Optical microscopy and electron microscopy have shown this resin to consist of roughly 2- $\mu\text{m}$  primary particles firmly agglomerated into porous 100–150- $\mu\text{m}$  grains. Molecular weights given by the supplier are  $M_n = 65\,000$  and  $M_w = 205\,000$ . Portions of this polymer were given the following thermal, vapor, and mechanical treatments:

**"Free-Cooled" Samples.** To erase effects of prior history, PVC powder samples were treated 30 min in a circulating-air oven at 120 °C and then allowed to cool to room temperature in the open air. Approximate cooling rates were 100 °C/min from 120 to 100 °C, 60 °C/min from 100 to 80 °C, 40 °C/min from 80 to 60 °C, and 25 °C/min from 60 to 40 °C.

**"DSC-Cooled" Samples.** To provide samples of more closely controlled cooling rate, 15-mg samples in DSC pans were heated 30 min at 120 °C in the DSC instrument, cooled at the maximum nominal cooling rate of 320 °C/min to -150 °C, and allowed to return to room temperature.

**"Liquid-N<sub>2</sub>-Quenched" Samples.** Portions of the PVC powder (~10 g) were heated 30 min at 120 °C and then poured directly into a large excess of liquid nitrogen in a Dewar vessel. Boiling of the liquid N<sub>2</sub> ceased within 2 s, suggesting an average cooling rate of roughly 10<sup>4</sup> K/min; assuming exponential cooling, the rate through the glass transition region may have approached 10<sup>5</sup> K/min.

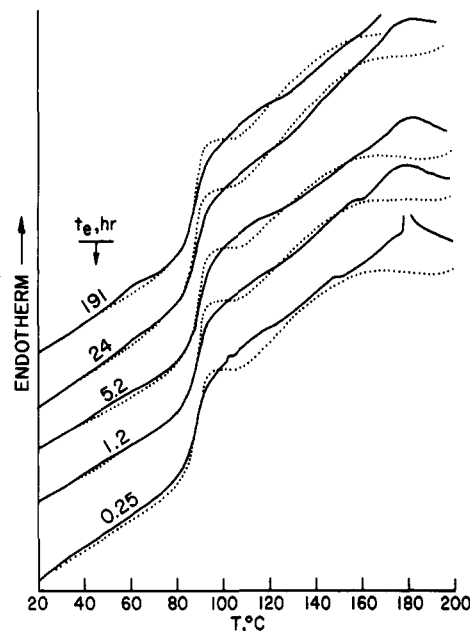
**Methyl Chloride Vapor Treatments.** For study of the effect of vapor swelling on enthalpy relaxations, CH<sub>3</sub>Cl vapor was chosen for its combination of relatively high diffusivity and appreciable solubility in PVC at convenient pressures. Gravimetric sorption measurements by methods previously described<sup>17</sup> showed the diffusivity of CH<sub>3</sub>Cl in PVC at 30 °C to be  $1 \times 10^{-11} \text{ cm}^2/\text{s}$  and its equilibrium solubility at 13-kPa (0.13 atm) pressure to be 3.6 mg/g of PVC. For the DSC study, samples of the PVC powder freshly free-cooled from 120 °C were evacuated in a stainless steel pressure vessel and then exposed to CH<sub>3</sub>Cl vapor at selected pressures (200–500 kPa) at 30 °C for up to 17 h. The vessel was then rapidly vented to atmospheric pressure and evacuated for 1 h at 30 °C; the absorbed CH<sub>3</sub>Cl was essentially all removed, since the half-desorption time under these conditions is approximately 30 s.

**Hot-Pressed Sheet.** Fused PVC sheets approximately 0.3 mm thick  $\times$  120 mm diameter were prepared by pressing portions of the powder sandwiched in aluminum foil between flat steel plates at 210 °C for 10 s under 133-kN (30 000 lb) force. The sheets were cooled by placing the hot steel plates and PVC sheet in a cold press without applying pressure; the cooling rates measured by a thermocouple were approximately 40 °C/min from 210 to 150 °C, 15 °C/min from 150 to 100 °C, and 7 °C/min from 100 to 50 °C. Samples for DSC measurements were punched from the center of the pressed sheets, where flow orientation was minimum.

**Cold-Drawn Sheets.** Strips about 2  $\times$  10 cm were cut from hot-pressed sheets and drawn at 1.3 cm/min in an Instron tensile tester, forming a stable neck with a draw ratio of about 2:1. DSC samples were punched from this drawn region.

**Cold-Pressed Powder.** Small portions of the PVC powder freshly free-cooled from 120 °C were compressed in a 1.1-cm-diameter piston mold under 517-MPa (75 000 psi) pressure for 10 min at room temperature, forming opaque, brittle pellets. Fragments of these pellets were used in the DSC measurements.

**Cold-Re-pressed Sheets.** Portions of the hot-pressed sheet described above were cut to ca. 1.1-cm diameter and re-pressed in the piston mold under 517-MPa pressure for 10 min at room



**Figure 1.** DSC scans on PVC cooled through  $T_g$  at 320 °C/min and aged at 20 °C for the indicated times: (—) first scan; (···) second scan.

temperature. DSC samples were cut from these disks.

**Annealing.** After each of the treatments listed above, samples were aged, or annealed, for varying time periods at room temperature ( $20 \pm 2$  °C), 40 °C, and 60 °C before DSC scans were run. Two sets of liquid-N<sub>2</sub>-quenched samples were annealed at 40 °C under 100-kPa (1 atm) pressure of CO<sub>2</sub> and CH<sub>3</sub>Cl; all other samples were annealed in air at atmospheric pressure.

**DSC Measurements.** DSC scans were carried out on 15-mg samples with a Perkin-Elmer DSC-2 instrument at a 20 °C/min heating rate from 0 to 200 °C. Samples were then cooled at 320 °C/min back to 0 °C, and a second scan was recorded at 20 °C/min to 200 °C. Figures showing DSC scans were traced directly from the charts recorded at 20-mm/min chart speed and 2-mcal/s full-scale sensitivity; the second scan for each sample, arbitrarily matched to the first at 20 °C, is shown as a reference for estimating magnitudes of endo- and exotherms.

## Results

**"DSC-Cooled" PVC Powder.** Figure 1 shows the full first-heat DSC scans for PVC powders aged at room temperature ( $T_e = 20 \pm 2$  °C) for the indicated times,  $t_e$ , after cooling in the DSC instrument at 320 °C/min. Also shown are second-heat scans after cooling at the same rate from 200 °C. Differences between the two scans above  $T_g$  presumably reflect changes in crystallinity, recrystallization, and melting behavior<sup>1</sup> resulting from the different temperatures (120 and 200 °C) at the start of the preceding 320 °C/min cooling stage. In the region below  $T_g$ , significant differences between first and second scans appear after several hours of aging. Although the changes are small, the first scans show a small sub- $T_g$  endotherm, which grows, narrows, and shifts to higher temperature with increased  $t_e$ .

**"Free-Cooled" PVC Powder.** For these samples, cooled through  $T_g$  at about 60 °C/min, DSC scans were obtained after various aging periods,  $t_e$ , at several temperatures,  $T_e$ . Figure 2 shows the 20–120 °C portions of the curves. For the samples aged at room temperature, a significant sub- $T_g$  endotherm is first apparent after  $t_e = 1$  week. For  $T_e = 40$  °C, the DSC curves closely resemble those obtained on the DSC-cooled samples at  $T_e = 20$  °C. A slight endotherm appears after a few hours of aging and grows and shifts up in temperature with increasing  $t_e$ . The temperature at the endotherm maximum,  $T_{max}$ , appears

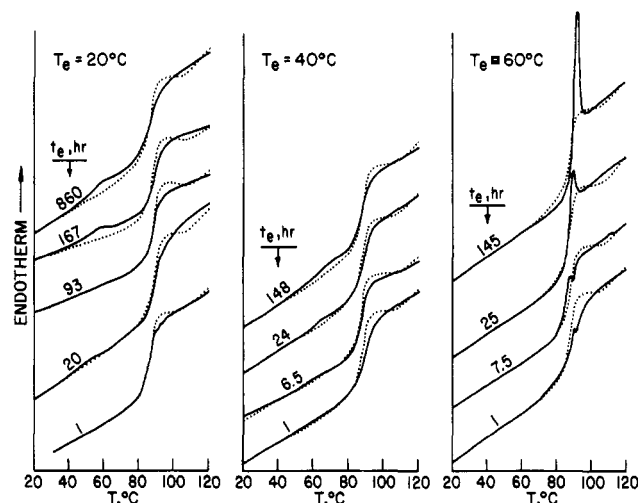


Figure 2. DSC, free-cooled PVC, varied  $T_e$  and  $t_e$ .

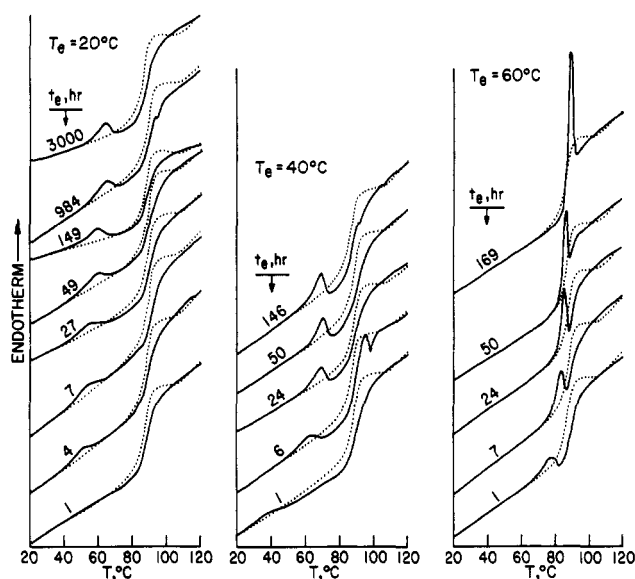


Figure 3. DSC, liquid- $N_2$ -quenched PVC, varied  $T_e$  and  $t_e$ .

somewhat higher for  $T_e = 40^\circ\text{C}$  than for  $T_e = 20^\circ\text{C}$ . When  $T_e$  was increased to  $60^\circ\text{C}$ , a slight endotherm appeared superposed on the  $T_g$  step after the first several hours of aging; for  $t_e \geq 24$  h, the endotherm appears as the " $T_g$  overshoot" widely reported<sup>3,4</sup> in studies of glassy polymers annealed near  $T_g$  and continues to grow with increasing  $t_e$ .

**Quenched PVC Powder.** DSC curves obtained after the indicated aging times and temperatures on PVC samples quenched from  $120^\circ\text{C}$  into liquid nitrogen are shown in Figure 3. In the series at  $T_e = 20^\circ\text{C}$ , a distinct sub- $T_g$  endotherm appears in the first few hours of aging; the growth, narrowing, and shift of this endotherm to higher  $T_{\max}$  with increasing  $t_e$  is now clearly apparent. Between this endothermal peak and  $100^\circ\text{C}$ , the first-heat curves lie below the second scan; it is not clear here whether this reflects an exothermal event or simply an upward shift in  $T_g$  by  $2\text{--}3^\circ\text{C}$  in the first-heat scan as a result of the initial rapid quench. With  $T_e = 40^\circ\text{C}$ , the endothermal peaks are more pronounced and narrower,  $T_{\max}$  is raised, and the "valley" following the peak appears to combine an exothermal process and a shift in  $T_g$  compared with the second scan. The series of curves for  $T_e = 60^\circ\text{C}$  clearly shows the progression of the endotherm, with increasing  $t_e$ , from a separate peak well below  $T_g$  to a spike superposed on the  $T_g$  step.

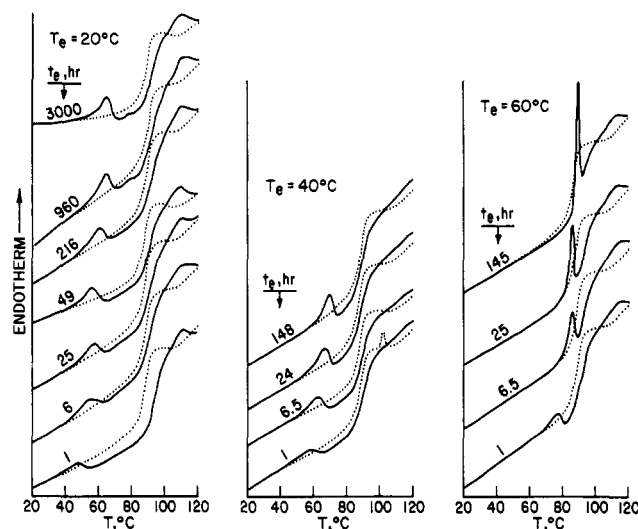


Figure 4. DSC,  $\text{CH}_3\text{Cl}$ -vapor-treated PVC, varied  $T_e$  and  $t_e$ .

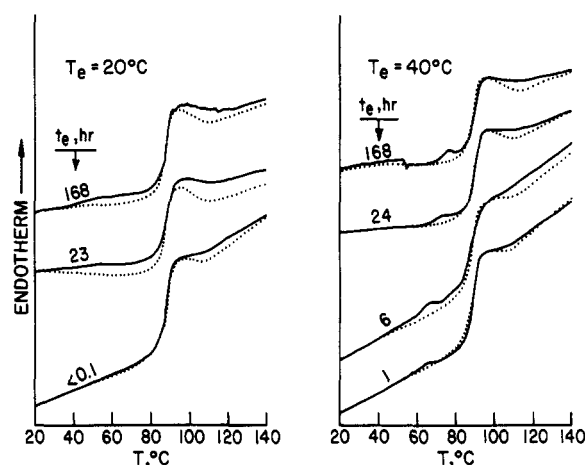


Figure 5. DSC, hot-pressed PVC sheet, varied  $T_e$  and  $t_e$ .

**Vapor-Treated PVC Powder.** Figure 4 shows the DSC curves obtained for free-cooled PVC powders which were subsequently treated overnight with  $\text{CH}_3\text{Cl}$  vapor at  $30^\circ\text{C}$  and 500-kPa pressure, evacuated and finally annealed under the same conditions as the free-cooled and quenched samples. The DSC curves for these vapor-treated samples are remarkably similar to those for the rapidly quenched samples. For equal  $T_e$  and  $t_e$ , the endotherm peak heights and positions, the exothermal valleys, and the  $T_g$  shifts are virtually superposable. The only noticeable difference is the somewhat stronger and narrower endotherms of the vapor-treated samples after annealing at low  $T_e$  and  $t_e$ . Samples treated with  $\text{CH}_3\text{Cl}$  vapor at lower pressure (200 and 300 kPa) show slightly weaker endotherms but otherwise parallel the trends shown in Figure 4. Vapor preswelling and rapid thermal quenching thus seem to have nearly identical effects on the development of enthalpy relaxations during aging of PVC.

In another series of experiments, the duration of the  $\text{CH}_3\text{Cl}$  vapor treatment at  $30^\circ\text{C}$  and 500-kPa pressure was varied from 1 min to 7 h, with annealing conditions fixed at  $24$  h and  $40^\circ\text{C}$ . The duration of the vapor treatment had virtually no effect on the DSC results; even 1-min exposure to  $\text{CH}_3\text{Cl}$  vapor caused the appearance of the pronounced sub- $T_g$  endotherm shown in Figure 4 ( $T_e = 40^\circ\text{C}$ ).

**Hot-Pressed PVC Sheet.** The  $20\text{--}140^\circ\text{C}$  portions of DSC scans on these samples for varied  $t_e$  at  $T_e = 20$  and  $40^\circ\text{C}$  are shown in Figure 5. Base line slope changes and

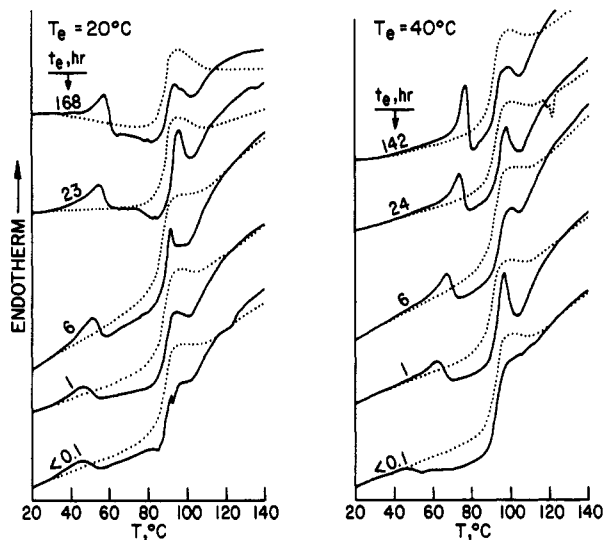


Figure 6. DSC, cold-drawn PVC sheet, varied  $T_e$  and  $t_e$ .

irregularities were particularly troublesome during these measurements. With estimated allowances for this problem, endotherms in the  $T_e = 20^\circ\text{C}$  series seem no more prominent than for the DSC-cooled or free-cooled powder samples (cf. Figures 1 and 2). At  $T_e = 40^\circ\text{C}$ , the sub- $T_g$  endotherms appear somewhat sharper but similar in magnitude and position to the corresponding peaks for the free-cooled powder (Figure 2). Conversion of the powder into a fused sheet, in itself, thus seems to have little effect on subsequent thermal behavior.

**Cold-Drawn PVC Sheet.** DSC scans on samples of the hot-pressed sheet elongated about 100% at room temperature and subsequently aged at 20 and  $40^\circ\text{C}$  are shown in Figure 6. These curves show all the features seen with the quenched and vapor-treated powders, but now in greatly magnified or accelerated form. For example, a significant endothermal peak is observed in a DSC scan run after only 5 min of room-temperature aging beyond the time of cold-drawing (the minimum time required to transfer the sample from the Instron tester to the DSC instrument). In 6 days' aging at  $40^\circ\text{C}$ , the endothermal peak is comparable to that for the quenched powder at  $t_e = 24$  h and  $T_e = 60^\circ\text{C}$ . The deep and randomly variable exothermal minimum above  $T_g$ , at  $95$ – $110^\circ\text{C}$ , may reflect macroscopic recovery of the cold-drawn samples and consequent changes of thermal contact with the calorimeter. It seems that the effects of cold-drawing upon DSC curves below  $T_g$  may differ in degree, but not in kind, from those of quenching or vapor swelling.

**Cold-Pressed PVC Powder and Sheet.** DSC scans of free-cooled PVC powder and hot-pressed sheet, both subsequently subjected to 517-MPa pressure at room temperature, are shown in Figure 7. Scans were run as soon as possible after the pressure treatment and also on samples annealed for 1 h at  $40^\circ\text{C}$ . While the sub- $T_g$  thermal events are somewhat more pronounced in the cold-pressed powder than in the sheet, in both cases the DSC curves below  $T_g$  are very similar to those for the cold-drawn samples (cf. Figure 6). Thus it seems that either tensile or compressive mechanical stress imposed on the polymer produces changes in the rate of relaxation which are similar to those produced by rapid thermal quenching and vapor preswelling.

**Effect of Vapor Presence during Annealing.** To determine whether the presence of  $\text{CH}_3\text{Cl}$  in the PVC during annealing affects the development of sub- $T_g$  endotherms, a sample of the PVC powder was quenched from

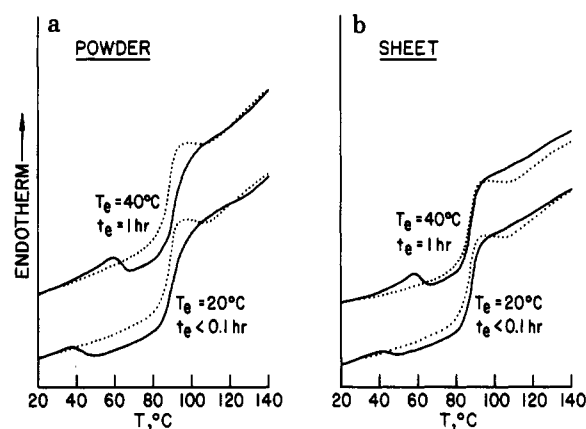


Figure 7. DSC: (a) cold-pressed PVC powder; (b) cold-re-pressed PVC sheet.  $T_e = 40^\circ\text{C}$ ,  $t_e = 0$  and 1 h.

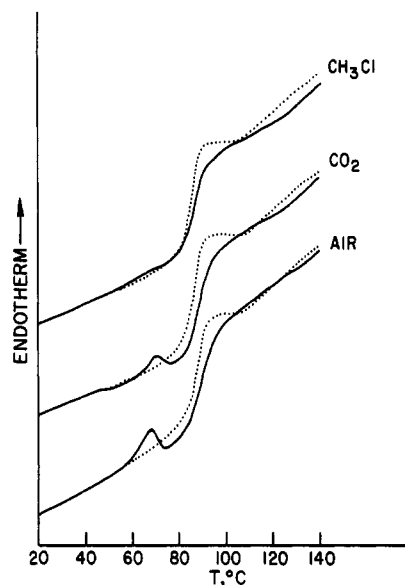


Figure 8. DSC, liquid- $\text{N}_2$ -quenched PVC, aged in air,  $\text{CO}_2$ , and  $\text{CH}_3\text{Cl}$  vapor.  $T_e = 40^\circ\text{C}$ ,  $t_e = 24$  h.

$120^\circ\text{C}$  into liquid  $\text{N}_2$ , allowed to warm to about  $0^\circ\text{C}$ , and then placed under  $\text{CH}_3\text{Cl}$  vapor at atmospheric pressure during annealing at  $40^\circ\text{C}$ . Another quenched sample was similarly aged under atmospheric pressure of  $\text{CO}_2$ . From independent gravimetric sorption measurements, the solubility of  $\text{CH}_3\text{Cl}$  in PVC at the annealing conditions was estimated to be  $\sim 15$  mg/g and that of  $\text{CO}_2$ ,  $\sim 2$  mg/g. DSC curves for samples annealed for 24 h at  $40^\circ\text{C}$  under  $\text{CH}_3\text{Cl}$  and  $\text{CO}_2$  atmospheres and in air are compared in Figure 8. It is evident that the presence of  $\text{CH}_3\text{Cl}$  vapor almost completely suppressed the development of the sub- $T_g$  endothermal peak, while  $\text{CO}_2$  significantly reduced its magnitude compared to the sample annealed in air.

**Endotherm Position and Magnitude.** Comparison of the DSC curves for PVC samples of differing pretreatments but similar  $t_e$  and  $T_e$  suggests that the temperature of the endothermal peak,  $T_{\text{max}}$ , varies systematically with annealing conditions but is nearly independent of the pretreatment. In Figure 9,  $T_{\text{max}}$  is plotted vs.  $\log t_e$  for all the samples showing definable peaks at each  $T_e$ . An approximately linear increase of  $T_{\text{max}}$  with  $\log t_e$  is evident, with a similar slope of about  $5^\circ\text{C}/\text{decade}$  at each  $T_e$ . The variation between the various pretreatments appears little greater than the experimental scatter for a given treatment. Included in Figure 9 are data of Prest et al.<sup>9,10</sup> for PVC vitrified under high pressure and for PVC samples com-

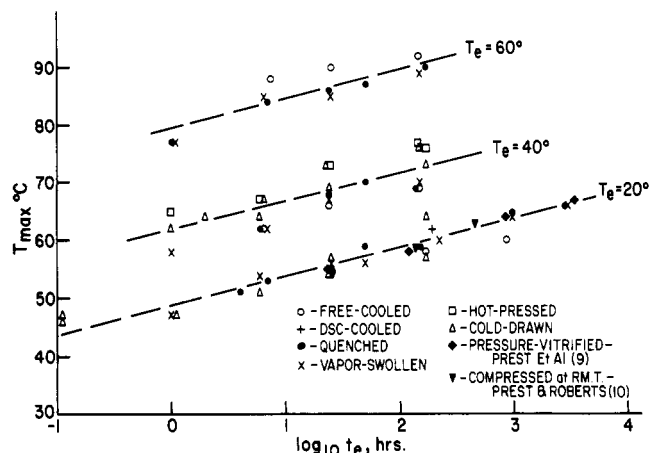


Figure 9.  $T_{\max}$  vs.  $\log t_e$  for PVC's with varied pretreatments.  $T_e = 20, 40$ , and  $60^\circ\text{C}$ .

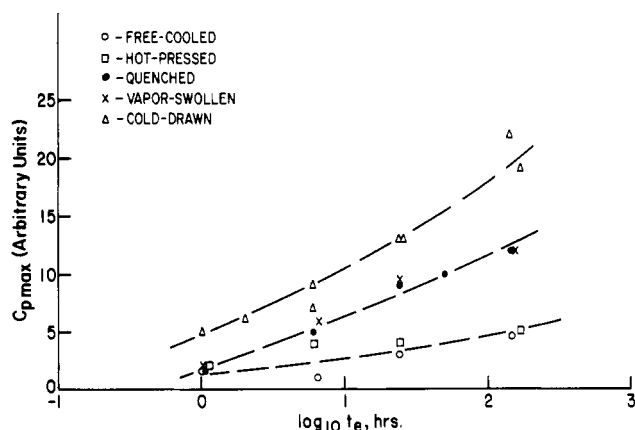


Figure 10.  $C_{p\max}$  vs.  $\log t_e$  for PVC's with varied pretreatments.  $T_e = 40^\circ\text{C}$ .

pressed at room temperature; these data also coincide with our results.

The magnitude of the endothermal peaks, on the other hand, is clearly dependent upon both the annealing conditions ( $t_e$  and  $T_e$ ) and the pretreatment. As an estimate of the peak size, the height of the maximum above the corresponding second-heat scan was measured, in arbitrary units, from Figures 2–6. In Figure 10, these peak heights ( $C_{p\max}$ ) for  $T_e = 40^\circ\text{C}$  are shown as a function of  $\log t_e$ . For each pretreatment,  $C_{p\max}$  appears to increase roughly in proportion to  $\log t_e$ , while the effects of the various pretreatments increase in the order free-cooling  $\approx$  hot pressing  $<$  quenching  $\approx$  vapor swelling  $<$  cold-drawing.

## Discussion

The foregoing experimental findings, in conjunction with previously published studies,<sup>1–14</sup> suggest that the development of endothermic maxima in DSC scans may be a completely general feature of the aging of PVC and other glassy polymers. The absence of such peaks in unaged samples and their growth and shift toward higher temperatures with increasing time and temperature of aging are now well documented for many polymers given a wide range of pretreatments before aging. Our observation that the peak grows in proportion to  $\log t_e$  at a given  $T_e$  agrees with the results of Petrie<sup>4</sup> for polystyrene annealed near  $T_g$ . The shift of peak position,  $T_{\max}$ , in proportion to  $T_e$  and to  $\log t_e$  is consistent with the few systematic studies<sup>5,6,9,10</sup> of samples and conditions producing sub- $T_g$  maxima. Perhaps the most interesting result of the present study is the demonstration that the magnitude of the ob-

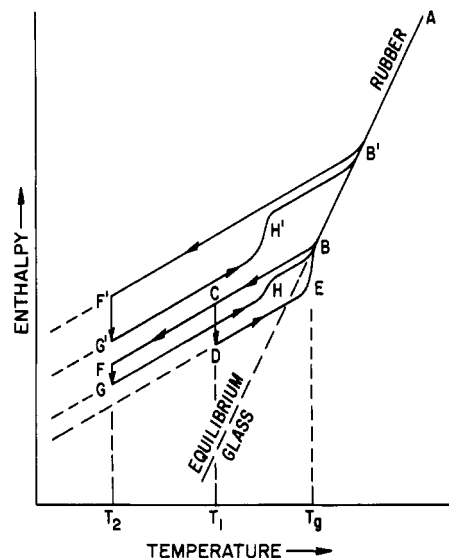


Figure 11. Schematic enthalpy vs. temperature diagram illustrating varied annealing and prior history.

served peaks is strongly dependent upon the pretreatment given the sample before annealing, while the peak position ( $T_{\max}$ ) is determined by annealing conditions ( $T_e$  and  $t_e$ ) and is essentially independent of the pretreatment.

The observed effects may be illustrated on the schematic enthalpy–temperature diagram shown in Figure 11. For a sample cooled into the glassy state, say along path ABC, and annealed at  $T_1$  somewhat below  $T_g$ , the enthalpy relaxes along CD; a subsequent DSC scan, tracing path DEBA, shows an endothermal peak superposed on the  $T_g$  step, i.e., the well-known “ $T_g$  overshoot”.<sup>1,4</sup> For a sample cooled to a lower annealing temperature  $T_2$ , the enthalpy relaxation along FG is recovered below  $T_g$  in a subsequent DSC experiment (path GHBA), as evidenced by the sub- $T_g$  endothermal peak. A more rapid rate of quenching into the glassy state would freeze in a higher level of enthalpy (ABF'), and the enhanced DSC peak (G'H'B'A) indicates that a greater degree of relaxation occurs during annealing (F'G').

Our experimental results suggest that other preannealing treatments also produce a high-enthalpy state and a consequent enhancement of relaxation during annealing. In the case of vapor preswelling, the source of the increased enthalpy is believed to be volume dilation; gravimetric sorption studies<sup>15,19</sup> have shown that a swelling vapor may be rapidly removed from a glassy polymer powder, while the additional volume produced by the swelling process relaxes out much more slowly. In cold-drawn samples, volume dilation is a consequence of a Poisson's ratio  $< 0.5$ .<sup>12</sup> For pressure-densified or compressed glasses, enthalpy can evidently be increased with a decrease of volume,<sup>6,9,10</sup> suggesting frozen-in compressive stress; the effect is again an enhancement of enthalpy relaxation and consequent DSC peaks. The presence of a soluble vapor during annealing imposes a swelling or dilation stress, which presumably opposes the tendency toward volume reduction of quenched samples during aging. Reduction of the magnitude of  $C_p$  peaks by annealing in a  $\text{CO}_2$  atmosphere and near suppression of the peaks by annealing in the more soluble  $\text{CH}_3\text{Cl}$  vapor may thus be regarded as calorimetric consequences of opposing dilational and consolidative effects.

Many of the effects of aging in glassy polymers have been explained as a consequence of the broad distribution of relaxation times and the self-retarding nature of volume relaxations. Struik<sup>18</sup> has emphasized that the short-time

portion of relaxations induced by a temperature quench can reach equilibrium rapidly, even far below  $T_g$ , while the slower relaxations continue for very long times. Moreover, the relaxation spectrum is shifted to longer times by a volume decrease and to shorter times by a volume increase.<sup>18</sup> A direct consequence of this shift is that the rate of relaxation during annealing should be markedly dependent upon the state of the polymer when annealing is commenced,<sup>23</sup> i.e., upon the quench rate or other treatments affecting enthalpy. Our experimental results qualitatively support this expectation.

A more quantitative treatment of the effects of the volume dependence and the distribution of relaxation times upon relaxation processes has been outlined by Moynihan et al.,<sup>20</sup> who employed Boltzmann superposition of nonexponential, nonlinear relaxations induced by successive temperature steps to model volume and enthalpy relaxations in glasses. In a preliminary communication,<sup>21</sup> we have shown that an adaptation of Moynihan's model, to include an annealing step in a rate cooling and heating cycle, predicts the appearance of sub- $T_g$   $C_p$  maxima under conditions approximating those of our experiments. A detailed exploration of this model and its comparison with experimental results will be given in part 2 of this series.<sup>22</sup>

### Summary

1. Sub- $T_g$  endothermal peaks are observed in DSC scans of PVC samples annealed below  $T_g$  or aged at room temperature after a wide variety of thermal, mechanical, or vapor pretreatments.

2. The temperature,  $T_{\max}$ , at which these peaks occur is determined primarily by the annealing temperature,  $T_e$ , and annealing time,  $t_e$ ;  $T_{\max}$  increases almost linearly with  $T_e$  and with  $\log t_e$ . For equal  $T_e$  and  $t_e$ ,  $T_{\max}$  is virtually independent of the pretreatment.

3. The magnitude of the endothermal peak,  $C_{p\max}$ , is highly dependent upon the pretreatment, i.e., upon the state of the sample at the start of the annealing process; for a given pretreatment,  $C_{p\max}$  increases with  $T_e$  and with  $\log t_e$ .

4. For given annealing conditions,  $C_{p\max}$  increases with an increased rate of prior cooling through  $T_g$ ; among varied pretreatments employed in this study,  $C_{p\max}$  increases in the order free-cooling < liquid- $N_2$  quenching  $\approx$  vapor preswelling < cold-drawing.

5. Increased  $C_{p\max}$  is generally accompanied by an increased apparent exotherm between  $T_{\max}$  and  $T_g$ .

6. The development of endothermal peaks below or near  $T_g$  may be a general feature of the physical aging of glassy polymers and can be qualitatively explained by the slow

approach toward equilibrium of a system with a broad relaxation time distribution.

7. Enhancement of sub- $T_g$  endothermal peaks results from pretreatments which produce a state of increased enthalpy at the start of the annealing process, including thermal quenching, mechanical compression, and dilation by tensile stress or by a swelling vapor.

8. Reduction or suppression of sub- $T_g$  endothermal peaks can result from the presence of a soluble vapor during annealing, as a consequence of a swelling stress which opposes the volume reduction during annealing.

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