Apparent Anomalous Thermal Behavior
of Polymers Undergoing a Glass Transition

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Synopsis

Glass transitions in certain polymer samples were detected as a step change in a DTA trace in the *exothermic* sense. This anomaly is explained as a manifestation of the volume relaxation shown to occur at the glass transition in internally strained samples.

Differential thermal analysis (DTA) is extensively used for the determination of glass transition temperatures in polymers. A polymer glass transition has some of the characteristics of an Ehrenfest second-order thermodynamic transition[1] being associated not with an enthalpy change but with an increase in the rate of enthalpy gain with temperature. Hence the DTA curves do not show peaks but merely a small step change in ΔT (the temperature difference between sample and reference) in the endothermic direction. A typical "ideal" DTA trace showing a polymer glass transition is shown in Figure 1(a). Observed glass transitions occur at temperatures at which molecular relaxation times become of the same order as the time scale of the experiment. Because of this kinetic nature, many authors have reported varying shapes for DTA traces through the glass transition. The most commonly encountered trace is shown in Figure 1(b), while that illustrated in Figure 1(c) occurs less frequently. Wunderlich et al.[2] have analyzed these two curves in detail, showing how curve 1(b) is obtained when the heating rate through T_g exceeds the prior cooling rate, while curve 1(c) is obtained with slow heating rates following fast cooling. On slow cooling, a relatively small fraction of free volume is frozen in at T_g. On subsequent fast heating the equilibrium free volume fraction is not immediately achieved, as the fast heating rate does not allow time for the necessary molecular rearrangements to occur. Once through the glass transition, molecular relaxation times decrease very rapidly and the polymer is able to achieve its equilibrium free volume fraction, absorbing heat as it does so and producing an endothermic peak in the thermogram. On fast cooling, a relatively large free volume fraction is frozen in. On subsequent slow heating, the polymer chains have sufficient time to rearrange to their equilibrium configurations having a smaller free volume fraction. This decrease in free volume is manifested by an exothermic peak in the thermogram.
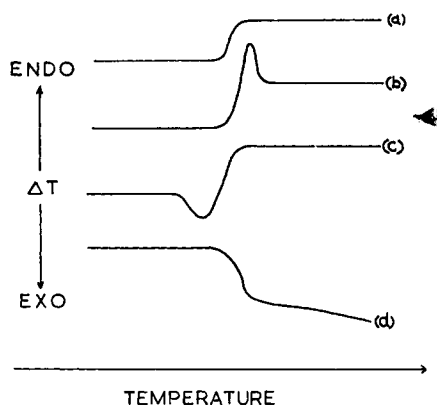
Fig. 1. DTA traces in the glass transition region.

We have, however, frequently obtained thermograms of polymers under-going a glass transition which do not fit into the above pattern. Thus Figure 1(d) shows a thermogram (obtained on a du Pont 900 Differential Thermal Analyzer, using a scan rate of 20°C/min) of a polyurethane in the glass transition region. On first heating, an *exothermic* step change in ΔT was observed followed by an exothermic drift in ΔT. After cooling in the instrument and reheating, no trace of any transition could be detected from the straight baseline. Further cooling and reheating produced a normal glass transition as an endothermic step in ΔT, as is shown in Figure 1(a). Subsequent reheating reproduced this curve. This phenomena has been observed with a very wide variety of polymeric types including polyesters, vinyl polymers, and polyamides. In all cases the polymer had either been isolated from solution, in some cases by freeze drying, or prepared in an expanded or strained form.

It has been shown[3] that changes in the DTA thermogram are reflections of changes in thermal diffusivity, k, of the sample ($k = \lambda/\rho \cdot C_p$ where λ is the thermal conductivity, ρ the density, and C_p the specific heat); i.e., the observed ΔT is a function of the ease of conduction of heat through the sample and the amount of heat needed to raise its temperature. At T_g the specific heat undergoes a step change, increasing in magnitude above T_g while both thermal conductivity and density merely have different temper-ature coefficients above T_g. Thus the net effect on the thermal diffusivity is to produce a step decrease at T_g the magnitude of which is determined by the change in specific heat. This decrease in thermal diffusivity is mani-fested in the DTA thermogram as an endothermic change in ΔT. The thermogram shown in Figure 1(d) would, therefore, appear to show a step decrease at T_g of the specific heat of the polymer, followed by the exothermic drift in ΔT. The thermal diffusivity of bulk material as used experimentally in DTA can, however, be very different from that of the solid polymer. We have found that polystyrene, freeze-dried from 10% solution in benzene, can have a bulk thermal conductivity of $\sim 1 \times 10^{-4}$ cal/cm sec °C as com-
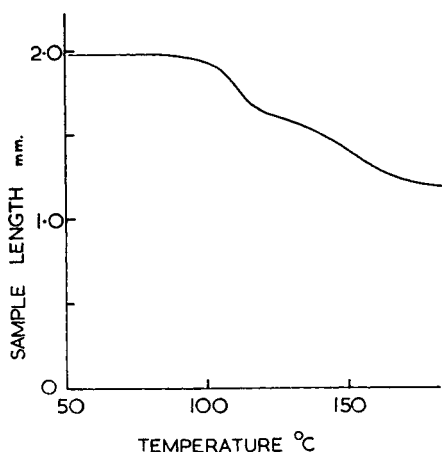
Fig. 2. Zero load length–temperature plot of expanded polystyrene.

pared with a value of 3.7×10^{-4} cal/cm sec °C for the solid polymer.[4] The polymer in this expanded state is highly strained and at T_g a bulk volume contraction occurs. Figure 2 shows a "zero load" length–temperature plot for the same freeze-dried polystyrene obtained on a du Pont Thermomechanical Analyzer using a heating rate of 20°C/min. The sample begins to contract in length (and hence volume) above 80°C, has decreased in length by ~20% at 130°C, and only approaches its normal density at 180°C when it will also have returned to its normal thermal conductivity. Thus, a sample having such a volume contraction at T_g would in effect show a step increase in thermal conductivity. Assuming that there were no change in the effective mass of the sample between the thermocouple and heat source, this fourfold increase in thermal conductivity would completely mask an increase in heat capacity at T_g of ~20% and result in a thermogram of the type shown in Figure 1(d). On cooling and reheating, there would be no volume contraction and a normal thermogram would be obtained. For a more dense sample, or one not completely relaxed, the volume change would be smaller and the increase in thermal conductivity could balance the increase in heat capacity resulting in no apparent deviation from the ΔT baseline. This could also be brought about by the volume change causing a decrease in the effective volume of the sample. If, in addition, the volume relaxation were to occur very slowly so that the thermal conductivity–temperature plot increased in slope above T_g, as shown by the polystyrene sample, a thermogram showing an apparent exothermic drift in ΔT would be obtained. We have found that such exothermic drifts in ΔT can persist on cooling and reheating and that as many as five or six cycles in temperature between 40°C above and below T_g or, alternatively, prolonged annealing above T_g sometimes is necessary to reduce curve 1(d) to 1(a). These conclusions are supported by the fact that this anomalous behavior is not generally observed when the samples have

been examined using a differential scanning calorimeter, in which effects of sample thermal conductivity are minimized by encapsulating a small sample in aluminum foil.

In conclusion, while DTA is an extremely useful technique for the rapid determination of polymer glass transition temperatures, care must be taken to ensure that these transitions are not obscured by other bulk changes in the polymer sample.

References

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