Letters

Enthalpy relaxation in amorphous polymers

There is at present considerable interest in the 'structure' of amorphous polymers as it becomes increasingly apparent that the properties of this large class of materials can be changed by a variety of thermal and mechanical treatments. Direct structural evidence is difficult to obtain and current views are culled from a variety of apparently contradictory circumstantial evidence[1].

One of the simplest indications of the structural changes on annealing is the enthalpy difference ΔH (enthalpy relaxation) between the original and the annealed (or relaxed) glass. This is conveniently obtained using a differential scanning calorimeter (d.s.c.) but the uncritical use of results from this type of apparatus can be very misleading. In this Note we show that the area of the peak observed near T_g, which is frequently taken as a measure of ΔH, is unrelated to this quality. The true value can only be obtained by allowing for the decrease of T_g with annealing.

At the glass transition temperature of a polymer there is a more-or-less abrupt discontinuity in the specific heat (c_p) so that the transition region is very easily observed with a d.s.c. as the instrumental output is directly proportional to c_p. However, the glass to liquid transformation is extremely sensitive to rate effects so that, since d.s.c. is a dynamic technique, the observed shape of the d.s.c. trace is very much a function of experimental conditions. The situation is most easily illustrated using enthalpy curves. *Figure 1a* shows an 'ideal' curve ABC and *Figure 1b* the corresponding c_p curve abb'c, for simplicity we have assumed that both glassy and liquid specific heats are independent of temperature and there is a sharp intersection of enthalpy curves which defines the glass temperature at B. ABC-type curves are found when the heating rate is low relative to the rate at which the liquid had previously been cooled through T_g. As the heating rate is increased the glass tends to superheat following the curve ADC and giving a peak on the corresponding c_p curve add'e'ec. For a given glass the peak area pd'e'e may be varied at will by

changing the d.s.c. heating rate[2], it simply represents the enthalpy needed to rejoin the equilibrium liquid curve BC i.e. bb'pd = pd'e'e. Results for an anionic polystyrene of molecular weight 36 000 (experimental details have been given in ref 2) illustrate the magnitude of the effect. For a glass formed by cooling through T_g at 2.5 K/min the peak area increased with subsequent heating rate (shown in brackets) as follows: 0.63(5), 0.75(10), 0.93(20), 1.13 J/g (40 K/min). Clearly the peak area alone has no thermodynamic significance. It is a useful qualitative indication of previous thermal history but a full description of enthalpy relaxation is only possible by considering the change of T_g on annealing. This has been discussed recently[2] where it was shown that, provided c_p data are known in the equilibrium regions below (this assumes a low temperature glass is stable with respect to the experimental time scale) and above T_g, together with the overall enthalpy change from one region to the other, T_g of a given glass is independent of experimental parameters. *Figures 2A* and *2B* show corresponding enthalpy and specific heat curves for two polystyrene glasses which differ only in their rate of cooling from the melt to the glass (α, 20 K/min; β, 2.5 K/day $\equiv$ 0.0017 K/min)

Figure 2 Enthalpy (A) and specific heat (B) curves for anionic polystyrene ($M_n = $ 36 000) glasses α (20 K/min) and β (2.5 K/day, 0.00176 K/min) formed by cooling through T_g at the rates shown in brackets. D.s.c. heating rate = 10 K/min Glass temperatures shown are calculated from the intersection of enthalpy curves extrapolated from regions where c_p is a linear function of temperature (for this reason $T_{g\alpha}$ lies below the *observed* intersection)

The enthalpy curve shows how T_g decreases on careful annealing (from T_g = 372.9K to T_g = 362.9K) whereas an increase would incorrectly be inferred from the discontinuity in the c_p curve. The enthalpy difference (*Figure 2a*) $\Delta H_\beta^\alpha = H_{g\alpha}(T_{g\beta}) - H_{g\beta}(T_{g\beta}) = 3.0$ J/g but peak areas for glasses α and β are 0.3 and 5.5 J/g, respectively so that on a 'peak' basis enthalpy relaxation is 5.2 J/g — almost double the true figure. Of course at some lower heating rate 'peak' data would give the correct figure but this would be entirely fortuitous since at even lower heating rates no peak is discernible for either glass. In the above example enthalpy relaxation of one glass relative to another is considered. A more basic reference state would be some point on the extrapolated liquid line but this has the disadvantage that the relaxation quantity thus defined is a strong function of temperature (compare δ_1 and δ_2, *Figure 1a*) whereas for $T < T_{g\beta}$ ΔH_β^α is almost independent of temperature since $c_{pg\alpha} \sim c_{pg\beta}$[2]. This last approximation has the practical
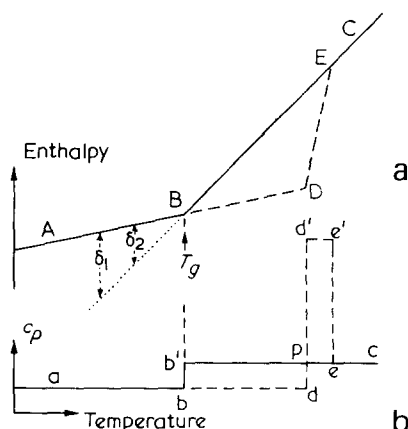
Figure 1 Schematic enthalpy (a) and specific heat (b) curves in the glass transition region. ——— and — — —, indicate behaviour at low and high heating rates respectively. . . . . . , equilibrium curve
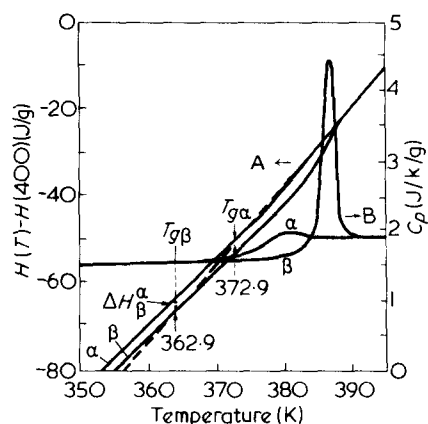
advantage that enthalpy relaxation can be measured directly by superimposing d.s.c. curves of glasses run under the same experimental conditions[3].

Because c_p for the glassy phase is nearly independent of thermal treatment enthalpy relaxation of one glass relative to another is given by $\Delta c_p \Delta T$ where Δc_p is the mean value of $c_{pl} - c_{pg}$ in the range $\Delta T = T_{g\alpha} - T_{g\beta}$ (c_p values are extrapolated from the 'equilibrium' regions above and below T_g). It is thus essential to have accurate values of T_g and these must be obtained using enthalpy, rather than specific heat, curves because the latter, even if unperturbed by rate effects, do not uniquely define T_g (see c_p *Figure 2B*). In the more familiar[4], but thermodynamically analogous, case of specific volume and coefficient of expansion (analogous to enthalpy and c_p, respectively) no attempt is ever made to extract T_g from the derivative, expansion, curve. There is, however, an important difference of scale between

the two cases since the ratio c_{pl}/c_{pg} is much less than that for the coefficients of expansion (for polystyrene the values are about 1.2 and 2.5, respectively) so that there is relatively little difference in slope between H_g and H_l and the extrapolation of each into the transition region to give T_g is far more critical than when using specific volumes. At this stage c_p curves are very helpful since for most homopolymers there is a fairly extensive region (30–40K, and often much wider) below T_g where c_p is a linear function of temperature. Departures from linearity clearly show the onset of abnormal energy requirements corresponding to the transition from c_{pg} to c_{pl} and may be used to define an upper limit to c_{pg}. Data below this limit can be integrated to give H_g which can then be extrapolated with some confidence into the transition region.

Sharanov and Volkenshtein[5] described the correct use of enthalpy

curves in fast calorimetric studies of the glass transition some years before the introduction of d.s.c. However the large number of recent publications which feature d.s.c. peak areas to characterize the thermodynamic state of glasses makes it essential to emphasize the errors inherent in this procedure.

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On structural transitions in polyethylene

Introduction

The widely applied methods for structural determination in crystalline polymeric materials are X-ray and electron diffraction[1].

Vibrational spectroscopy has, however, been applied[2] and has the advantage over diffraction methods that it can detect and characterize short range and/or transient order, and hence it is an attractive technique for investigat-

ing certain types of structural problem.

Experimental

Films ~30 μm in thickness were melt cast from a linear high density commercially available polyethylene which contained less than one CH_3 group per 1000 carbon atoms.

Infra-red spectra were recorded on a Perkin–Elmer 225 grating infra-red spectrophotometer over the temperature range 77–405K (melt), using a Beckmann/RIIC variable temperature sample cell.

Results and Discussion

Crystalline polyethylene forms a primitive orthorhombic lattice, of space group Pnma (D_{2h}^{16}), in which two chains traverse the crystalline unit cell. Vibrations of adjacent chains interact and as a result the vibrational spectrum characteristically contains a series of closely split doublets[3] (correlation or Davydov splitting).

The infra-red active CH_2 rocking mode is observed as a doublet close to 720–730 cm^{-1}. A plot of frequency against temperature for the two bands is shown in *Figure 1*. The results are
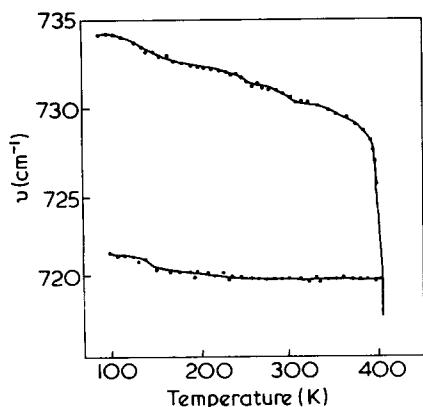

Figure 1 The frequencies of the CH_2 rocking modes in crystalline polyethylene as a function of temperature. Comparative error ~±¼ cm^{-1}
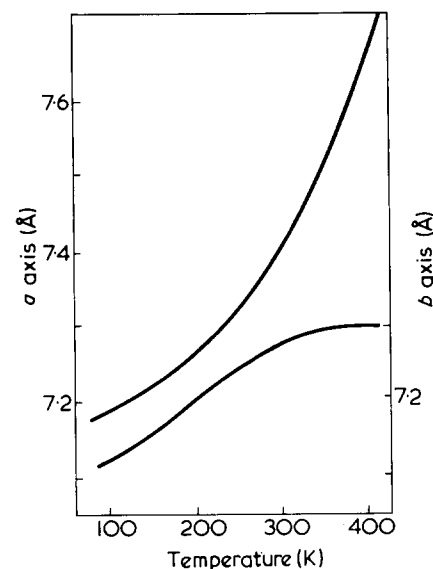

Figure 2 Thermal expansion of the 'a' and 'b' axes in crystals of linear polyethylene

broadly in line with those of previous workers[4–6], although the present study includes high temperature data for the first time. It is clear from X-ray data (*Figure 2*), that the frequency of these bands near 720 and 730 cm^{-1} follow changes in the b and a axes respectively, of the crystalline unit cell as a