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 investigating certain types of structural problem.

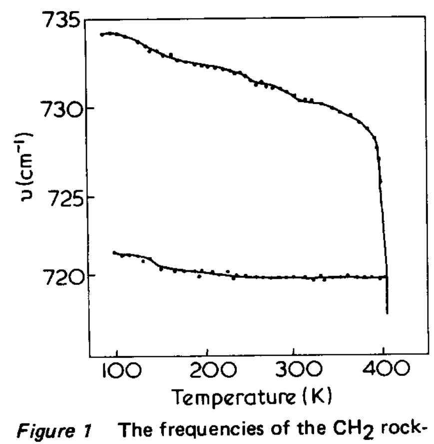

Figure 1 The frequencies of the CH_2 rocking modes in crystalline polyethylene as a function of temperature. Comparative error ~±¼ cm^{-1}

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 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

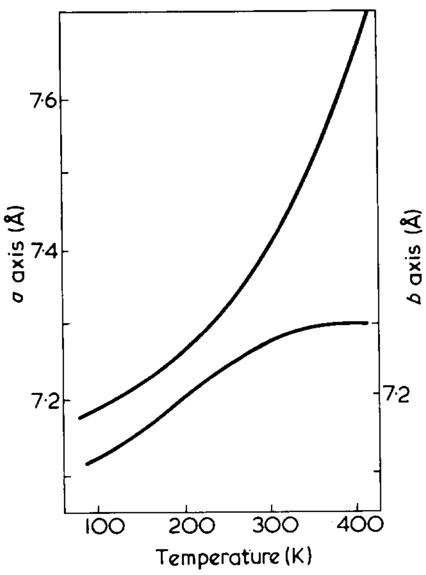

Figure 2 Thermal expansion of the '*a*' and '*b*' axes in crystals of linear polyethylene

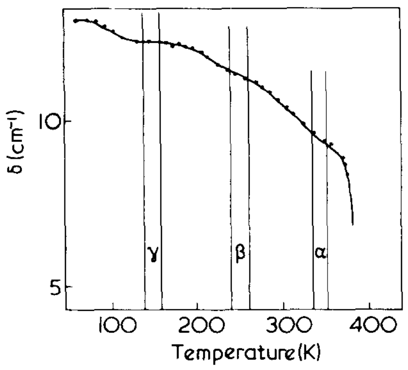

Figure 3 Splitting in the CH_2 rocking mode doublet of crystalline polyethylene as the temperature is raised towards T_m. Error ±½ cm^{-1} or better

function of temperature[7]. However, discontinuities, apparent in the infrared frequency *versus* temperature plots have not been detected in the X-ray experiment.

The discontinuities become more pronounced if the magnitude of the correlation splitting δ, is plotted as a function of temperature, (*Figure 3*). It can be seen that marked changes of slope occur in the curve at temperatures known to be typical of dynamic–mechanical transitions, namely ~395K (α′), ~335K (α), ~250K (β) and ~150K (γ).[8–10]

The dynamic–mechanical transitions are normally detected by experimentally slow techniques. Vibrational spectroscopy is, however, very fast, the lifetime of a vibrational state is probably $<10^{-12}$ sec, hence we expect on this basis to observe the effects.

It is surprising, however, to note that even those transitions which are normally associated with changes in the disordered regions (γ and β transitions) and the α′ transition which has been said to be due to lamellar slip[11], are detected, since correlation splitting is a phenomenon which is exclusive to the crystalline domains of polyethylene.

Thus we suggest that the structural interpretation of the dynamic mechanical transitions of polyethylene may require re-appraisal.

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