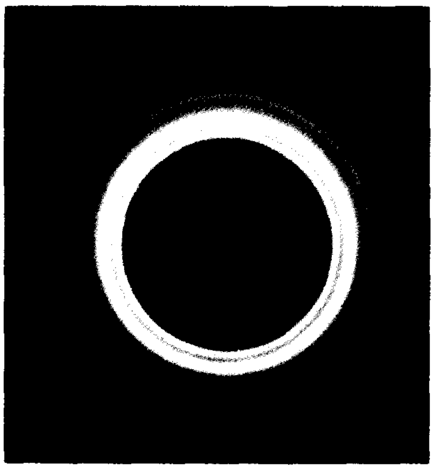

Figure 2 WAXS pattern of an IPS film, cast from a mesitylene solution, as described in ref 1

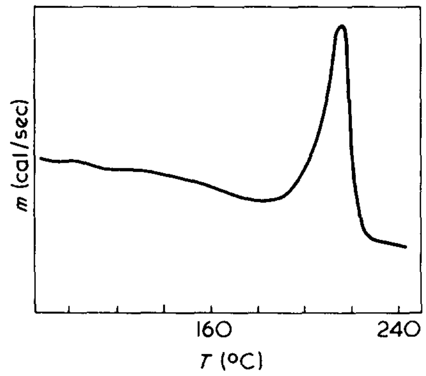

Figure 3 D.s.c. thermogram of the IPS film, cast from a mesitylene solution, scan rate 20° C/min

solvent concentration allowing crystallization.

When samples of IPS crystallized by this technique are dried under vacuum and are brought again in contact with dichloromethane or acetone, no maximum in the absorption curves is observed (*Figure 1*). This corresponds to an absorption of Case II of ref 1. This absorption behaviour is also obtained with thermally crystallized samples (*Figure 1*). We conclude therefore that when completely dried, semicrystalline samples are used, the degree of swelling increases continuously until an equilibrium value is reached. No maximum can be seen in the curves. It is also clear from these remarks that the desorption reported by us (ref 2) is only the consequence of crystallization.

The situation is completely different when IPS samples are prepared by casting films from solutions of the polymer in high boiling solvents as mesitylene or *o*-chlorotoluene. Samples prepared as described in ref 1 are crystalline. This can be easily shown by X-ray diffraction (*Figure 2*) and d.s.c. (*Figure 3*). This is due to the very slow rate of evaporation of the solvent. It is also possible that the residual solvent concentration is high enough to allow further crystallization at room temperature. Annealing of these samples can even increase the crystallinity. The presence of this crystalline fraction can be directly deduced from the densities reported in ref 1, *Figure 1*. After annealing for 48 h, pure IPS has a crystallinity fraction of 0.18, calculated from the density reported in this Figure, using 1.057 and 1.125 g/cm^3 as the densities of amorphous and completely crystalline IPS. Starting then with an already crystallized sample, a maximum in the absorption kinetics of their dried samples cannot be expected. Furthermore, we have observed that n-hexane is unable to crystallize IPS by swelling at 35°C. Probably the maximum degree of absorption at this temperature is too low to allow any crystallization.

From these observations and remarks, we can reach the following conclusions. Samples partly crystalline and containing some amount of casting solvent, will show a maximum in the absorption kinetics as a consequence of desorption of trapped casting solvent. The difference in absorption rate can be explained by the presence in IPS of a crystalline fraction. Starting with amorphous, dried samples, a maximum is only observed when crystallization is possible. This requires a minimum concentration of solvent in the sample depending on the partial vapour pressure and the temperature. This is clearly illustrated in ref 2, *Figure 2*.

The fundamental difference between the results of Faulkner *et al.* and our work results from the difference in the sample preparation techniques. They also used an organic liquid that is incapable of crystallizing IPS under the reported experimental conditons.

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Fine structure of the low temperature relaxation in linear polyethylene

In linear polyethylene the low temperature (γ) relaxation occurs at about −120°C (depending upon the frequency of measurement) and is thought to consist of components from both amorphous and crystalline parts of the polymer. Illers[1] identified three separate relaxations termed γ_I, γ_{II} and γ_{III} centred (at 1 Hz) at −110°, −135° and −165°C, respectively. The interpretation of these relaxations has led to considerable difference of opinion[2] and in addition, in a paper published in 1972, Cooper and McCrum[3] pointed out the importance of thermal history on the position and magnitude of these low temperature relaxations.

In this Letter we give results of some preliminary studies on the low temperature mechanical behaviour of ultra-high drawn polyethylene which suggest that there may indeed be multiple γ relaxations in these materials.

Sample preparation

The samples used in this work were from a batch previously prepared during the work reported elsewhere[4]. They had been made from Rigidex 50 which had been moulded at 160°C into a sheet, cooled at 1.5°C/min to 110°C and then quenched in cold water. Tensile test samples, 20 x 4 x 1 mm, had

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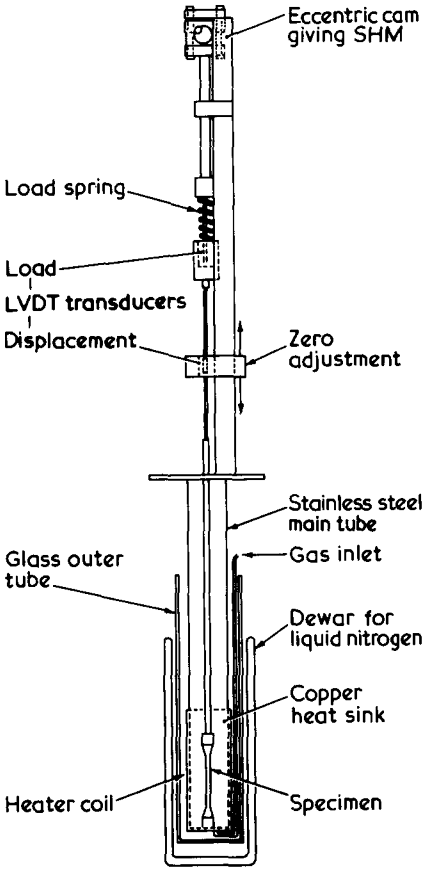

Figure 1 Layout and schematic diagram of the tension apparatus

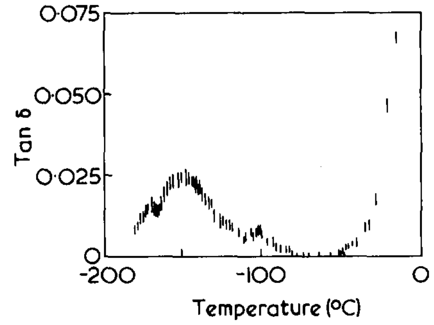

Figure 2 Loss factor $\tan\delta$ in tension for unannealed fibre in the temperature range −200° to 0°C (N_2 atmosphere)

then been cut from this sheet and drawn at 75° ± 1°C for 3–4 min at 50 mm/min. Drawing was stopped before whitening occurred so that the resulting specimens were transparent. Draw ratios between 20 and 30x were achieved and the tensile modulus in the unannealed material then lay between 400 and 800 kbar.

Some of this material had been annealed at constant strain at temperatures between 129° and 132°C until the retractive forces had relaxed, and then cooled to room temperature. This procedure caused the 'self-hardening effect' referred to in ref 4. The two types of sample are here referred to as unannealed and annealed, respectively.

Two samples were used in the work reported here. Sample 1 (annealed) was tested in tension and in torsion and had the dimensions: 109 x (1.82 ± 0.03) x (0.12 ± 0.01) mm. Sample 2 was tested in tension unannealed, then annealed and retested in tension. Its dimensions were 105 x (1.01 ± 0.05) x (0.09 ± 0.01) mm.

For measurement of E and $\tan\delta$ in tension the specimens were mounted in a mechanical straining device which applied a constant frequency (0.1 Hz) constant amplitude displacement to a load spring and the sample connected in series. The displacement of the sample was measured by a *LVDT* and the load by a second *LVDT* which recorded the extension of the load spring. A schematic diagram of the apparatus is shown in *Figure 1.* The load spring–*LVDT* combination is of comparable hardness to the specimen itself over the temperature range studied. The maximum sample strain was (0.1 ± 0.01)%.

The output from the two *LVDTs* is displayed as a stress–strain diagram on an *XY* recorder thus giving an elliptical trace from which, assuming linear viscoelasticity, E and $\tan\delta$ may be found and thus E' and E'' if required. The system was calibrated and checked for linearity using a hard-drawn stainless steel wire specimen.

Measurements in torsion were made using a conventional inverted free torsion pendulum in which end-loads are minimized by a counter balance and the amplitude and period of torsional vibrations (at ∼0.1 Hz) measured by optical means. The maximum strain was 0.1%.

Both the tensile and the torsion apparatus allow control of specimen temperature in the range −190° to +100°C in any environment to better than 2°C. Noting Cooper and McCrum's strictures[3] on the effect of thermal history on the magnitude and even the presence of the γ_{II} peak, we took care to make measurements extremely slowly over the required range, and approached the γ region from both above and below with no discernible difference in the fine structure observed.

Figure 2 shows the variation of the loss factor $\tan\delta$ in tension as a function of temperature for the unannealed sample (sample 2). Three relaxation regions may be tentatively assigned, following Illers[1] as γ_I, γ_{II} and γ_{III}. In *Figure 3,* which is a plot of $\tan\delta$ in tension against temperature for the same sample after annealing, the γ_{III} peak is seen to have become very much more intense while γ_I and γ_{II} are little altered. In torsion the evidence for three peaks is less convincing, the γ relaxation being a broad curve of maximum $\tan\delta$ ∼0.02 at ∼−140°C, with a slight shoulder at ∼−120°C.

Discussion

Illers' tests[1] were carried out in shear at 1 Hz and his specimens were not as highly drawn as ours. His later results[2] on material drawn to 3, 15 and 30x do not show convincing fine structure in the γ region.

In ref 1 activation energies of 16, 12 and 5 kcal/mol were assigned to the γ_I, γ_{II} and γ_{III} relaxations, respectively. Assuming the usual rate process theory the temperatures at which these relaxations should appear at our frequency of 0.1 Hz are −117°, −142° and −175°C, respectively. These are in fair agreement with the positions of the maxima in our work.

Interpretation of the γ relaxation is not unequivocal. It seems to be generally accepted, however, that it may be comprised of contributions from amorphous and crystalline regions.

The present work indicates that the annealing at constant strain reported in ref 4 to produce the self-hardening effect and to remove the contractile forces present in the unannealed, as-drawn material also causes a pronounced change in the low temperature γ peak.

Further work now in progress should cast more light upon the nature of the low temperature relaxation but it seems at this stage reasonable to associate the γ_{III} peak with the recrystallization demonstrated in ref 4. The fact that the remainder of the structure of the γ re-

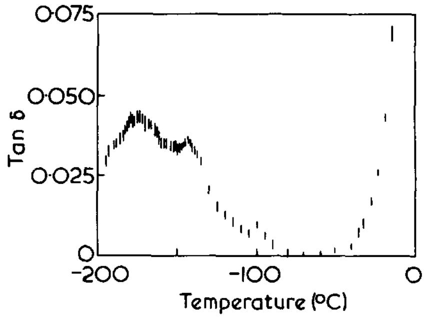

Figure 3 Loss factor $\tan\delta$ in tension for annealed fibre in the temperature range −200° to 0°C (N_2 atmosphere)

laxation is unchanged on annealing is consistent with our interpretation of the structure of ultra-high drawn polyethylene in terms of a fibre composite model as detailed by us[5]. In this model the self-hardening is explained by a change in the 'matrix' phase of the composite resulting from recrystallization, while the 'fibre' phase remains unaltered.

Acknowledgements

P. J. B. wishes to thank ICI Ltd for financial support during this work.

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revised 19 December 1977)*

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