polymer communications

Chain extension from neutron scattering in high modulus oriented polyethylene

D. M. Sadler and J. A. Odell
H. H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, UK
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Mechanical properties of crystalline polymers are closely correlated with structure, especially chain orientation; with the advent of neutron scattering we are now able to measure directly chain extension and assess its influence. The technique enables chain dimensions in the condensed state to be derived by virtue of the ability of the technique to 'see' individual chains with contrasting isotopes, for example see refs 1–3. For crystalline polymers the technique has so far been used to assess the types of folding, whether adjacent or randomly re-entrant (e.g. ref 2). In brief, it is now clear that melt-quenched polyethylene folds in a rather random way, although it remains to be found precisely what degree of randomness is involved. Work in ref 4 has already shown that chain dimensions can be derived in different directions in an oriented mat of solution grown crystals. The preliminary results presented here are not primarily concerned with fold re-entry. Rather, we wish to show how a high degree of chain orientation can exist both when the chains are stretched out and when they occupy approximately the same volume as in the unoriented material.

To achieve these two different degrees of chain elongation, two distinct methods of orientation have been employed, both of which give near perfect *c*-axis alignment. First, solid state extrusion of the heat-softened polymer was used to produce a sample which probably has a high degree of chain elongation. Second, pressure-induced crystallization of the melt onto a small amount of fibrous nuclei formed during elongational capillary flow produced a material in which the vast majority of the material was of a lamellar nature with the chains not extended. It seemed likely that for the lamellar material the chains were not extended[6].

Both of these techniques are capable of producing extremely high modulus materials (Young modulus greater than 50 GPa along the draw direction) although the precise interrelation between mechanical properties and morphology is clearly different in the two cases[6,7].

The hydrogenous Rigidex 9 and deuterated polyethylene were blended in the usual way[2]. The molecular weight averages of the latter were 4.4 × 10^5 (M_w) and 2 × 10^5 (M_n); it was present as 3% of the total polymer. The starting material for the solid state extrusion was obtained by melting the as-crystallized polymer in the barrel of an Instron rheometer at 150°C and then rapidly pressure-quenching at 200 GPa, and lowering the temperature. This material was then extruded under 100 GPa pressure through a tapering Instron die using a deformation ratio (the ratio of the area of unextruded plug to that of the extrudate) of 20:1 and a temperature of 100° C[8]; at this temperature the polymer is softened but not molten. The second method of sample preparation is in two stages. First, the melt is extruded, again in an Instron rheometer, through a 1 mm tapering capillary die at 140°C. The elongational flow in the capillary entrance produces fibrous crystals; the extrusion rate and temperature are controlled so that in the fibrils are present in extremely small quantities and do not block the flow system. The second stage is to block the capillary exit, and rapidly increase the pressure in the rheometer to 200 GPa. The bulk of the molten polymer in the capillary is then pressure-quenched, and crystallizes using the previously formed fibrils as nuclei. The whole assembly is cooled to room temperature before the pressure is released, and the extrudate removed from the capillary.

These two preparation techniques yield samples which are suited to neutron scattering studies. The extruded plugs are almost transparent, with a few voids which may contribute to extraneous background scatter[2,3]. Also, since both types of sample are crystallized from the melt by rapid pressure-quenching, fractionation leading to partial segregation of the deuterated material is minimized. Even quite small fluctuations in isotope concentration as a result of fractionation can give rise to problems in the measurement of radii of gyration from the neutron scattering of polyethylene[2,3]. The low-angle neutron scattering instrument D11 at the Institut Laue Langevin (Grenoble) was used with a specimen-to-detector distance of 10.5 m and with a wavelength of 10 Å. Measurements were made on the blend, on purely hydrogenous samples and on the empty cell, and the counter response was calibrated using H_2O.

Contour plots of difference intensities are shown in *Figures 1* and *2*. The units of intensity are arbitrary; a detailed analysis to be published elsewhere shows that the extrapolated 'forward intensity' is consistent with the molecular weight of the labelled material as measured by gel permeation chromatography.

The difference between the two methods of orientation is quite striking. *Figure 1* corresponds to the 'blocked plug' method[6], and we see that the reduction in intensity as a function of angle, expressed in the diagram as the distance from the centre of the contour plot, is nearly independent

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During the preparation of this note preprints of *Faraday Meeting Number 68* have become available, in which Ballard *et al.*[9] also show differences in chain dimension in different directions in a fibre sample. The work here was available as an I.L.L. report during 1979.

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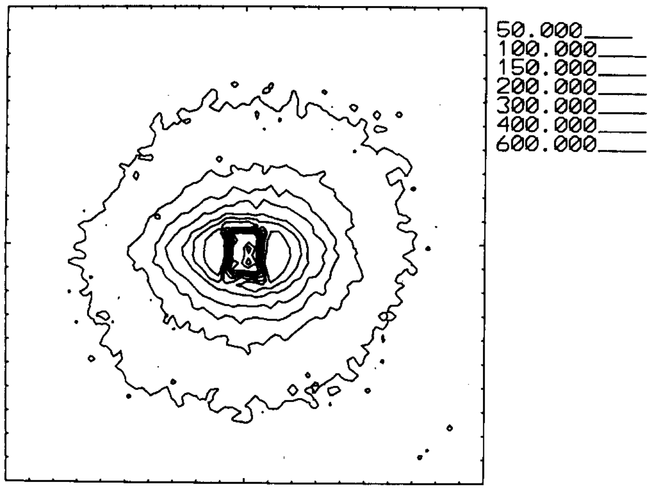

Figure 1 Contour plot of difference intensities for the 'blocked plug' fibres (axis vertical). The scale marks on the perimeter correspond to 2 cm intervals on the detector which was 10.5 m from the sample. The wavelength was 10 Å. Hence the inverse of the Bragg spacing varies from 3.4×10^{-3} Å^{-1} near the corners to 4×10^{-4} Å^{-1} at the extreme edge of the beam stop. This means a q range of 2.1×10^{-2} to 2.5×10^{-3} Å^{-1}, where $q = 4\pi \sin \theta/\lambda$, 2θ being the angle of scatter. The count rate levels for the contours are indicated (in arbitrary units)

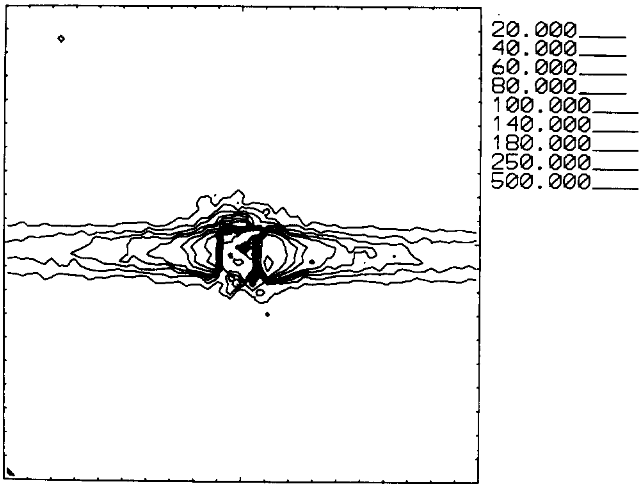

Figure 2 Contour plot as in *Figure 1* but for solid-state extruded fibres

of the azimuthal angle (the chain-axis corresponds to the vertical). However, for solid state extrusion (*Figure 2*) we have a very prominent 'streak' of intensity at right angles to the chain axis. This shows that the molecules are scattering as very long cylinders. The average diameter of these cylinders is not that of the hydrocarbon zig-zags of the chain itself, since the intensity along the streak decreases with increasing angle. Different parts of the molecule must be displaced with respect to each other in the equatorial plane, and the projected dimensions in this plane are found to be comparable with those of the chain in the blocked plug experiment and in quiescent crystallization. A more detailed analysis of these dimensions, including variations with molecular weight will be published elsewhere.

This experiment confirms directly what was deduced previously[6], that for blocked plug samples, high modulus can be obtained without the chains being stretched out into parallel 'bundles'. Rather, the mere shape and mutual arrangement of the crystallites is sufficient to prevent the disordered lamellae deforming preferentially and leading to a low overall modulus. Solid state extrusion, however, is efficient in extending the molecules. It is not known whether the molecules are completely extended with no folding whatever. The degree of folding can, in principle, be assessed by the width of the meridional streak. This will be the subject of further work. With the present data, the largest contribution to the width of the streak is the collimation of the incident beam (about 4 cm on the detector for the full width at half maximum intensity). The observed width provides a lower limit for the length of the molecule, which is of the same order as the length of the deuterated chain in the fully extended conformation (3.4×10^4 Å).

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