Structure of drawn fibres: 2. Neutron scattering and necking in single-crystal mats of polyethylene

The late D. M. Sadler and P. J. Barham
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK
(Received 30 January 1989; revised 20 April 1989; accepted 24 April 1989)

Results of neutron scattering experiments on polyethylene fibres prepared by drawing oriented mats of isolated single crystals through a neck are reported. It is shown (from the appearance of an isotopic segregation signal) that, as the temperature of drawing is raised above ~90°C, there is an increasing degree of local melting within the neck. It is further shown that, in contrast to the situation pertaining to the drawing of melt-crystallized material, the molecules do not deform affinely through the neck.

(Keywords: necking; drawing; fibre formation; neutron scattering; polyethylene)

INTRODUCTION

In the first paper of this series[1] we showed, using evidence of isotopic segregation, how local melting occurred during necking of melt-crystallized polyethylene when drawn at high temperatures. We also showed that, when drawing was performed at low enough temperatures, no segregation occurred and the molecules deformed affinely with the sample through the neck. The purpose of the present paper is to undertake a similar survey of the behaviour of solution-crystallized polyethylene. In the third part of the series[2], we shall address the issue of further drawing beyond the neck where strong, stiff, fibres may be formed.

Polyethylene single crystals (and single-crystal mats) have been used as model materials for studies of polymer deformation[3–8], their advantages lying both in the well defined crystal orientations and in the more or less regular chain folding within them. Individual single crystals have been stretched at room temperature[7,8] and examined by electron microscopy. Such studies have revealed 'micro-necks' with microfibrils being drawn from the individual single crystals. Annealing studies have revealed a striated morphology within the microfibrils. This has been associated with the presence of crystalline blocks, which are said to be remnants of the original crystal[8,9]. Oriented mats of single crystals have been drawn at elevated temperatures and the variations in crystal orientations studied during the drawing process[4,5]. Most recent studies have concentrated on the achievement of very high draw ratios and moduli[10,11]. However, owing to the brittleness of single crystals, most studies have only been carried out at a high drawing temperature and consequently, unlike the situation of melt-crystallized material, little is known of the variation in properties with the drawing temperature.

In the present paper, we are concerned only with the first stage of drawing: the neck. We have used neutron scattering techniques to follow the changes in molecular configuration on necking. The situation for single-crystal mats is more complex than that for melt-crystallized material. In melt-crystallized material, each molecule in the undrawn material has an approximately Gaussian distribution of segments and, apparently, deforms affinely with the sample. In single-crystal mats in the undrawn material, the crystals are oriented with their c axes normal to the draw direction, and within the crystals the molecules are arranged in superfolded sheets[12]. Thus, before drawing, we can picture the molecules in the way illustrated schematically in *Figure 1* (taken from ref. 12). During drawing, the crystals rotate so that the c axes are parallel to the draw direction. Neutron scattering from isotopic blends permits us to estimate R_x and R_z values (i.e. the average radii of gyration of the molecules projected normal to, and parallel to, the crystal c axis), both before and after necking. However, owing to the complex, anisotropic, trajectories of the molecules, we cannot use these data to determine molecular draw ratios. In the case of melt-crystallized material, we found a very well defined change from unsegregated to segregated material on drawing, as the drawing temperature was raised. This change could easily be seen by a very large increase in the scattering at low angles, and led to very large increases in the extrapolated values of R_x. As we shall show, the case is quite different in the drawing of single-crystal mats, where only low anisotropy is observed, and where, while segregation does occur, its effect is much smaller.

EXPERIMENTAL TECHNIQUES

Single-crystal mats: preparation and drawing

Blends of hydrogenated polyethylene (HPE) ($\bar{M}_w \sim 67\,500$, $\bar{M}_n = 15\,000$) with 2% of deuterated polyethylene (DPE) ($\bar{M}_w \sim 64\,500$, $\bar{M}_n \sim 30\,500$) were prepared in xylene solution at 0.2% (w/v). The solutions were cooled to 70°C and left to crystallize. The resulting suspensions were filtered slowly to form oriented single-crystal mats.

The dry mats were quite brittle; in order to reduce their brittleness before attempting to draw them, we passed them through a pair of hot rolls. The roll surface

0032-3861/90/010043-03$03.00

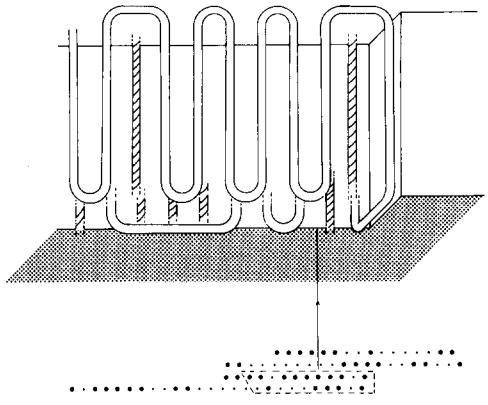

Figure 1 A diagram illustrating the arrangement of polyethylene molecules in a single crystal—the superfolding model from Spells and Sadler[12]

temperature was 85°C and the gap was adjusted so that on passing through the rolls the mats had an extension ratio of 1:1.1 or less. After this process, the orientation of the mats (assessed by wide-angle X-ray diffraction) was essentially unchanged, but the previously opaque, brittle material became transparent and tough. The mats were then cut into strips approximately 5 mm wide and stretched, by hand, across a heated bar at the desired temperature. Only the undrawn material was kept in contact with the bar so that drawing was confined to the neck.

Neutron scattering results

The low-angle facilities (D11 and D17), at ILL, Grenoble, were used with camera distance of 1 to 20 m. The usual subtractions and corrections were made. The undrawn mats were analysed according to previously described methods[12]. The drawn samples gave slightly anisotropic signals and were analysed by the methods we have described previously[13]. Zimm plots were fitted to the equations:

$$I(0,0)/I(q_x,0) = 1 + q_x^2 R_x^2$$
$$I(0,0)/I(0,q_z) = 1 + q_z^2 R_z^2 \qquad (1)$$

where the z direction is along the fibre normal and parallel to the draw direction. Thus for both undrawn and drawn material, the z direction is parallel to the crystal c axis.

RESULTS AND DISCUSSION

We show in *Figure 2* a typical contour plot of the scattering from a drawn single-crystal mat, and in *Figure 3* the resulting Zimm plots along the meridian and equator. The results for the whole range of drawn mats are given in *Table 1*, where we show the drawing temperature and draw ratio, the R_x and R_z values derived from the Zimm plots, and the 'effective molecular weight' of the DPE derived from the $I(0,0)$ values of equation (1), as well as the crystal thickness derived from Raman LAM measurements[14]. The data from the undrawn mat are $R_x \simeq 70$, $R_z \simeq 48$, the fold length is ~ 110 and the effective molecular weight 60 000. These results are in marked contrast to the data we have reported for melt-crystallized material[1]. First, at low temperatures of drawing, while there is a small increase in R_z on drawing, there is virtually no decrease in R_x, i.e. the molecules do not appear to deform affinely. Secondly, there is no sudden onset of a segregation signal as the drawing temperature is raised; rather it appears from the $I(0,0)$ values that segregation begins at drawing temperatures above ~ 95°C and becomes progressively more pronounced as the temperature is raised. We also note

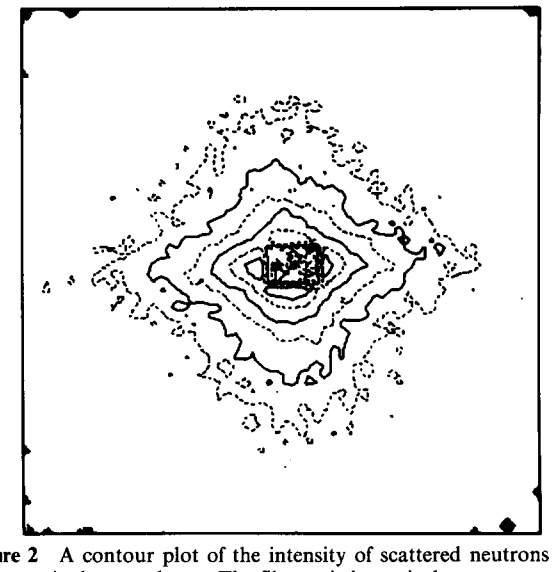

Figure 2 A contour plot of the intensity of scattered neutrons from a drawn single-crystal mat. The fibre axis is vertical

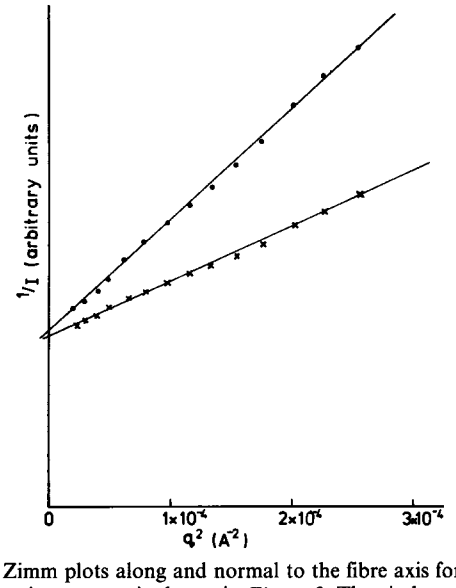

Figure 3 Zimm plots along and normal to the fibre axis for the fibre whose scattering pattern is shown in *Figure 2*. The circles refer to the fibre axis and give an R_z value of 80 Å and the crosses refer to the equatorial direction and give $R_x \simeq 56$ Å

Table 1 Data on drawn single-crystal mats[a]

Temperature of drawing (°C)	Draw ratio across neck	R_x (Å)	R_z (Å)	Molecular weight (from $I(0,0)$) ($\times 10^{-3}$)	Raman fold length (Å)
78	4.8	64	76	56	150
88	5.2	56	80	52	180
93	5.1	57	94	68	185
98	5.3	68	124	83	180
106	5.7	74	130	126	190
115	5.4	85	146	175	185
120	5.3	98	180	210	200

[a] Prior to drawing the mats had $R_x \simeq 70$ Å, $R_z \simeq 48$ Å and Raman fold length 110 Å

that the crystal thickness (as derived from Raman spectroscopy) has increased on drawing in all the samples.

We suggest that the increase in R_x, R_z and apparent molecular weight values at drawing temperatures above $\sim 95°C$ indicate that isotopic segregation can then occur, i.e. that there is some local melting within the neck. The gradual increase in the amount of local melting may be due to the different crystalline orientations in the undrawn material. It is well established from electron microscopic studies of individual crystals that yielding and necking occur along well defined directions (i.e. along the fold planes), while in other directions (normal to the fold planes) the crystals fracture cleanly. Thus, those crystals which are aligned so that the fold planes are parallel to the draw direction will yield, while those whose fold planes are normal to the draw direction will fracture. Such differences will lead to very different local energy dissipations, and hence temperature rises. Accordingly, as the draw temperature is raised progressively, more of the crystals will be in a suitable orientation so that they will dissipate sufficient elastic energy to melt, and hence permit isotopic segregation to occur.

We argue that the lack of any significant change in R_x values on drawing at temperatures below $\sim 95°C$ indicates that the lateral extent of molecules in the crystals is substantially unchanged on drawing, while the increase in R_z is due to the observed increase in crystal thickness. This increase in crystal thickness is, we suggest, an annealing phenomenon; if at drawing temperatures of $\sim 100°C$ crystal melting can take place, then the local temperature in the neck will be $\sim 30°C$ higher than ambient, i.e. the crystals in the neck are hot enough to thicken by an annealing process.

The model that we propose for the necking of single-crystal mats is therefore as follows. On drawing, the crystals are broken up into blocks (whose lateral extent is greater than the extent of the molecules—at least for the molecular weight we have used). These blocks are rotated so that the crystal c axes lie in the draw direction. During the plastic deformation in the neck zone, the temperature rises—this causes annealing and crystal thickening at lower drawing temperatures and melting and recrystallization at higher drawing temperatures.

REFERENCES

1 Sadler, D. M. and Barham, P. J. *Polymer* 1990, **31**, 36
2 Sadler, D. M. and Barham, P. J. *Polymer* 1990, **31**, 46
3 Statton, W. O. *J. Appl. Phys.* 1967, **38**, 4149
4 Ishikawa, K., Miyasaka, K. and Maeda, M. *J. Polym. Sci. (A-2)* 1969, **7**, 2029
5 Maeda, M., Miyasaka, K. and Ishikawa, K. *J. Polym. Sci. (A-2)* 1970, **8**, 355
6 Barham, P. J. and Keller, A. *J. Mater. Sci.* 1976, **11**, 27
7 Holdsworth, P. J. and Keller, A. *J. Polym. Sci. (A-2)* 1968, **6**, 707
8 Geil, P. H. *J. Polym. Sci. (A-2)* 1964, **2**, 3814, 3835, 3857
9 Geil, P. H. 'Polymer Single Crystals', Polymer Review, Vol. 5, Wiley, New York, 1963
10 Kanomoto, T., Tsurata, A., Tanaka, K., Takeda, M. and Porter, R. S. *Polym. J.* 1983, **15**, 327
11 Furuhata, K., Yokokawa, T. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 133
12 Spells, S. J. and Sadler, D. M. *Polymer* 1984, **25**, 739
13 Sadler, D. M. and Barham, P. J. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 309
14 Fraser, G. V. *Ind. J. Pure Appl. Phys.* 1978, **16**, 344