

Structure of drawn fibres: 1. Neutron scattering studies of necking in melt-crystallized polyethylene

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Results of neutron scattering experiments performed on fibres of polyethylene drawn through a neck from melt-crystallized sheets are reported. It is shown, from the appearance of an isotopic segregation signal, that at drawing temperatures above ~ 70 – 90°C (depending on polymer molecular weight) there is some local melting during necking. At lower drawing temperatures there is no evidence for any local melting, and the molecules appear to deform affinely with the sample through the neck. The implications of these results for various models of necking are discussed.

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

David Sadler

The experiments reported in this and the two subsequent papers were carried out by David Sadler and myself at ILL, Grenoble, over a period of five years. Although the results often seemed confusing and contradictory, David continually encouraged me to prepare more different samples—he was confident that we would eventually be able to understand fibre structures from such neutron scattering experiments. It was during our last visit to Grenoble over Easter 1988 that David at last recognized the pattern underlying the many experiments we had already carried out. We quickly prepared some fresh samples to test his hypotheses while we still could use the instruments at ILL; these experiments seemed to confirm his ideas.

David's tragic and untimely death came before we had a chance to complete the reanalysis of old and new data, or to write up the work. I have tried as best I can in these three papers to complete the work along the lines David intended, and to express, as clearly as I can, the ideas and conclusions that we arrived at in Grenoble and discussed several times later. I wish to make it quite clear that all credit for this work should go to David Sadler and, at the same time, that all responsibility for any errors or omissions is entirely mine.

Peter Barham

INTRODUCTION

In this series of papers we wish to re-examine the structure of drawn fibres in molecular terms. The basis for this reappraisal is the use of neutron scattering techniques to determine changes in the shapes and relative positions of individual molecules during drawing. In the first two papers of the series we shall be concerned with the transformation from isotropic, undrawn material to a fibrous morphology, through a neck. In this paper we shall deal with the case where the initial material is crystallized from the melt and has a spherulitic texture, while in the following paper¹ we shall address the drawing of solution-crystallized material, specifically oriented single-crystal mats. The third paper of the series² will be concerned with further ultra-drawing beyond the neck.

There is already a wealth of literature concerning the transformation of initially isotropic melt-crystallized polymers into fibrous structures, by a variety of routes including drawing, rolling and extrusion, and various combinations of these methods. For the purposes of the present study we shall restrict ourselves to a brief review of the most relevant literature concerning the deformation of spherulitic polyethylene. Probably the most striking, and important, result on the drawing of polyethylene through a neck is the frequently made observation that the X-ray long period in the drawn material depends on

the temperature of drawing, and is not in general related to the long period in the undrawn material^{3–10}. This observation is usually interpreted as being due to local melting and recrystallization in the neck¹⁰; such a view is supported by the observed dependence of the long period l on temperature, which follows the same relation as that for crystallization from the melt (i.e. $l \propto 1/\Delta T$, where ΔT is the supercooling)³. Further, calculations of the energy dissipated in a neck show that in many cases sufficiently large temperature rises could be generated to cause melting¹¹. Indeed, it has even been suggested that local melting actually causes the neck^{12,13}. On the other hand, it has been shown that necking occurs even at extremely low rates where melting is very unlikely to occur^{11,14}. Studies that have followed wide-angle^{6,14} and low-angle^{5,6,10} X-ray diffraction throughout the change from isotropic to fibrous structure show apparently continuous, although complex, changes in crystal orientation and in the low-angle pattern, rather than the discrete jumps that might be expected from melting and recrystallization.

The simplest, and most commonly quoted, model for the drawing of a polymer through a neck is due to Peterlin^{15–17}. In this model the necking process is envisaged as the breaking away of small blocks of crystals from the lamellar stacks in the unoriented material, and

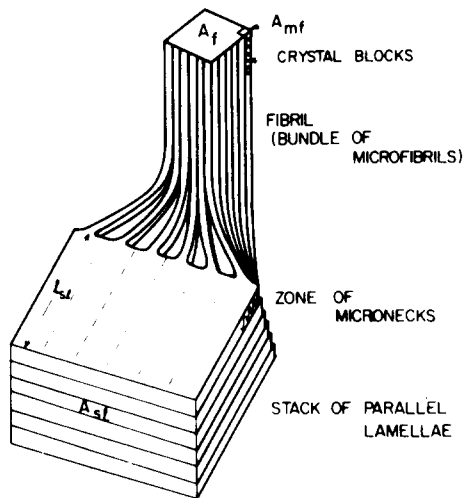


Figure 1 A sketch illustrating Peterlin's model of neck formation (from ref. 16)

their subsequent reorientation and restacking to form microfibrils of oriented material. This is illustrated in Figure 1, taken from Peterlin's own work¹⁶. While this model has many obvious attractions, most notable among which is its simplicity, it cannot be used to explain the observed dependence of long period on drawing temperature. Indeed, the model implies that the long period in the fibrous structure should be close to that in the undrawn material. Other models, most notably those from the Russian school^{18–20}, which do allow the long period to change during necking, are much less specific—usually they invoke some sort of local melting and recrystallization.

The purpose of the present paper is to determine whether or not local melting occurs during necking. In order to achieve this we have taken advantage of the usually deleterious effect of isotopic segregation in blends of hydrogenated (HPE) and deuterated (DPE) polyethylene. The segregation of an initially random blend of HPE and DPE into a non-random mixture is readily observed by neutron scattering techniques, as we discuss in detail below. In order for a system to change from random to non-random, there must be large-scale motion of molecules, i.e. there must be regions within the sample where the molecules are highly mobile. Further, to achieve any significant degree of segregation, these regions must be larger than the size of an individual molecule. We argue that such regions, where molecular mobility is high, may properly be described as molten. Hence, whenever we observe that segregation occurs during necking, we assert that some local melting must have also occurred. Such an approach to the study of a solid-state deformation (by compression rather than by drawing) has been adopted by Wignall and Wu²¹. In that case, blends of HPE and DPE were prepared in which segregation was deliberately introduced. These segregated blends were then deformed by a compressive technique. The authors found that the degree of segregation, as inferred from the apparent molecular weights and radii of gyration, decreased during the deformation; from this they deduced that some local melting must have occurred to permit the required movement of molecules. We have chosen to use a similar technique to study the melting during necking in a range of polyethylenes over a range of drawing temperatures. In most cases, however,

we have carefully prepared well mixed, unsegregated blends and observed whether segregation occurs on necking; when it does, we suggest that it is indicative of local melting. Although, as we shall show, the effects that we observe are very large and, in most cases, easy to interpret, we nevertheless feel that we should present some background to the details of neutron scattering from segregated systems.

INTER- AND INTRAMOLECULAR CORRELATIONS

Partial coherence

A straightforward way of understanding the labelling technique is by analogy with coherent and incoherent scattering. That incoherence occurs is due to the fact that there are no spatial correlations in the nuclear spin and the scattering length depends on the spin orientation. The incoherent signal is obtained, which depends on the difference between the spin-dependent scattering lengths. The coherent signal comes from the average. In the absence of inelastic effects, the incoherent signal is independent of scattering angle 2θ , since it depends on the self-correlation of the nucleus (much smaller in size than the neutron wavelength). The isotopic blend can be considered in the same way, in this case the scattering lengths being dependent on isotope:

$$|A(q)|^2 = |A(q, \langle b_i \rangle)|^2 + (\langle b_i^2 \rangle - \langle b_i \rangle^2) I(q) \quad (1)$$

where A is the scattering amplitude, $q = 4\pi \sin \theta / \lambda$ and b_1 and b_2 are scattering lengths for polymer species with ^1H and ^2H respectively. The second term, analogous to the usual incoherent signal, depends on the Fourier transform $I(q)$ of a correlation function $g(r)$. The correlation function $g(r)$ is proportional to the probability, given a pair of nuclei separated by r , that they will be of like isotopes. (For the analogous case of spin incoherence, this is given just by the average concentrations, independently of r .) In equation (1), $I(q)$ is the net 'intensity', which is usually derived for the isotope labelling technique. The first term is a coherent background, which is usually small (e.g. for isotope mixtures with a few per cent of ^2H isotope).

For random mixing of two isotopic species of a polymer (identical, apart from the isotope), the spatial variations of $g(r)$ are given by the intramolecular correlation function $g_0(r)$, and for different molecules the probabilities are again independent of r (as in the case of incoherent scattering). For random mixing, the correlation functions $G_{ij}(R)$ for the separation R of molecular centres of gravity of species i and j are given by:

$$\begin{aligned} G_{11}(R) &= (1-C)^2 G_0(R) \\ G_{12}(R) &= C(1-C) G_0(R) \\ G_{22}(R) &= C^2 G_0(R) \end{aligned} \quad (2)$$

where $G_0(R)$ is the total intermolecular correlation function irrespective of isotope, and C is the volume concentration of the ^2H species.

(Note that $G_{22}(R)$ is not required to be even approximately independent of R , as is implied by the solution scattering analogy for neutron scattering (^2H species = 'solute', ^1H species = 'solvent'). This explains why for the method to work there is no limit to C , as long as the two isotopic species are identical apart from the isotope.

On the other hand, this explanation is only precise for a precise matching of the two components. It has been found that for different molecular weights (for example), the intramolecular scattering is obtained only if C is sufficiently small. The solution scattering analogy for the analysis is then more appropriate.)

Segregation and deformation

Equations (2) do not hold for non-random mixing (e.g. like molecules tending to be nearer than unlike ones, i.e. partial or complete segregation). In the limit of $q \rightarrow 0$ and $g_0(q) = n$ (n being the number of hydrogens in a molecule), each molecule can be considered as a point scatterer and $G_0(R)$ is constant for $R > 1/q$. The contribution to $g(r)$ from intermolecular correlations is then given by $G_{22}(R)$. The net entropy (from the second term in equation (1)) is then:

$$I(q) = nG_{22}(q) \quad (q \rightarrow 0) \quad (3)$$

where $G_{22}(q)$ is the Fourier transform of $G_{22}(r)$, and has been obtained from both the Porod²² and Debye²³ formulae. This presumes that the segregation can be described in terms of zones of two different (uniform) isotope concentrations. It has been found that a very similar result is obtained even when q is not small enough to give $g_0(q) = n$, as long as q is in the Guinier regime (i.e. $qR_g \leq 1$, where R_g is the radius of gyration). The result for the intensity is the product of $g_0(q)$ and a segregation term $G'(q)$:

$$I(q) \approx g_0(q)G'(q) \quad (q < R_g^{-1}) \quad (4)$$

This analysis was mainly concerned with the isotropic case.

Deformation will of course change the molecular conformations and $g_0(r)$. For example, our previous paper on neutron scattering and deformation of PE²⁴ measured molecular deformations, and mixing appeared to be effectively random both before and after deformation. In the general case of non-random mixing, both before and after deformation, there is no reason to suppose that there will be a simple relationship between $G'(q)$ before and after deformation; zones of different isotope concentration would presumably deform (e.g. amalgamate or split up and/or change shape).

In this paper we are not concerned with such relatively small effects: mixing was effectively random before deformation; after, it was either still random or very dramatically non-random. In order to change from random to non-random there must be effectively some interchange of molecules so as to increase the probability of like molecules being nearer. This demonstrates that there must have been, during deformation, mobile regions larger than the size of an individual molecule. The issue is not directly whether molecular centres move: they must do on deformation, regardless of segregation.

Calibration of intensities

Most experiments involving absolute measurements of intensity have been concerned with isotropic samples. We mentioned previously²⁴ that, for highly anisotropic samples, instrumental resolution effects can affect not only measurements of molecular dimensions, but also the absolute intensity. Once the actual intensity I is convoluted with the instrumental function, the maximum in the observed intensity peak is reduced. By performing

this convolution numerically for the case of polyethylene fibres using the D11 spectrometer at the Institut Laue-Langevin (ILL), Grenoble, it was found that this decrease in intensity is typically by a factor of 2. For other situations (e.g. a one-dimensional detector where the resolution in q is much coarser), the decrease could be much larger. No such decrease in intensity applies for isotropic samples (I independent of σ).

EXPERIMENTAL PROCEDURES

Preparation of unsegregated isotropic samples

HPE samples of various molecular weights were blended in 0.2% (w/v) xylene solution with DPE of various molecular weights. In all cases, the DPE concentration was 2% by weight. The actual molecular weights determined by g.p.c. analysis of all HPE and DPE samples are included in Table 1 in the 'Results' section. The polymer was precipitated from the solutions by cooling to room temperature; after filtering and drying the blends were melted into sheets (approximately 0.1 mm thick) at 160°C for 2 min and crystallized by quenching into water at 0°C.

Preparation of segregated isotropic samples

The blending and melting procedures described above were used, the only difference occurring in the final crystallization: the molten samples were placed in a vacuum oven at 125°C and allowed to crystallize slowly overnight. This procedure produced sheets of well segregated material.

Drawing procedures

A few samples were drawn in an oven using an Instron tensile testing machine. These samples were initially 5 mm wide by at least 20 mm long. They were drawn at 5 cm min⁻¹. The remaining samples were drawn while in contact with a bar at the required drawing temperature at a rate of between 1 and 5 cm min⁻¹. In all cases the drawing was stopped once the neck had run through the whole sample. Draw ratios were measured by comparing the mass per unit length of drawn and undrawn portions of the same sample.

Modulus measurements

The tensile moduli of all the fibres were measured using an Instron tensile testing machine. The fibres typically had widths of 2–3 mm and lengths of ~300 mm; thus they should have aspect ratios high enough to avoid complications due to end effects²⁵. The moduli were taken as the secant modulus at a strain of 10⁻³ and measured at an initial strain rate of 10⁻⁴ s⁻¹.

Neutron scattering measurements

All the measurements reported here were taken using the D11 diffractometer at ILL, Grenoble. The fibres (in the form of tapes ~3 mm wide) were wound onto bobbins so that they occupied an area of ~1 cm² and filled the beam (approximately 80 mg of material was used in each sample), the draw direction being kept horizontal. Data reduction comprised subtraction procedures to remove from the sample signal the incoherent scattering and the (generally small) coherent background. For these purposes a purely hydrogenous sample was used. A correction involving the signal from an empty sample

holder was made to allow for the slightly different transmission of sample (blend) and background (HPE sample). The counter response was normalized by the scattering from water.

RESULTS

The neutron scattering data enable us to distinguish cases where segregation occurs during necking from those where it does not. In general, we find that, on drawing at temperatures well below the α -relaxation (i.e. $< 60^\circ\text{C}$), no segregation occurs during necking, while drawing at temperatures well above the α -relaxation (i.e. $> 90^\circ\text{C}$) induces segregation during necking. In the intermediate temperature range, segregation depends on the polymer molecular weight.

The details of the segregation may be presented in several different ways. For the higher draw temperatures, a very large segregation signal appears (i.e. $G'(q)$ increases by a factor of at least 10 and typically 150 at low q). This produces a remarkable and unmistakable change in the scattering pattern, which is illustrated in *Figure 2*. *Figure 2a* shows a contour plot of the scattering from a fibre drawn at 81°C to a draw ratio of 7.2 ± 0.5 , while *Figure 2b* shows the scattering from a fibre drawn from the same starting material to a similar draw ratio, 7.1 ± 0.4 , but at 89°C . The large, most or less isotropic, segregation signal in the latter sample is immediately evident. We should note that the wide-angle X-ray diffraction shows a more or less identical degree of crystalline orientation

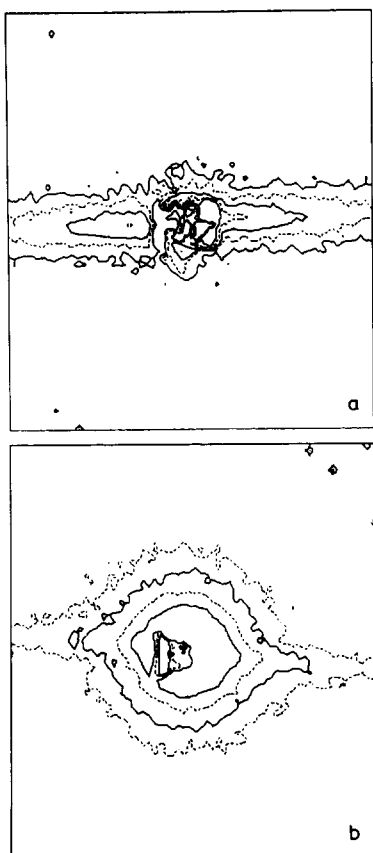


Figure 2 Contour plots of intensity of neutron scattering for two drawn polyethylene fibres. The fibre direction is vertical in both cases. (a) A fibre drawn at 81°C to a draw ratio of ~ 7.2 . (b) A fibre drawn at 89°C to a draw ratio of ~ 7.1 . Note the large, isotropic, segregation signal in the fibre drawn at the higher temperature

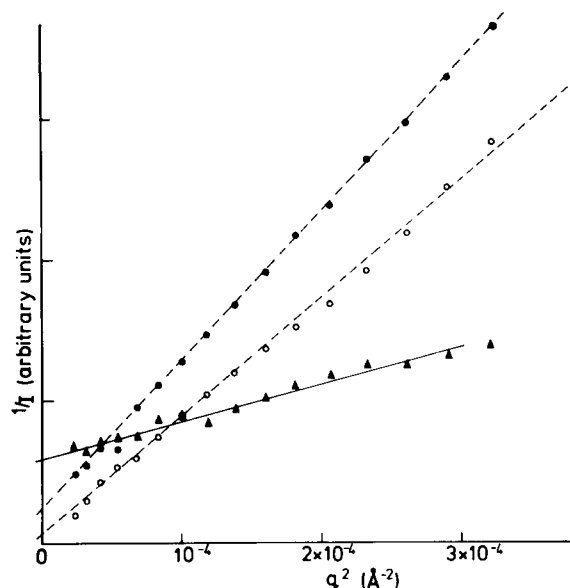


Figure 3 Zimm plots (along the horizontal direction) for both the fibres whose contour plots are shown in *Figure 2* and of the initial isotropic sheet from which they were drawn: (●) from the undrawn sheet; (▲) from the fibre drawn at 81°C , $R_x \sim 68 \text{ \AA}$; (○) from the fibre drawn at 89°C , $R_x \sim 400 \text{ \AA}$

in both these fibres; indeed, the only way we can distinguish between them is by their neutron scattering patterns. Another way to look at such data is to make Zimm plots along the x direction (i.e. perpendicular to the draw direction) to obtain values of R_x , as described in our previous paper²⁴. This we have done in *Figure 3*, where we show Zimm plots for the undrawn sheet and for the two drawn fibres shown in *Figure 2*. These give R_x values (note that $R_x^2 = \frac{1}{3}R_g^2$) of 170 \AA for the isotropic sheet, 68 \AA for the fibre drawn at 81°C and $\sim 400 \text{ \AA}$ for the fibre drawn at 89°C . An affine deformation by a factor of 7.2 would lead to the reduction of R_x from 170 \AA in the isotropic sheet to 64 \AA in the drawn fibre. Thus we may deduce that at 81°C no segregation occurs in the neck, while at 89°C the molecules are sufficiently mobile to cause segregation.

We have studied fibres drawn at a range of temperatures and from polyethylenes with a range of different molecular weights. The results are summarized in *Tables 1* and *2*. *Table 1* is for a series of samples all using the same HPE ($\bar{M}_w \sim 67\,500$; $\bar{M}_n \sim 15\,200$) and doped with 2% DPE of molecular weight ranging from 35 000 to 220 000. *Table 2* is for a series of different HPEs with \bar{M}_w ranging from 55 000 to 399 000, all doped with 2% DPE of $\bar{M}_w \sim 189\,000$. In addition to quoting the draw ratios of the fibres and the R_x values measured by neutron scattering, we also quote the molecular draw ratio $(R_{x,\text{undrawn}}/R_{x,\text{drawn}})^2$, the X-ray long period, where measured, and the tensile modulus.

It is immediately noticeable that the draw ratios and tensile moduli are more or less independent of the drawing temperature, and, as illustrated in *Figure 4*, that the X-ray long period varies continuously with drawing temperature. The only discontinuous changes occur in the neutron scattering patterns.

While we can argue that the observation of segregation implies a large degree of molecular mobility in the neck (which is equivalent to local melting), the inverse, i.e. that observation of no segregation implies no mobility

Table 1 Neutron scattering data, X-ray long periods and moduli of drawn fibres (host: hydrogenated polyethylene, $\bar{M}_w \sim 67\,500$, $\bar{M}_n \sim 15\,200$)

Molecular weight of DPE ^a	Drawing temperature (°C)	Draw ratio ^b	R_x values		Molecular draw ratio ^c	Segregation ^f	Long period ^g (Å)	Modulus ^h (GPa)
			Isotropic ^c (Å)	Drawn ^d (Å)				
\bar{M}_w 64 000	21	8.6 ± 0.2	98	33	8.8	N	160	4.0
\bar{M}_n 30 500	42	7.2 ± 0.2	98	36	7.4	N	165	3.9
	61	7.0 ± 0.5	98	40	6.0	N	180	3.9
	69	6.8 ± 0.2	98	43	5.2	N	—	3.8
	78	6.0 ± 0.4	98	(130)	(0.6)	S	190	3.8
	86	6.2 ± 0.4	98	(175)	(0.3)	S	205	3.6
	96	5.8 ± 0.6	98	(160)	(0.9)	S	210	3.7
\bar{M}_w 95 000	22	5.6 ± 0.5	130	56	5.4	N	155	3.9
\bar{M}_n 48 000	68	6.8 ± 0.4	130	61	4.5	N	—	4.0
	77	7.0 ± 0.2	130	85	2.3	N	185	4.1
	86	6.5 ± 0.4	130	(190)	(0.5)	S	—	3.6
	95	6.8 ± 0.6	130	(230)	(0.3)	S	205	3.8
\bar{M}_w 218 000	20	6.2 ± 0.4	170	76	5.0	N	165	4.1
\bar{M}_n 69 000	54	5.8 ± 0.4	170	72	5.6	N	—	4.0
	72	6.9 ± 0.3	170	65	6.8	N	175	3.6
	81	7.2 ± 0.5	170	68	6.3	N	—	3.7
	89	7.1 ± 0.4	170	(400)	(0.2)	S	—	3.8
	98	7.0 ± 0.2	170	(380)	(0.2)	S	215	3.5
	\bar{M}_w 34 800	60	8.0 ± 0.5	77	29	7.0	N	—
\bar{M}_n 17 600	65	7.2 ± 0.2	77	31	6.2	N	—	3.7
	70	7.5 ± 0.6	77	(130)	(0.4)	S	—	3.8
\bar{M}_w 189 000	80	6.1 ± 0.5	165	69	5.7	N	—	3.7
\bar{M}_n 78 700	84	6.6 ± 0.4	165	74	5.0	N	—	3.6
	90	6.8 ± 0.6	165	(280)	(0.3)	S	—	3.2

^a Molecular weights of DPE dopant as measured by g.p.c.

^b Draw ratios across the neck—the errors refer to the range of measured draw ratios (several fibres were used in each sample)

^c From Zimm plot ($R_x^2 = \frac{1}{3}R_g^2$)

^d Values in brackets correspond to cases where segregation has occurred, and should not be taken to be representative of the molecules

^e Molecular draw ratio calculated from R_x values and assuming an affine deformation

^f N indicates no evidence for segregation in drawn fibre. S indicates the presence of a large (isotropic) segregation signal as shown in *Figure 2b*

^g Long period as measured by low-angle X-ray diffraction; error is typically 15 Å

^h Fibre tensile modulus; error is typically 0.1 GPa

Table 2 Neutron scattering data, X-ray long periods and moduli of drawn fibres (host: hydrogenated polyethylene, \bar{M}_w 55 000 to 399 000)

Host polymer molecular weights	Drawing temperature (°C)	Draw ratio	R_x values		Molecular draw ratio	Segregation signal ^a	Tensile modulus (GPa)
			Undrawn	Drawn			
\bar{M}_w 67 500	80	6.1 ± 0.5	165	69	5.7	N	3.2
\bar{M}_n 15 200	84	6.6 ± 0.4	165	74	5.0	N	3.2
	90	6.8 ± 0.6	165	(280)	(0.3)	S	3.2
	\bar{M}_w 55 600	80	5.8 ± 0.6	162	71	5.2	N
\bar{M}_n 10 300	85	6.1 ± 0.2	162	(270)	(0.4)	S	4.1
	90	5.9 ± 0.4	162	(340)	(0.2)	S	3.6
\bar{M}_w 116 000	85	5.6 ± 0.5	168	73	5.3	N	4.2
\bar{M}_n 15 500	90	5.9 ± 0.3	168	88	3.6	N	4.4
	95	5.5 ± 0.6	168	(180)	(0.9)	S	4.0
\bar{M}_w 349 000	90	5.2 ± 0.4	170	78	4.8	N	4.8
\bar{M}_n 24 400	95	4.6 ± 0.2	170	84	4.1	N	4.6
	100	5.1 ± 0.3	170	(210)	(0.7)	S	4.0

^a N, not present; S, present

in the neck, it is not necessarily true, since it may be the 'recrystallization temperature' that determines whether or not segregation occurs. Accordingly, we prepared segregated, isotropic sheets and drew these. If mobility occurs during necking at low temperatures, then we should expect to see some remixing in such samples. In these experiments we used just one blend, the HPE with $\bar{M}_w \sim 67\,500$ and DPE with $\bar{M}_w \sim 34\,000$. The results, in terms of R_x values derived from Zimm plots, are shown

in *Table 3*. These results show no evidence for remixing on drawing at any temperature, nor is there any evidence based on the $I(0, 0)$ values, which may be used to give very approximate 'molecular weights'. In the undrawn samples we estimate a 'molecular weight' of the segregated DPE clusters to be $\sim 10^6$, while in the drawn samples it is $\sim 4 \times 10^5$. The apparent reduction in molecular weight can easily be explained in terms of the finite instrumental resolution²⁴. The data in *Table 3* suggest a change in

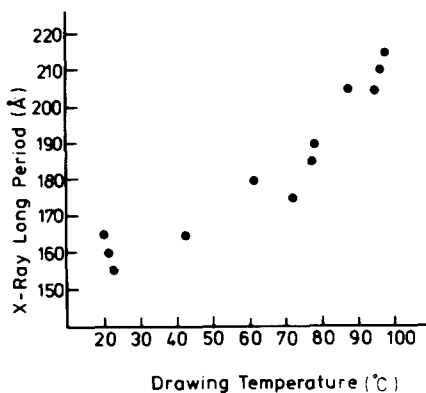


Figure 4 A graph showing the variation in the measured X-ray long periods of the drawn fibres with the drawing temperature

Table 3 Data on drawing of initially segregated samples

Initial R_x (Å)	Drawing temperature (°C)	Draw ratio	R_x in drawn material (Å)	'Molecular draw ratio'
290	20	6.8	170	2.9
360	50	7.1	210	2.9
400	60	7.2	190	4.4
340	64	6.3	180	3.6
380	70	6.7	400	0.9

behaviour, with the possibility of additional segregation occurring at a drawing temperature between 64°C and 70°C, which is in good agreement with the data in *Table 1* for the polymers of the same molecular weight. Accordingly, we may deduce that, on drawing at low temperatures, necking does not lead to any high mobility of the molecules, i.e. there is no local melting.

DISCUSSION AND CONCLUSIONS

The data in *Tables 1* and *2* show clearly that, for all molecular weights studied, there is high molecular mobility within the neck on drawing at high temperatures (>90°C); they also show that if there is high mobility on drawing at lower temperatures, then it does not lead to any isotropic segregation. The data in *Table 3* again show that there is molecular mobility on drawing at high temperature (R_x actually increases on drawing at 70°C), but show no evidence for a decrease in isotropic segregation at lower drawing temperatures. These two sets of data, in combination, permit us to deduce that high molecular mobility, on the scale of the whole molecules, occurs during necking at high draw temperatures; this we argue is equivalent to local melting during necking.

It is also noticeable, from *Tables 1* and *2*, that the temperature of drawing above which this local melting occurs increases with increasing molecular weight, both of the DPE dopant and of the HPE host material. The results are shown graphically in *Figure 5*, where we show regions of molecular weight and drawing temperature in which necking does, and does not, cause local melting. In both cases (host molecular weight varying and dopant molecular weight varying) there appears to be a plateau value for the 'transition temperature' at high molecular weights. It is, however, probably more meaningful to look at the value of the 'transition temperature' where

the molecular weights are matched. Thus we can deduce that, for a molecular weight of ~70 000, drawing above 75°C will cause local melting in the neck, while for a molecular weight of ~90 000, a drawing temperature of 95°C is needed before local melting will occur. A possible explanation of these molecular-weight effects would be to argue that the volume over which local melting occurs increases with increasing drawing temperature and that our neutron scattering technique will only observe melting once the volume of local melting is of the order of the size of a molecule. Thus, if the DPE is of similar or greater molecular weight than the host HPE, we should observe an increase in the transition temperature with increasing molecular weight. Accordingly, we have plotted in *Figure 6* the radius of gyration of the deuterated molecules as a function of the 'transition temperature'. If we extrapolate such a plot, we can see that there is a drawing temperature at which the volume of local melting tends to zero; depending on the extrapolation used, this will occur at ~40–60°C.

The work on the changes in X-ray long period (and Raman LAM mode) reported previously by other workers^{3–10} and confirmed by results in this paper show that the long period is determined, in the first instance, by the drawing temperature rather than by the initial morphology. The usual explanation of this phenomenon is that local melting (and recrystallization) has taken place during necking. However, these changes in long period have been reported on drawing at temperatures where, by our present neutron scattering criteria, no

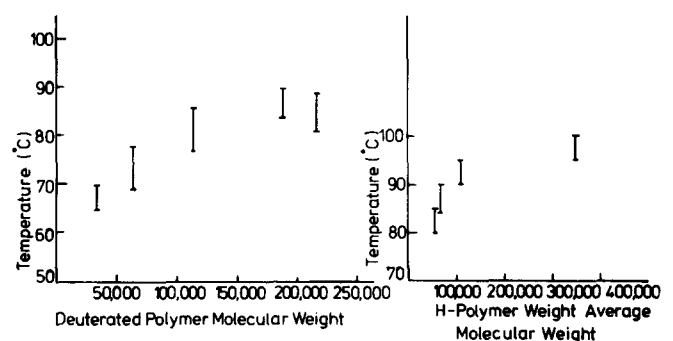


Figure 5 Two diagrams showing the transition temperatures below which melting does not occur on necking and above which melting does occur as a function of both dopant polymer molecular weight and host polymer molecular weight

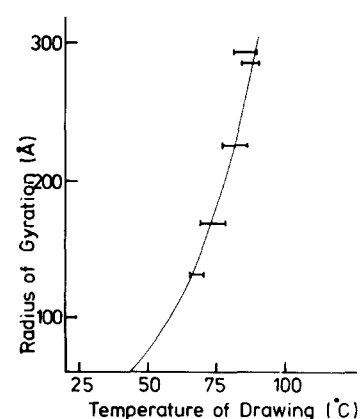


Figure 6 A diagram illustrating the same data as in *Figure 5*, where we have used the radius of gyration, rather than the molecular weight, to define the size of the molecules

melting can take place. Thus, we must face up to the situation where data from neutron scattering, and X-ray long periods, offer contradictory conclusions as to molecular mobility in the neck during drawing at low (i.e. $<60^{\circ}\text{C}$) temperatures. One possible way to resolve this conflict would be to suggest that the two techniques are sensitive to melting on different distance (and possibly time) scales. However, in order to cause changes in long period the melting would have to occur on a size scale at least as great as the initial lamellar thickness; and since (at least for low-molecular-weight material) this is a similar scale to the size of the molecules, we should anticipate that isotopic segregation would occur.

We wish to propose an alternative resolution of the problem. One fact that is not always made clear in studies of the long period is that the intensity of the peaks is very much lower in samples drawn at low, rather than high, temperatures. For example, in order to obtain any discernible diffraction from the samples drawn at 20°C requires (on our apparatus) exposure times of up to 24 h, whilst using the same apparatus diffraction patterns from samples drawn at $\sim 80^{\circ}\text{C}$ can be obtained in 2 h. Similar observations have been made by other authors^{5,6,10}. We suggest that on drawing at low temperatures there is no melting in the neck and the Peterlin model is followed. However, we also suggest that as the crystalline blocks are broken away and rotated into microfibrils, so they lose their regular stacking, and the surfaces become less well defined so that the X-ray diffraction signals are smeared out. Also, we anticipate that the shearing applied to these crystals will cause a wide spread in stem lengths and hence smear out the Raman LAM signal. Further, we suggest that some of the thinner crystals (remember there will be a range of crystals of differing thicknesses) are not broken up within the neck, but are simply rotated (note that the total force on a thin crystal is likely to be less than that on a thick one). Thus, in the drawn sample there will be some remnants of stacks of thin lamellae, and it is these which provide the observed, weak diffraction signals.

The fact that no physical properties of the drawn fibres show an abrupt change when drawing takes place with, rather than without, high mobility in the neck, suggests that the change in mobility does not cause any large changes in the structure and morphology of the drawn fibres. We should note that while neutron scattering provides information about the configuration of the molecules in fibres drawn at low temperatures, once segregation occurs we can no longer make any deductions about the shape of individual molecules. We can only assume, since the overall properties show no significant changes when the DPE molecules are segregated on drawing, that the changes in the shapes of the individual molecules on drawing are similar to those which occur without segregation.

Thus we now assert that on necking the molecules deform more or less affinely with the whole sample. We should note that for two samples studied in greater detail in our earlier work²⁴ (not specifically concerned with necking), we measured both R_x and R_z values. In that case we found for macroscopic draw ratios of 5.4 and

6.5 molecular draw ratios of 3.9 and 4.9 from R_z measurements and of 3.6 and 7.5 from R_x measurements. We also found that the best fit to the data was observed if we used a model that assumed a Gaussian segment distribution, both before and after (affine) deformation.

To sum up, the experiments reported here, and supported by our earlier studies²⁴, show that on drawing through a neck individual molecules deform more or less affinely with the whole sample; the data reported here also show that above some drawing temperature ($70\text{--}90^{\circ}\text{C}$, depending on molecular weight) local melting occurs in the neck. We also observed, as has often been reported by others³⁻¹⁰, that the X-ray long periods depend on the drawing temperature.

We argue that the affine deformation of the molecules is consistent with the 'Peterlin' model of breaking up and rotating crystalline blocks to form microfibrils. However, in order to explain the observed long-period changes, even at low drawing temperatures where the present work shows there is no local melting, we propose two additional features to the model. First, as described above, we suggest that the thinnest lamellae escape the breaking up stage and are simply rotated and aligned; thus, providing for the observed reductions in measured long period and intensity at low drawing temperatures. Secondly, we propose that at high drawing temperatures (when the molecules become mobile) refolding (or annealing) occurs during necking and causes increases in the lamellar thickness. Further, the high mobility permits better stacking of the crystalline blocks within the microfibrils so that a strong X-ray signal is observed.

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