Plastic deformation in linear polyethylene

P. J. Hendra, M. A. Taylor* and H. A. Willis
Department of Chemistry, University of Southampton, Southampton SO9 5NH, UK
(Received 8 November 1984; revised 1 February 1985)

A detailed study has been made of drawn linear polyethylene using vibrational spectroscopy. The proportion of a monoclinic crystal modification and its dependence on draw ratio is determined by draw temperature, rate and medium (air or water). This is explained by the role of mechanical energy increasing local temperatures within the samples and the corresponding loss of heat to the environment. Monoclinic material acts as a sensitive molecular level thermometer and indicates that temperatures in the vicinity of the melting point can be generated by drawing.

(Keywords: polyethylene; plastic; deformation; vibrational spectroscopy; draw ratio)

INTRODUCTION

The draw process

Plastic deformation of crystalline polymers invariably produces a profound series of changes in the morphology of the material. When a material is drawn, deformation is substantially localized into a 'neck' region and it is here that a discontinuous change occurs from the normal lamellar structure to a fibrillar one. Two structural descriptions of this complex set of processes are relevant to this paper.

The descriptive model of Peterlin[1–3] is well established and very widely accepted. The model assumes firstly that the precursor undeformed material consists of chain folded lamellae connected by relatively rare tie molecules. According to Peterlin, application of stress results in tilting, orientation and ultimately fragmentation of the lamellae. This is associated with chain unfolding as molecules are pulled out of their parent lamellae. The fibrillar material produced consists of bundles of microfibrils. These microfibrils are therefore the remnants of the original lamellae and contain crystal blocks connected by molecules of unfolded chains.

The model proposed by Harrison[4,5] is of a very different nature; it has attracted considerable interest but very little support. In Harrison's view deformation occurs by a stress activated transition to the melt phase. Drawing involves melting followed by extension of molecules in the melt phase and recrystallization at the draw temperature. In this model, melting and recrystallization produce the fibre structure and its crystalline material forms from the recrystallization of chains extended in the amorphous phase.

Although Harrison's model must be considered extreme in that it involves melting under any conditions of draw, it is clear that significant temperature rises do occur on drawing[7,8]. Drawing becomes increasingly adiabatic at high strain rates and the heat produced by the action of mechanical work can affect the fibre structure. Peterlin has modified his theory to account for changes in crystal thickness on drawing, most notably at elevated environmental draw temperatures[2,3]. According to Peterlin crystal thickness is adjusted following extension and this requires substantial molecular mobility. However, Peterlin has calculated the maximum temperature rise on drawing[3] and concludes that it is insufficient for complete melting. Melting and recrystallization is implicated in a recent SANS study[6]. Deuterated and protonated polyethylene were cocrystallized to produce isotopic segregation. Samples were then either deformed in compression or melted and rapidly cooled. In either case there was a pronounced loss of segregation indicating that deformation involves extensive molecular rearrangement such as occurs during melting.

This study aims at placing theories of the structural transitions involved in the deformation process in perspective by supplying new data on the temperature rise that occurs within the sample as drawing proceeds. In particular, we comment on the molecular level temperatures achieved during deformation at strain rates and in environments typical of commercial practice.

The monoclinic phase

Linear polyethylene is a highly crystalline polymer where crystallization from the melt normally produces an orthorhombic crystal structure with two chains per unit cell[9]. However, the appearance of a single chain per unit cell structure has also been reported.

Certain alkanes can be crystallized[9–21] exclusively in the single chain per unit cell form[9–11] and this form can also be found coexistent with the two chain per unit cell form in deformed single crystals[10–16] and in deformed melt crystallized material[17–21]. Seto *et al.*[20] suggest that the single chain per unit cell structure, which they designate as monoclinic, can be produced from orthorhombic material by a phase transformation involving a diffusionless process similar to twinning.

The single chain per unit cell structure has been referred to as both monoclinic and triclinic in the literature and there is some confusion. In this paper it will be denoted as monoclinic and defined by its spectral characteristics.

It is widely accepted that single chain per unit cell material produces a single band near $717\ \mathrm{cm}^{-1}$ in the infra-red spectrum[10–12]. In addition the two forms have

---

* Current address: Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

0032-3861/85/101501-06$03.00

different band profiles in the 1400–1500 cm^{-1} region of the Raman spectrum with a band near 1416 cm^{-1} arising only from the two chain per unit cell form[22].

Some characteristics of the monoclinic form in single crystals have been reported. It appears to be sensitive to elevated temperatures in that it can be converted to the orthorhombic form at 70°C (ref. 13). Also, the monoclinic form persists in crystals following stripping of their surfaces by nitric acid thus indicating that it lies at least partially within the orthorhombic crystal core, possibly existing as a lattice imperfection[14]. There has been no detailed study of the monoclinic form in melt crystallized material; the exact nature of its situation within the fibre structure and formation and the details of its stability remain uncertain.

In this paper, we present the results of a spectroscopic study of drawn linear polyethylene produced under various draw conditions. There is a detailed characterization of the crystalline material in the fibre structure and this is followed by deductions on temperature rises associated with drawing.

EXPERIMENTAL

Two grades of linear polyethylene were used in this study, both supplied by British Petroleum PLC. Rigidex 006-60 was chosen as a widely available commercial grade with typical properties. It is 'particle formed' by the Phillips process and the molecular weight characteristics are $\bar{M}_w = 130\,000$, $\bar{M}_n = 19\,500$. Rigidex 50 was used for comparison it is 'solution formed' and currently out of production; $\bar{M}_w = 101\,450$, $\bar{M}_n = 6180$.

Both grades were supplied as pellets and were pressed into film between aluminium foil sheets in a hydraulic press at 160°C and then rapidly air cooled. The films produced were 80–100 μm thick and thus suitable for infra-red spectroscopy in both their undrawn and drawn state.

Dumbell samples with a parallel section 32.5 mm long and 6.25 mm wide (ASTM D638) were cut from the films and heated for 1 h at 100°C to remove residual stresses. These samples were then drawn in an Instron test machine at three draw rates: 25, 5 and 1.25 mm/min. Drawing was conducted either in an environmental cabinet with an air temperature between 0 and 90°C or with the samples immersed in water at 20°C. Once drawn, all samples however produced, were immediately returned to ambient conditions in the laboratory. Draw ratio was determined from the increase in spacing of 1 mm transverse ink divisions on the undrawn samples.

Raman spectra were recorded on a Coderg T800 spectrometer using 90 mW of 415.5 nm radiation and a spectral band pass of 1 cm^{-1}. Samples were maintained at $-150°C \pm 1°C$ in a specially designed Raman cold cell.

Infra-red spectra were recorded at a resolution of 1 cm^{-1} on samples maintained at room temperature with the draw axis vertical. A Nicolet MX1 FTIR was used throughout the work. When polarization data were required, a wire grid polarizer was used in the beam and rotated so that the electric vector was either parallel or perpendicular to the sample draw axis. To restrict the viewed area in the inhomogeneous specimens, a sample holder was employed with an aperture of 2 × 2.5 mm. Spectra were recorded for specimens prepared under various conditions and also for a variety of draw ratios. In addition, spectra were recorded before, during and after heat treatment of samples in a purpose-built hot cell. The hot cell facilitated *in situ* measurements which proved necessary to achieve the accuracy and reproducibility in band intensity required for quantitative analysis. Heat treatments were conducted between 60°C and 100°C and spectra were recorded at 10 min intervals up to a total time of 60 min.

Wide-angle X-ray scattering diffractograms were recorded on film using Nickel filtered CuKα radiation incident perpendicular to the sample plane and draw axis.

Analytical techniques

Features in the X-ray scattering pattern and Raman and infra-red spectra attributed to monoclinic material will be discussed in order to establish their usefulness in detecting and quantifying monoclinic material. In connection with this, we considered it desirable to confirm the assignment of certain spectral features to monoclinic material. This was achieved by correlating them with X-ray data which are considered definitive. Unambiguous spectroscopic assignments together with a knowledge of the spectra produced by systems of varying relative proportions of orthorhombic and monoclinic material were then available. This enabled us to detect and quantify monoclinic material with ease using a spectroscopic technique and this is discussed subsequently.

Wide-angle X-ray scattering

Rings or sectors characteristic of the monoclinic phase[17–19] appeared in addition to those associated with orthorhombic material. In particular, the (001) monoclinic reflection corresponding to a spacing of 4.522 Å, although less intense than its orthorhombic (200) and (110) counterparts, was very strong and since it lies at the lowest Bragg angle appeared distinctly from the other reflections.

Drawn samples were highly oriented and produced anisotropic scattering; the intensity of diffraction rings varied considerably around their circumference and this ruled out the possibility of quantitative analysis based on X-ray scattering as a method of determining the relative proportions of the two crystal forms.

Infra-red spectroscopy

The spectral region of interest is that characteristic of the CH_2 rocking mode between 700 and 800 cm^{-1} where bands are indicative of crystalline environment (*Figure 1*). In the orthorhombic lattice molecules are mutually perpendicular with two chains/unit cell (point group D_{2h}). This produces a band pair due to correlation splitting with components near 731 and 720 cm^{-1} arising from in-phase and out-of-phase interactions between adjacent molecules respectively[23]. In the monoclinic lattice all molecules are parallel with a single chain/unit cell and so all interactions are in-phase and a single band arises at 716 cm^{-1}.

We correlated the appearance of the 716 cm^{-1} band with the X-ray features mentioned above and thus confirmed its assignment to monoclinic material. This band provides a convenient means of quantitative analysis once the effect of molecular orientation on the band intensity is accounted for.

Unfortunately the 716 cm^{-1} band is not completely resolved from the overall band profile even at cryogenic

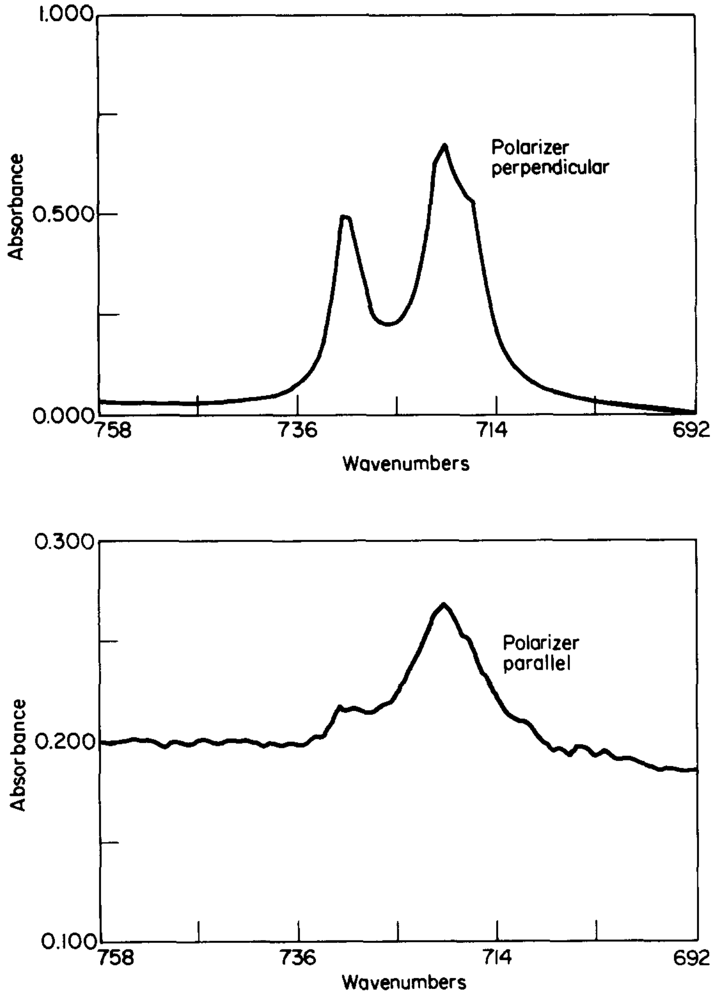

Figure 1 Infra-red spectra of drawn polyethylene

temperatures, because it is eclipsed by the relatively broad predominant feature near 720 cm^{-1}. However, it does appear as a distinct shoulder and deconvolution is possible.

A quantitative analysis of the infra-red band profile centred on 725 cm^{-1} can be used to determine the proportion of monoclinic material at different draw ratios. However, the effect of molecular orientation, which varies across the sample neck, must first be accounted for. For a transversely isotropic sample, this is best done by using structural absorbance values for band intensity. The structural absorbance value (A) for a vibration consisting of components of parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) polarization is $(2A_{\perp}+A_{\parallel})/3$ (ref. 22).

Values for the relative proportions of the monoclinic and orthorhombic material can be found from the ratio of structural absorbance values of the 716 and 731 cm^{-1} bands. These bands originate in monoclinic and orthorhombic material respectively. Any difference in extinction coefficient between the two bands would affect the result. However, any effect can be accounted for since a value for the ratio of the two extinction coefficients can be found from a consideration of the heat treating experiments.

This analysis is based on a heat treatment which completely removes the monoclinic material (*Figures 3* and *4*) and further assumes that monoclinic material transforms exclusively to the orthorhombic crystal form. The ratio of extinction coefficients is given by the ratio of band areas before and after annealing since any loss of intensity at 716 cm^{-1} produces a corresponding increase at 731 cm^{-1}.

$$\frac{e_{731}}{e_{716}}=(A_{731\,\text{after}}-A_{731\,\text{before}})/(A_{716\,\text{before}}-A_{716\,\text{after}}) \qquad (1)$$

An average values of 1.2 was obtained. The Beer–Lambert law applies to both crystal forms

$$A=ecl \qquad (2)$$

(A is absorbance, e extinction coefficient, c concentration, l sample thickness) and the relative proportions of the two forms is given by

$$\frac{C_{\text{mc}}}{C_{\text{or}}}=\frac{A_{716}}{A_{731}}\times\frac{e_{731}}{e_{716}} \qquad (3)$$

The percentage of crystalline material in the monoclinic form can thus be found.

To obtain the structural absorbance of the 716 cm^{-1} band, deconvolution from the overall band profile is necessary for each polarized component. This was achieved on a Du Pont curve analyser using the infra-red spectrum of fully heat treated material to provide a suitable background profile.

Raman spectroscopy

Raman bands show a correlation splitting effect clearly related in origin to that observed in the infra-red spectrum. Doublets appear at 1062/1064 cm^{-1} due to skeletal motions of the carbon chain and at 1293/1295 cm^{-1} from CH_2 twisting motions, both in the orthorhombic 2 chain per unit cell material[24]. Monoclinic material has been reported to produce corresponding singlet bands[22]. In the spectra reported here we do not see triplets when orthorhombic and monoclinic species are present in appreciable quantities. Instead a partial but very obvious loss of the 'normal' splitting occurs when samples are drawn (*Figure 2*). This is apparent in spectra

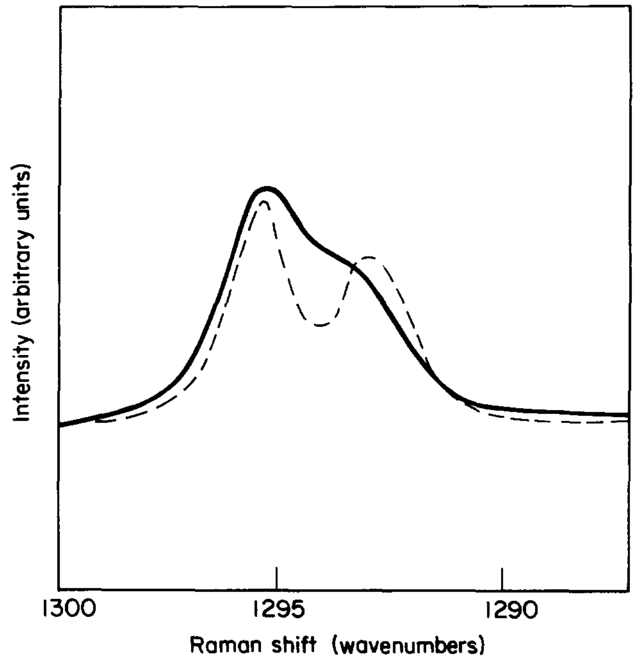

Figure 2 Raman spectra of undrawn (---) and drawn (—) polyethylene

recorded with the sample axis both parallel and perpendicular to the incident radiation. We interpret our observation by proposing that the frequency of a mode in a single chain per unit cell structure lies between the pair of frequencies characteristic of the 2 chain per unit cell phase. Overlapping then leads to the apparent loss of splitting.

The complex band profile in the region 1400–1500 cm^{-1} is reported to be different for one and two chain/unit cell material[22]. However, no changes were recorded which could be reliably correlated with the relevant X-ray features.

Quantitative analysis of the Raman spectrum is unsatisfactory because no band due exclusively to monoclinic material can be isolated by deconvolution. In addition, the effect of molecular orientation on band intensity complicates any analysis and makes the method particularly unattractive.

RESULTS

Draw behaviour

Of the two polyethylene grades used in this work, Rigidex 006-60 had a more consistent draw behaviour, with a higher attainable maximum draw ratio and lower incidence of fracture. Accordingly, Rigidex 50 was used only for a limited number of experiments but in all cases the results confirmed those of Rigidex 006-60.

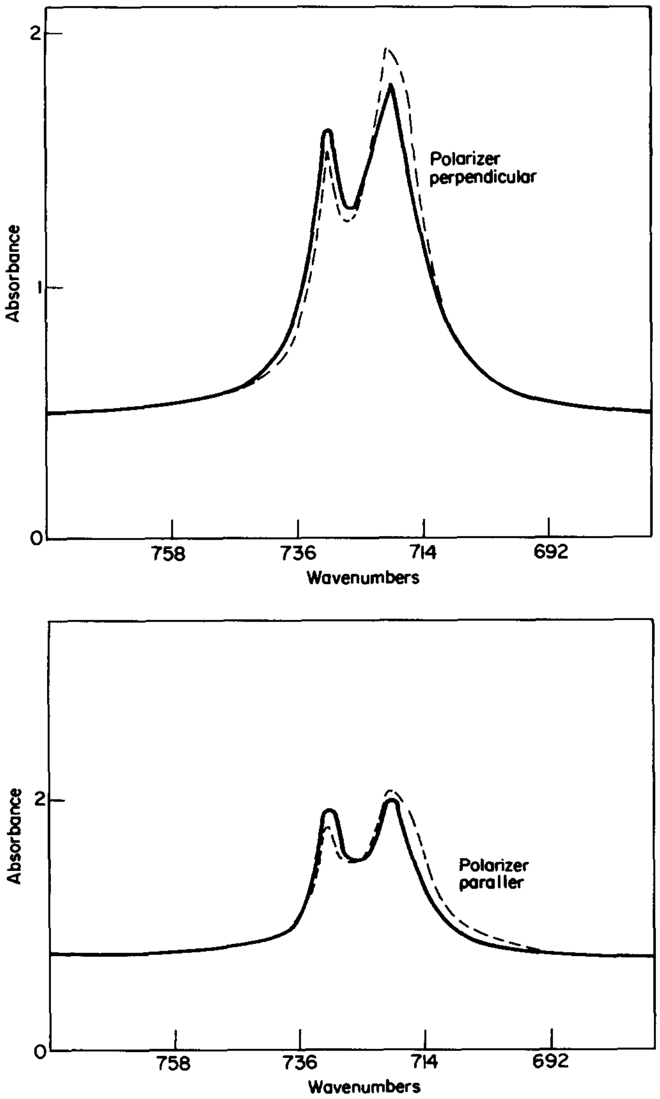

Figure 3 Infra-red spectra of as drawn (– – –) and drawn/annealed (1 h at 100°C) (———) polyethylene

Heat treatment effects on monoclinic material

Samples containing monoclinic species stored at room temperature for periods in excess of 6 months exhibited little or no measurable loss of monoclinic content. However, significant effects were apparent at elevated temperatures.

In response to heat treatment, samples containing monoclinic material exhibited a decrease in 716 cm^{-1} band intensity but very little change in both 720 and 731 cm^{-1} bands (*Figure 3*). Polarized measurements indicated no loss of dichroism for bands independent of the orthorhombic and monoclinic phases and the X-ray diffraction rings remained unchanged in extent indicating no loss of overall orientation. Therefore, heat treatment did not introduce any overall sample relaxation and any spectral changes could be related exclusively to the loss of the monoclinic phase. In addition it is clear that heat treatment transforms the monoclinic material predominantly to the orthorhombic crystal form since an increase in the 1416 cm^{-1} band area of about 10% is apparent when the spectra are normalized with respect to the 1295 cm^{-1} region band area. It is useful to compare spectra of the same sample recorded before and after heat treatment.

From a comparison of the relevant Raman spectra, there is confirmation that there are no new bands or profile changes in the 1400–1500 cm^{-1} region. However, there is an apparent loss of correlation splitting in the 1295 cm^{-1} region (*Figure 2*) and this has already been discussed. This effect arises from an additional band due to monoclinic material and not from the effect of molecular orientation on band intensity.

The time dependence of the annealing process is a useful indication of the stability of the monoclinic phase as a function of temperature. The time taken for intensity of the 716 cm^{-1} band to fall below 10% of its as-drawn value was measured at three temperatures and the results are shown in *Table 1*.

The influence of draw conditions

Monoclinic material appears only for highly specific draw conditions (*Table 2*).

The influence of draw ratio: in the infra-red spectrum, the different effects of relative crystal proportions and molecular orientation on band intensity are obvious when structural absorbance values and band dichroism are considered as a function of draw ratio. Band dichroism is defined as the ratio of parallel to perpendicular polarized elements and was calculated for 716, 720 and 731 cm^{-1} bands. Structural absorbance values for the three bands were found and were used to find the percentage of crystalline material in the monoclinic form.

Table 1 Times taken for intensity of 716 cm^{-1} band to fall below 10% of its as-drawn value measured at 3 temperatures

Temperature (°C)	Time (min)
60	40
70	20
100	10

Table 2 Occurrence of monoclinic material as a function of draw conditions

Draw medium	Draw temperature (°C)	Draw rate (mm s^{-1}) 0.02	0.08	0.4
Air	0	mc	–	–
	10	mc	mc	–
	22	mc	mc	none
	50	mc	mc	none
	70	none	none	none
	90	none	none	none
Water	22		mc	mc

Key: –, sample not prepared; mc, substantial amount of monoclinic material present; none, monoclinic material absent or less than 2% of total crystalline material

The dichroic ratio for the 710 and 731 cm^{-1} bands increases uniformly with draw ratio up to the maximum draw ratio of the samples of 4. The dichroism and structural absorbance for the 716 cm^{-1} band exhibited three different types of behaviour with draw ratio according to the particular draw conditions, which were:

(A) constant;
(B) increasing;
(C) rising to a maximum followed by a decrease.

Values for the percentage of monoclinic material and the trend with draw ratio for the three sets of samples are tabulated in *Table 3*. In the case of the sample drawn in air at 20°C and 5 mm/min there is a maximum at a draw ratio of 2; this is a similar result to that of Siesler[25].

The situation of monoclinic material within the overall structure: from a detailed analysis of the infra-red spectra of a variety of samples it is possible to deduce the location of the monoclinic species. Considering first as-drawn samples (*Figure 1*) it is clear that the dichroism of the 716 cm^{-1} band is considerably larger than that of the 731 cm^{-1} band. This is because the 716 cm^{-1} band is stronger than the 731 cm^{-1} for parallel polarization. The difference in dichroism indicates that the orthorhombic and monoclinic material are oriented either in a different way or to a different extent. Monoclinic material must therefore be situated outside the orthorhombic crystal core.

A comparison of infra-red spectra recorded before and after heat treatment (*Figure 3*) reveals that the band at 731 cm^{-1} increases in intensity during heat treatment. The increase is roughly equal for both polarization conditions indicating that the orthorhombic material formed during heat treatment is oriented in a different way or to a different extent to the pre-existing orthorhombic material. It must therefore be formed outside the crystals in order that it is not forced to comply with the existing orientation within the crystal cores. The monoclinic material which gives rise to this orthorhombic material on heat treatment must therefore also be outside the crystal cores. Some samples were subjected to digestion by fuming nitric acid. This was done at 30°C to avoid heat treating the samples. At this temperature, the reaction rate is normally very low but was increased by the addition of 10% by volume concentrated sulphuric acid. Under these conditions, digestion for 2 weeks removed about 20% of the total sample weight.

A comparison of infra-red spectra recorded before and after digestion indicates that the 716 cm^{-1} band falls in intensity by about 50% whilst bands due exclusively to amorphous material at 1330, 1375 and 2658 cm^{-1} lose about 25% of their intensity.

Digestion removes both amorphous and monoclinic material so that they must be integrated within the fibrillar structure to some extent. However, their digestion rates are very different and this indicates that the monoclinic material is embedded only partially in the amorphous zones.

In order to explain data on both polarization behaviour and digestion rate it is necessary to conclude that the monoclinic material is located on the crystal surfaces.

DISCUSSION OF RESULTS

It is clear that a significant proportion of crystalline material within a drawn sample may be in the monoclinic form, but that its presence and quantity will depend on draw conditions and draw ratio. In particular, the drawing process can produce three unexpected effects involving monoclinic material.

Firstly, high temperatures and/or draw rates either do not allow the formation of monoclinic material, or else, lead to its destruction during the overall draw process. Secondly, varying the draw rate and temperature produces materials showing different trends in the proportion of monoclinic material produced *versus* the draw ratio achieved. Thirdly, drawing under water appears to enhance the formation of the monoclinic material apparently by overriding the effects of draw ratio and draw rate and temperature.

An attractive explanation is that severe draw conditions (particularly rapid drawing at high ambient temperatures) causes sufficient local heating that the monoclinic phase is disrupted, i.e. that the drawing process always generated monoclinic material, but that this is subsequently destroyed in some cases. That the phase should be formed and then destroyed rather than that it is in some way prevented from forming under rapid drawing conditions, seems more likely because of the wide range of techniques described in this paper. Thus, for example, drawing in air at 20°C produces an increasing proportion of monoclinic material if the draw rate is less than 1.25 mm min^{-1}, but a lower value above this rate. At 25 mm min^{-1} the monoclinic material vanishes. Further, evidence supporting our view comes from the experiments involving drawing under water. Water is unlikely to have even subtle chemical or structural effects on polyethylene, thus we conclude that it simply acts here as a heat sink.

Excess of heat generated within the sample during drawing is lost to the water, thus preventing heating effects and allowing the full amount of monoclinic material to form and remain intact across the neck.

One other possible explanation for the loss of mono-

Table 3 Percentage of crystalline material in the monoclinic form and its dependence on draw ratio

Draw medium and temperature	Draw rate (mm s^{-1}) 0.02	0.08	0.4
Water at 22°C		39% Constant	44% Constant
Air at 22°C	36% Increasing	36% Maximum	No monoclinic material present
Air at 10°C	–	36% Increasing	

, indicates sample not analysed

clinic material is that it is due to disruption by molecular orientation, i.e. monoclinic material is lost when draw rate/temperature produces a high degree of molecular orientation and that orientation increases with draw ratio. This explanation can be rejected with confidence since we see the monoclinic material in samples drawn rapidly under water. Water cannot reasonably be expected to affect the molecular orientation equilibria except by completely indirect means.

A heating effect can account for the lack of monoclinic material in the relevant samples and also for the three different trends in its proportion as a function of draw ratio. Drawing under water removes the heating effect completely producing a constant and high proportion of monoclinic material. Moderate draw conditions produce an increasing proportion of monoclinic material with draw ratio limited, in the absence of any heating effect, only by its rate of formation.

Intermediate conditions produce a maximum in the proportion of monoclinic material reflecting the balance between creation during draw and destruction due to heating. If a heating effect is thought to cause the loss or reduction of monoclinic material during drawing, then it is possible to apply data on the annealing behaviour of monoclinic material to the draw process itself. The monoclinic phase can act as a kind of molecular level thermometer indicating the maximum temperature achieved locally during the deformation process.

In order to destroy monoclinic material completely in the very limited time whilst the neck is resident over a particular mass of material, the maximum temperature achieved must be well in excess of 100°C. This point is demonstrated in the earlier part of this paper. The reduction of monoclinic phase shown here as draw rate, and temperature, is raised suggests that, locally, this temperature is reached easily and hence temperature rises to 140°C, i.e. the melting point of polyethylene, must be easily achieved in real cases. In fact, the condition required to produce melting would appear to be routine in commercial practice.

The source of energy required is, of course, the work of deformation. It is suggested that the work becomes concentrated on zones where the modulus is low, which are of small size, and hence rapid heating and hence local melting occurs. Stress (and hence strain) concentration then occurs round the boundaries of these 'islands' of melt, feeding energy into them and retaining their existence against heat loss to the surrounding relatively undeformed polymer mass. The minute melt 'islands' then suffer distortion and freezing under melt elongation, the 'islands' of melt progressing steadily through the whole polymer mass. Clearly the size of these 'islands' will be related to the draw rate and ambient temperature. Further work is now in progress along these lines but it is already clear that the Raman longitudinal acoustic mode (*LAM*) is affected by draw temperature and, notably, draw rate. Samples drawn under moderate conditions (which produce monoclinic material) have a very broad and indistinct *LAM*, which is not resolvable. Conversely, samples drawn under severe conditions (which do not produce monoclinic material) have a well-defined *LAM*. The distribution in crystal thickness as indicated by the *LAM* is, we contend, determined by the size of the melt islands. Severe conditions are responsible for relatively complete melting of crystalline material and the melted material is then consolidated by recrystallization to produce a distinct *LAM* and a narrow distribution in lamella crystal core thickness. Joderate conditions, produce either a less extensive melt zone which leads in turn to partial melting or to 'islands' thinner than the equilibrium core thickness dictated by the melt temperature and cooling rate. Either phenomenon would produce a broad distribution in crystal thickness and hence a diffuse *LAM* band in the Raman spectrum.

CONCLUSION

The quantity of monoclinic material and its dependence on draw ratio in polyethylene is determined by the role of mechanical energy in increasing local temperatures within the sample and the corresponding loss of heat to the environment. Monoclinic material acts as a sensitive molecular level thermometer and indicates that the temperatures generated by drawing are in the vicinity of the melting point in even quite mild drawing situations. This appears to be inconsistent with the well-established Peterlin model. A model involving melting in numerous small zones within the neck can account for experimental observations on crystal structure and the distribution in crystal size.

Clearly, the real structural conclusion of this work is negative. We do not feel that the well-established model for plastic deformation is adequate. Our suggested explanation is speculative. A programme of research into this more positive contribution aimed, we hope, at the eventual production of a new structural scheme, is in hand.

ACKNOWLEDGEMENTS

We wish to express our thanks to the US Navy Office of Naval Research for generous financial support and to British Petroleum PLC for the supply of polymer samples.

REFERENCES

1 Peterlin, A. *Colloid. Polym. Sci.* 1975, **253**, 809
2 Peterlin, A. *Polym. Eng. Sci.* 1969, **9**, 172
3 Peterlin, A. *J. Mater. Sci.* 1971, **6**, 470
4 Juska, T. and Harrison, I. K. *Polym. Eng. Rev.* 1982, **2**, 13
5 Juska, T. and Harrison, I. K. *Polym. Eng. Sci.* 1982, **22**, 766
6 Wignall, G. D. and Wu, W. *Polymer* 1983, **24** (*Commun.*), 354
7 Vincent, P. I. *Polymer* 1960, **1**, 7
8 Allison, S. W. and Ward, I. M. *J. Polym. Sci. A-2* 1968, **6**, 607
9 Bunn, C. W. *Trans. Faraday Soc.* 1939, **35**, 482
10 Snyder, R. G. *J. Mol. Spectr.* 1961, **7**, 116
11 Holland, R. F. and Nielsen, J. R. *J. Mol. Spectr.* 1962, **8**, 383
12 Martin, J. M., Johnston, R. W. B. and O'Neal, M. J. *Spectrochim. Acta* 1957, **12**
13 Kikuchi, Y. and Krimm, S. *J. Macromol. Sci. Phys.* 1970, **B4**, 461
14 Koenig, J., private communication
15 Kiho, H., Peterlin, A. and Geil, P. H. *J. Polym. Sci. Polym. Lett. Edn.* 1965, **3**, 157
16 Kiho, H., Peterlin, A. and Geil, P. H. *J. Polym. Sci. Polym. Lett. Edn.* 1965, **3**, 257
17 Terre, P. W. and Holmes, P. *J. Polym. Sci.* 1957, **24**, 496
18 Turner-Jones, A. *J. Polym. Sci.* 1962, **62**, 553
19 Marsden, E. *PhD Thesis*, University of Southampton
20 Seto, T., Hara, T. and Tanaka, K. *Jpn. J. Appl. Phys.* 1968, **7**, 31
21 Kiho, H., Peterlin, A. and Geil, P. H. *J. Appl. Phys.* 1964, **35**, 1599
22 Koenig, J. and Boerio, F. *J. Chem. Phys.* 1970, **52**, 3425
23 Schochtschneider, J. and Snyder, R. *Spectrochim. Acta* 1963, **19**, 117
24 Hendra, P. J., Jobic, H. P., Marsen, E. P. and Bloor, D. *Spectrochim. Acta* 1977, **33A**, 445
25 Siesler, H. W. *Infrared Phys.* 1984, **24**, 239