Lamellar structure in heat-treated polyethylene. A Raman spectroscopic study

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Measurement of the low frequency Raman spectrum of polyethylene affords a method of following the effects of sample deformation on lamellar structure and of the process of annealing on lamellar thickness.

1. Introduction

It is now generally accepted that most simple hydrocarbon polymers crystallize from the melt in the form of spherulites composed of lamellar units involving polymer chains folded on the lamellar surfaces. There is also some evidence to suggest that there are folded chain structures in drawn fibres [1, 2] of polyethylene. Electron microscopy and X-ray diffraction techniques have been used extensively to investigate lamellar structures in crystalline polymers.

In Raman spectroscopy of polymers we are measuring the frequency and importance of molecular vibrations. Colloquially these are divided into three classes, the "internal modes", i.e. vibrations of the atoms within the molecules considered as isolated units, "lattice modes", vibrations of one polymer segment against its surroundings and defined with reference to the unit cell and acoustic motions to be discussed here.

Recently, it has been proposed that the Raman active longitudinal acoustic vibrational mode (LA mode) [3] in polyethylene can be used to measure lamellar thickness [4]. The LA mode has a frequency inversely proportional to the length of the extended (CH_2) sequence [4] within a lamellar unit and, hence, is a measure of a parameter close to the lamellar thickness. Results are available on the LA mode frequencies of polyethylene crystallized from solution [4] and more recently from the melt crystallized homopolymer [5]. These results have been compared with those from small-angle X-ray

diffraction techniques and it has been reported [4-6] that the values for lamellar thickness are in good agreement.

In this report the use of low frequency Raman spectroscopy as a rapid and convenient method of following changes in lamellar structure is described with particular reference to deformation and annealing of polyethylene.

2. Experimental
2.1. Preparation of samples

All samples were prepared from a batch of granular polyethylene having a density of 0.95 $g\ cm^{-3}$ and a methyl group content of 2 per 1000 carbon atoms.

Samples of polyethylene in the form of bars were prepared by heating the granules to 160°C in a mould, followed by cooling to room temperature at 25°C min⁻¹. Samples in the shape of a dumb-bell were prepared similarly. The frequencies of the primary acoustic mode of the undrawn samples prepared as above were identical; 12.5 ± 1 cm⁻¹. The bars were rolled successively in the same direction along the long axis at room temperature. Dumb-bell shaped samples were drawn to extensions of 100 and 400% at room temperature using a Hounsfield tensometer.

2.2. Spectroscopy

Raman spectroscopy is an inelastic light scattering process of very weak intensity. The scattered radiation lies very close to the wavelength of the laser source. Raman spectra of

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polymers in the higher shift frequency range (typically 100 to 3500 cm^{-1} from the source) have been available for some years. Recently, it has become possible to investigate the region very close to the exciting wavelength.

Earlier work by others in this field [4-6] has been carried out using argon ion lasers operating at 5145 Å in a single mode. The Raman and Rayleigh scattered radiation has then been optically filtered by a cell containing iodine vapour [7] to remove the elastically scattered and reflected radiation at 5145 Å. The resultant spectrum has then been analysed with a commercially available double monochromator-Raman Spectrometer.

This method has certain experimental disadvantages including the difficulty of keeping the laser locked permanently in the single mode and the power limitations resulting from single mode operation. Further the iodine vapour filter, although very effective at attenuating the source wavelength, is far from an ideal optical filter as it possesses undesirable absorptions and fluorescent emissions. In the experiments reported here these difficulties are avoided by analysing the scattered and reflected radiation at 5145 Å in a completely routine manner using a commercial Raman spectrometer containing a triple monochromator. It would appear that this approach is most likely to be the one adopted in future since one report exists on its application to biopolymers [14] and we have been able to show that both the Cary 82 and the recently announced Coderg T800 instruments both perform adequately for the purpose and would seem to be much more convenient and if anything slightly more effective than the iodine filter double monochromator alternative.

In order to minimize heating of the sample by the laser, low intensities of exciting radiation were used; typically less than 100 mW.

3. Results

Calculations and experimental experience show that the internal vibrational modes [8] and the lattice vibrations [9] of the crystalline polymer should occur well above 80 cm^{-1}. Furthermore, most lattice modes have frequencies which are temperature dependent.
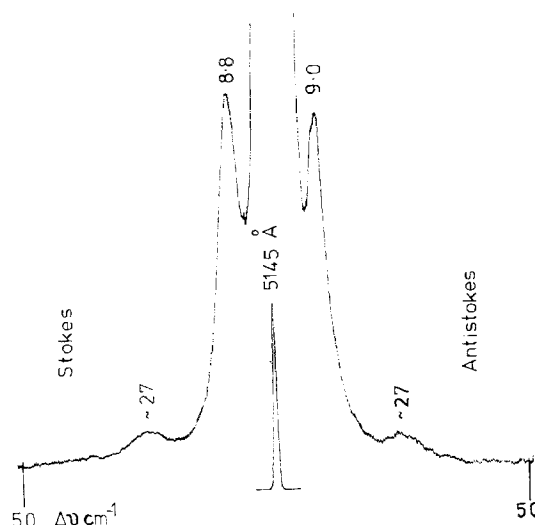

Figure 1 The low frequency Raman spectrum of a sample of crystalline high density polyethylene recorded on a Cary 82 spectrometer using 100 mW of 5145 Å excitation and a constant spectral bandwidth of 2 cm^{-1}.

A representative Raman spectrum of the low frequency region is given in Fig. 1. The lowest frequency line is observed well below 50 cm^{-1} and since its decrease in frequency on annealing is consistent with the thickening of lamellae inferred from low-angle X-ray data as shown by

TABLE I Frequencies and half-widths of the LA modes recorded for samples of quenched and annealed samples of bulk crystallized polethylene

Sample	$m = 1$ (cm^{-1})	$W_{\frac{1}{2}}$ (cm^{-1})	$m = 3$ (cm^{-1})	$W_{\frac{1}{2}}*$ (cm^{-1})	Lamellar thickness†
As supplied	16.0	9.0	50.0	~10.0	199
Cooled from melt at 10°C min^{-1}	11.8	7.0	37.0	~ 7.0	269
Annealed at 128°C	9.0	6.0	27.5	~ 8.0	357
Annealed at 130°C	7.0	6.0	20.5	~ 7.0	454

*Calculated as in [10]
†It is difficult to assess the half-width of this band accurately due to its relatively low intensity

earlier workers [4-6], it can be reliably ascribed to an LA mode. The theory of the frequency and activity of the mode [10] allows all odd order vibrations to be Raman active with intensities decreasing with mode order, m. From the data in the table it is clear that a weak band at the frequency very close to three times that of the $m = 1$ LA mode is observed in all cases, and this supports the assignment. As yet no bands due to higher odd order modes have been found.

3.1. Effect of heat-treatment

The frequency of the $m = 1$ LA mode for a particular sample remains constant from liquid nitrogen temperature until the temperature approaches the melting point. Near the melting point the primary LA mode is found against an intense background emission which becomes more pronounced as the temperature is raised. The latter is probably due to "Rayleigh Wing Broadening" resulting from motional freedom in the structurally disordered zones within the specimen. The LA mode for a quenched sample moves to lower frequency at temperatures below the melting point. Subsequent cooling of the specimen leaves the band unchanged in frequency, i.e. irreversible thickening is indicated.

In the case of an annealed sample the LA mode is unchanged in frequency up to the melting temperature (135°C). At this temperature the lattice modes and LA mode bands are not apparent. A broad Raman feature which does not appear at lower temperatures is centred on 210 cm^{-1}. The latter has been observed for liquid n-paraffins and appears to be characteristic of a polymethylene chain containing a high proportion of gauche sequences [11]. Since the frequency of the LA mode remained constant up to the melting point, it appears that the extended chain length was the same up to the melting temperature. This result is not expected on the basis of the theory of premelting [12]. In this respect we are in agreement with Koenig and Tabb who found no evidence of premelting during the annealing of polyethylene single crystals [6].

3.2. The width of the low frequency Raman lines

The width of the Raman band due to the LA mode should be a simple precise indication of the distribution of lamellar thickness. In this respect the parameter of interest would be the (width of the band at half weight $W_{\frac{1}{2}}$) (frequency shift of

the band head)$^{-1}$. Caution is required in the interpretation of band width data, since the band profiles at very low frequencies may be distorted by the Rayleigh wing. Furthermore, experience with pure isomeric normal paraffins and with a wide range of polyethylene samples leads to the suggestion that the minimum band width is close to 4 cm^{-1}. The reason for this is certainly not instrumental as typical slit widths in this type of work are 1 to 2 cm^{-1} and thus the cause is obscure. Band broadening beyond 4 cm^{-1} is probably significant at this stage.

3.3. Effect of sample deformation

When a sample is rolled to extensions of less than 200% the band head of the LA mode remains at a fixed frequency and no appreciable broadening of the band can be detected. Thus it would appear that the lamellae remain dimensionally intact when the sample is rolled to extensions of 200%. For extensions of between 200 and 300% the band becomes broader until at 350% extension it appears as a shoulder on the Rayleigh wing. At these extensions, therefore, lamellar breakdown occurs to give a structure consisting of chains in which some folded sequences remain. This is consistent with the model of deformation developed by Peterlin [13]. From the broadness of the LA mode it can be inferred that the chain lengths between the folds have a greater distribution than in the sample before rolling.

Each of the stretched samples was investigated by recording spectra at various points on the sample as it was moved across the laser focus and, hence, the point viewed by the spectrometer as shown in Fig. 2. The spatial resolution in these measurements was 0.050 in.

In the undrawn part of the specimen an LA mode was observed at 12.5 cm^{-1}. Near the neck in the undrawn part of the specimen, the band is reduced in intensity but appears to be unchanged in frequency. In the neck, it has been reduced to a weak shoulder on the Rayleigh Wing. On the fibre side of the neck and well out into the fibre itself no distinct LA mode is observed. Nevertheless, the appearance of the spectrum suggests that a relatively weak LA mode is present and that this band is buried in the profile of the Rayleigh Wing. Thus it appears that there is a progressive breakdown of the chain-folded structure through the necking region with the possibility of some residual folded material.
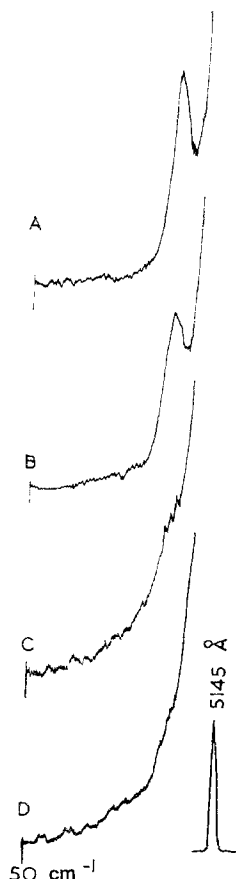
Figure 2 Low frequency Raman spectra of drawn polyethylene at various points through the necking region; A, in the undrawn part of the sample; B, close to the neck in the undrawn part; C, in the neck; D, in the fibre side of the neck.

The above examples demonstrate that the original chain-folded structure is retained or alternatively destroyed to different extents depending upon the type of deformations and that the LA mode is able to provide information on this point. At this stage we do not attempt to account for the differences displayed by rolling and stretching in more specific terms.

When the fibre is annealed at 118°C for five min a very broad shoulder is observed at $\sim$ 13 cm^{-1} on the Rayleigh Wing. Annealing for longer periods of time at the same temperature does not significantly alter the appearance of this band. Thus on annealing the fibre it would appear that the distribution of trans(CH$_2$) sequences between the folds is narrowed.

As stated above, no distinct LA modes were observed in the fibre part of the specimens. In the theory [3] of the LA mode an effective vibrator is considered to be a single chain and chain-chain interaction is thought [10, 15] to have little influence on the frequency of the vibration, i.e. would not appear necessary to have a cluster of (CH$_2$) trans sequences of identical length for the appearance of the LA mode. Therefore, the non-appearance of a distinct mode in the fibre would at this time, indicate that a very wide distribution of interfold lengths is typical of the structure of the fibre.

4. Conclusion

In this note we have shown very briefly how information on the morphology of bulk crystallized polyethylene can be obtained from the low frequency Raman spectrum. The results obtained so far confirm that, in rapidly cooled high density material irreversible thickening of the lamellae occurs at temperatures below the melting point. No evidence of premelting is found. The Raman method provides a means of studying the degree of disruption in the course of plastic deformation.

Acknowledgements

References

1. I. L. HAY and A. KELLER, *Nature* **204** (1964) 862.
2. G. MEINEL and A. PETERLIN, *J. Polymer Sci.* **A2** (1968) 587.
3. S. I. MIZUSHIMA and T. SHIMANOUCHI, *J. Amer. Chem. Soc.* **71** (1949) 1320.
4. W. L. PETICOLAS, G. W. HIBLER, J. L. LIPPERT, A. PETERLIN and H. OLF, *Appl. Phys. Letters* **18** (1971) 87.
5. H. OLF, A. PETELIN and W. L. PETICOLAS, *J. Polymer Sci.* **12** (1974) 359.
6. J. L. KOENIG and D. L. TABB, *J. Macromol. Sci.*, in press.
7. G. E. DEVLIN, J. L. DAVIS, L. CHASE and S. GESCHWIND, *Appl. Phys. Letters.* **19** (1971) 138.
8. J. H. SCHACHTSCHNEIDER and R. G. SNYDER, *Spectrochim Acta* **19** (1963) 117.
9. M. TASUMI and S. KRIMM, *J. Chem. Phys.* **46** (1967) 755.
10. R. F. SCHAUFELE and T. SHIMANOUCHI, *J. Chem. Phys.* **47** (1967) 3605.
11. J. D. BARNES and B. M. FANCONI, *J. Chem. Phys.* **56** (1973) 5190.
12. E. W. FISCHER, *Kolloid. Z. Poly.* **218** (1967) 97.

13. A. PETERLIN, *J. Polymer Sci.* **C15** (1966) 427.
14. R. G. BROWN, S. C. ERFORTH, E. W. SMALL and W. L. PETICOLAS, *Proc. Nat. Acad. Sci. USA* **69** (1972) 1467.
15. M. TASUMI, T. SHIMANOUCHI and R. F. SHAUFELE, *Polymer J.* **2** (1971) 740.