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The structure of crystalline polyethylene sulphide - a laser Raman study

P. J. HENDRA, H. A. MAJID
Department of Chemistry, The University, Southampton, UK

That polyethylene sulphide crystallizes in lamellar units within spherulites, has been presumed. In this paper further evidence for lamellae from Raman spectroscopy is presented and discussed. Thickening of the lamellae between $T_M - 90$ and $T_M - 15$ is also demonstrated.

1. Introduction

The most widely accepted methods for the identification of lamellae in melt-crystallized polymers and for the measurement of their thickness are electron microscopy and low-angle X-ray diffraction (LAXD). However, although widely applied, some confusion exists in the interpretation of electron micrographs of fracture surfaces. Density and thermochemical data tend to be only vaguely connected to the presence or otherwise or or the nature of lamellar features [1]. Recently, a new method has received some prominence, namely the observation of bands due to acoustic vibrations in the Raman spectra of polyethylene [2] (and a few other systems [3]) and the relationship of their frequency with lamellar thickness.

The Raman spectrum of polyethylene contains features at very low energy where frequency ν is inversely related to the lamellar thickness l and obeys $l \sim 3000/\nu$. This versatile technique does not provide an accurate measure of lamellar thickness, at this time, as debate continues regarding the precise relationships between ν and l, but as a method of identifying the presence or otherwise of lamellae and as a rough indication of thickness, the method is of considerable value [4]. It can be applied to minute samples over great ranges of temperature and pressure, whilst in large samples, the method has excellent spatial resolution [5]. It has recently been used to demonstrate lamellar build up at low temperatures in quenched polyethylene melt in specimens quite inaccessible to study by other techniques [6].

In this paper we use the Raman method to support a suggestion that lamellae are probably present in polyethylene sulphide and that they thicken on annealing. The significance of this observation centres on the fact that repeated attempts to use low-angle X-ray diffraction in several laboratories on this material have failed to produce viable patterns and thus this paper provides support for the hitherto assumed existence of lamellae in polyethylene sulphide.

2. Experimental details

Three samples of polyethylene sulphide were examined, two provided by the Thiokol Corporation and one produced at Southampton. For our purpose, it may be assumed that all behaved identically. The polymer was melted at 220° C and then slowly cooled or quenched into water. Where appropriate, samples were annealed for 2 to 9 h at temperatures between 120 and 190° C in a thermostatted oven under nitrogen atmosphere. Raman spectra were recorded on a Cary Model 82 spectrometer fitted with a triple monochromator and powered by an Argon ion laser (at 514.5 nm) on samples maintained at room or cryogenic temperatures using standard sampling techniques [7].

3. Results and discussion

The Raman spectra at low energies of a typical polyethylene sulphide specimen when quenched into water and then annealed at 120, 150, 170 and 190° C are shown in Fig. 1. The bands of interest are those which change from spectrum to spectrum, namely those lying within the frequency range 20 to 5 cm^{-1}.

Polyethylene sulphide is known to solidify with a high degree of crystallinity and with the familiar spherulitic morphology [8–10]. The molecular structure is known [space group *pbcn* – D_{2h}^{14} (orthorhombic)] and has the rotameric form

$$-CH_2\underset{t}{-}CH_2\underset{g}{-}S\underset{g}{-}CH_2\underset{t}{-}CH_2\underset{g}{-}S\underset{g}{-}$$

with an identity period of 6.7 Å, i.e. the material exists as semi-extended and non-helical chains. The vibrational behaviour and infra-red and Raman spectra have been reported and analysed [11, 12], but have been confined to modes of vibration involving contortions of the molecular structure, i.e. at much higher frequencies than those displayed in Fig. 1. It is apparent that a rich Raman and infra-red spectrum of this species is to be anticipated within the frequency range 3200 to 100 cm^{-1} [10, 11]. It is also clear that since two chains translate the unit cell, several lattice vibrational modes of low frequency are to be expected (normally in this type of polymer within the frequency range 20 to 150 cm^{-1}). Tadokoro *et al.* [12] observed two Raman bands near 36 cm^{-1} and 65 cm^{-1} in this region and tentatively assigned them to lattice modes. Whilst the band near 36 cm^{-1} is not observed in the present study, the band near 60 cm^{-1} in Fig. 1 is thought to have its origin in this type of motion and thus to involve the movement as an entity of one chain with respect to its neighbour within the unit cell. This hypothesis is confirmed by cooling the specimen to –180° C when the Raman bands at 62, 19.6 and 6.5 cm^{-1} shifted to 67, 20 and 7 cm^{-1} respectively. On the other hand, when the specimen was heated to 180° C the 62 cm^{-1} band fell in frequency to 52 cm^{-1}. In this experiment, cooling causes the lattice to contract, stiffening the force field and hence forcing up the frequency of the lattice type vibrations; the reverse happens on heating.

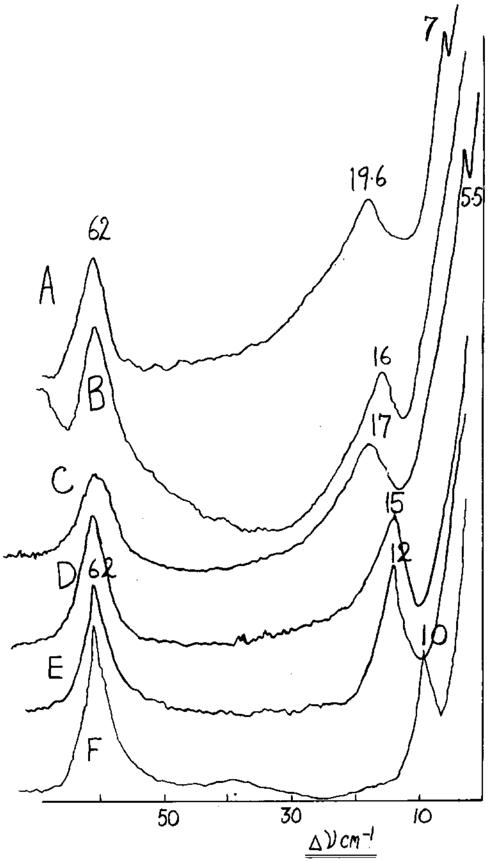

Figure 1 Low frequency Raman spectra of polyethylene sulphide. (A) Melt, rapidly quenched; (B) melt, slowly cooled, (C) to (F) specimen A annealed for 2 h at 120, 150, 170 and 190° C respectively. The Raman bands between $\Delta\nu = 10$ and 20 cm^{-1} are due to 3rd order longitudinal acoustic vibrations.

Turning now to the bands below 25 cm^{-1}; their sensitivity to thermal history, their indifference to sample cooling and their low frequency, all point convincingly to an origin in longitudinal acoustic vibrations (LAM). It is probable that the lowest frequency band arises from the fundamental motion (with a single node at the central plane of the lamellar unit) and the higher frequency one to the third order vibration, i.e. with three nodes within the lamellar core. The relationship between frequency and thickness ($\bar{\nu}$ and l) in this case is unknown, but it can be concluded with confidence that annealing causes a gradual increase in thickness as a function of annealing temperature until at 190° C the original thickness has doubled.

If one assumes that Young's modulus for the isolated chain in polyethylene sulphide is close to that in polyethylene the Raman data would indicate a lamellar core thickness in quenched polyethylene sulphide of ~ 400 Å. It is far more likely, however, that the modulus is lower than this value by a factor of two or more since the backbone is non-planar. We must, therefore, assume that the core (and hence, approximately, the long spacing) in the quenched material probably lies in the range 100 to 300 Å.

Conventional lamellar/spherulitic crystallization would require that disordered and hence low-density material would be provided predominantly by the lamellar surface zones. We are encouraged by the plot of density against the third order LAM

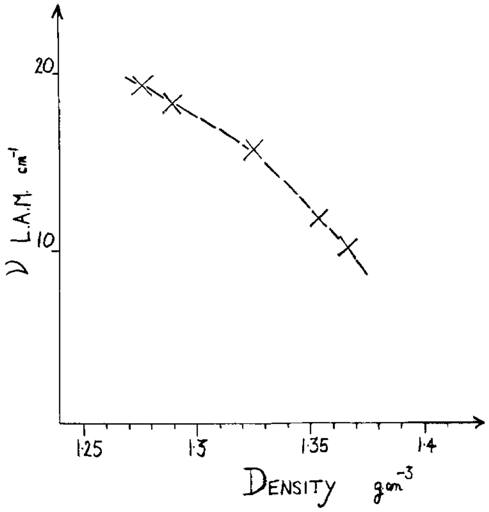

Figure 2 Densities of annealed polyethylene sulphide specimens plotted against their 3rd order longitudinal acoustic mode frequencies.

frequency shown in Fig. 2. We also find that annealing increases the D.S.C. derived melting point within the range 202 to 217° C. Thus, we can conclude that the Raman data provide novel evidence for the existence of lamellar units in polyethylene sulphide and that lamellae thicken on annealing at temperature in excess of 120° C.

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References

1. A. KELLER, *Kolloid Z. u.Z. Polym.* **231** (1967) 386.
2. H. G. OLF, A. PETERLIN and W. L. PETICOLAS, *J. Polymer Sci. Polymer Phys.* **12** (1974) 359.
3. M. J. FOLKES, A. KELLER, J. STEIGNY, P. L. GOGGIN, G. V. FRASER and P. J. HENDRA, *Kolloid, Z. u.Z. Polymer,* in press, and Authors' unpublished data on a range of polyoxy- and polythioethers.
4. P. J. HENDRA, E. P. MARSDEN, M. E. A. CUDBY and H. A. WILLIS, *Makromol. Chem.,* in press.
5. P. J. HENDRA, in "Polymer Spectroscopy", edited by D. O. Hummel (Verlag, Chem., Berlin, 1974) pp. 151–187.
6. P. J. HENDRA, H. JOBIC and K. HOLLAND-MORITZ, *J. Polymer Sci. C Polymer Letters,* in press.
7. M. J. GALL, P. J. HENDRA, D. S. WATSON and C. J. PEACOCK, *Applied Spec.* **25** (1971) 423.
8. S. ADEMEK, D. MACKILLOP and H. SCHNECKE, *J. Appl. Polymer Sci.* **16** (1972) 2511.
9. E. BALCERZYK, H. PSTRECKI and G. WLODARSKI, *J. Appl. Polymer Sci.* **11** (1967) 1179.
10. Y. TAKAHASHI, H. TADOKORO and Y. CHATANI, *J. Macromol. Sci. Phys.* **B2** (1968) 361.
11. A. C. ANGOOD and J. L. KOENIG, *J. Macromol. Sci. Phys.* **B3** (1969) 321.
12. M. YOKOYAMA, H. OCHI, A. M. UEDA and H. TADOKORO, *ibid* **B7** (1973) 465.

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