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Structure

The structure of linear polyethylene crystals formed in dilute solution

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Summary

Raman LAM and internal mode studies have been made on crystals of linear polyethylene formed in dilute solution. The molecular weight range, $5 \times 10^4 - 1.5 \times 10^6$, was much greater than has been studied heretofore. The crystallite core thickness and degree of crystallinity was found to be independent of molecular weight for a given crystallization mode. The internal mode analysis indicates a substantial disordered overlayer, which is primarily isotropic in character.

Introduction

There is a substantial body of evidence which demonstrates that crystals formed from dilute solution contain a significant disordered overlayer (1)(2)(3). Small-angle x-ray studies have shown that the total lamellar periodicity is constant over a wide range in molecular weight for a fixed isothermal crystallization temperature (4)(5). The question then arises as to whether the disordered overlayer is also independent of molecular weight. This problem can be addressed directly by determining the crystallite core thickness, as a function of molecular weight, from an analysis of the Raman low frequency longitudinal acoustical mode (LAM). The polyethylenes are particularly amenable to this kind of measurement and analysis. Such measurements have heretofore been restricted to a relatively small molecular weight range (6). In another region of the Raman spectrum the internal mode gives a very accurate measure of the fraction of non-crystalline material and can also discriminate as to what proper portion of this region is isotropic, or liquid-like (7)(8). Consequently we report here the results of a Raman spectroscopic study of crystals of linear polyethylene formed in dilute solution and covering a much greater molecular weight range than has been previously studied.

Experimental

Five of the six linear polyethylene fractions used in this work were obtained from Societé Nationale Elf Aquitaine; the other was prepared in this laboratory by liquid/liquid fractionation of Hifax 16 (9). The molecular weight characteristics of the fractions are given in Table 1. Crystallization of 0.1% w/v solutions from p-xylene was

Table 1. Molecular Weights and Experimental Results for Linear Polyethylene Fractions

Sample #	Crystallization Temperature (°C)	M_n x 10^{-3}	M_w x 10^{-3}	Ordered Sequence Length from LAM		Internal Mode Analysis			$(1-\lambda)_{\Delta H}$ (%)
				Most Probable (Å)	Half Height Range (Å)	α_c (%)	α_a (%)	α_b (%)	
1	87	49.5	52.6	127 ± 2	119-135 ± 2	80 ± 3	16 ± 2	4 ± 5	77 ± 4
2	87	107	115	127 ± 2	118-138 ± 2	77 ± 3	14 ± 3	9 ± 6	83 ± 5
3	87	153	161	136 ± 4	125-147 ± 4	78 ± 4	16 ± 3	6 ± 7	69 ± 5$^{(a)}$
4	87	207	225	127 ± 2	117-136 ± 2	78 ± 3	19 ± 3	3 ± 6	69 ± 4
5	87	720	800	134 ± 2	123-139 ± 5	79 ± 4	15 ± 3	6 ± 7	72 ± 4
				128 ± 3$^{(b)}$					
6	87	1,500$^{(c)}$	---	126 ± 2	117-138 ± 2	73 ± 3	18 ± 2	9 ± 5	71 ± 4
5	0	720	800	93 ± 3	81-104 ± 3	68 ± 3	26 ± 3	7 ± 6	66 ± 5

(a) DSC sample possibly contaminated

(b) secondary peak

(c) M_η

carried out as previously described (6). All the fractions were crystallized at an isothermal temperature of 87°C ± 0.1°C. Fraction 5 was also crystallized by quenching a dilute solution to 0°C.

Raman LAM spectra were recorded in the range 10-60 Δcm^{-1} using a SPEX 1403 double monochromator equipped with gratings ruled at 2,400 lines mm^{-1}, controlled by a SPEX Scamp. Solution crystals packed into a thin walled capillary tube were illuminated by the beam from an argon ion laser operating at 514.5 nm. Plasma lines were removed from the laser beam using a pre-monochromator. The power at the sample was 50-150 mW with the scattered light being collected at right angles to the exciting beam. A spectral slit width of 1 cm^{-1} was used in all cases. All LAM peaks were superimposed on the Rayleigh wing of the exciting line. A baseline was drawn under each peak by hand. The data was analyzed according to the method of Snyder and Scherer (10) to yield a straight chain length distribution. A value of 2.9 x 10^{11} Nm^{-2} was used for the elastic modulus of the ordered (all trans) polyethylene chain (11).

Raman internal modes were recorded in the range 950-1550 Δcm^{-1} on a SPEX 1403 double monochromator spectrometer equipped with gratings ruled at 1,800 lines mm^{-1}, controlled by a SPEX Datamate. A spectral slit width of 2.5 cm^{-1} was used in all cases. Other conditions were similar to those used for recording LAM spectra. A typical internal mode spectrum is shown in Figure 1a. These spectra were analyzed, as described in the literature, to yield the fractions of ordered (crystalline), disordered (isotropic) and partially ordered interfacial material (α_c, α_a and α_b respectively) (7)(8). We have computerized this method to remove any subjectivity from the analysis. In this procedure the background is first removed by subtracting a pedestal of varying height from the raw data as shown in Figure 1a to yield the spectrum shown in Figure 1b. A spectrum of molten disordered high molecular weight linear polyethylene at 150°C ± 2°C, as shown in Figure 1c, is scaled to match the spectrum under investigation using the trailing edge of the CH_2 twisting band at 1294 Δcm^{-1} for comparison, as shown in Figure 1d. The ratio of the areas of the CH_2 twisting band in the disordered spectrum to that of the total CH_2 twisting band in the partially ordered spectrum yields the fraction of disordered material (α_a) directly. The CH_2 twisting region of the spectrum was chosen for the calculation of α_a because the shape and intensity of the disordered CH_2 twisting band remain constant with temperature (7)(8) permitting direct comparison with the molten spectrum. The very broad C-C stretching band at ≈1080 Δcm^{-1} was found to vary in shape and height depending on crystallization conditions and hence was unsuitable for computer analysis. The scaled disordered spectrum is subtracted from the sample spectrum to yield the spectral components due to the crystalline and partially ordered regions. The CH_2 bending band at 1416 Δcm^{-1} is due solely to the crystalline component so that the area of this band can be used to calculate α_c, after subtraction of the disordered spectrum to yield the spectrum as shown in Fig. 1e. The area of the 1416 Δcm^{-1} band is

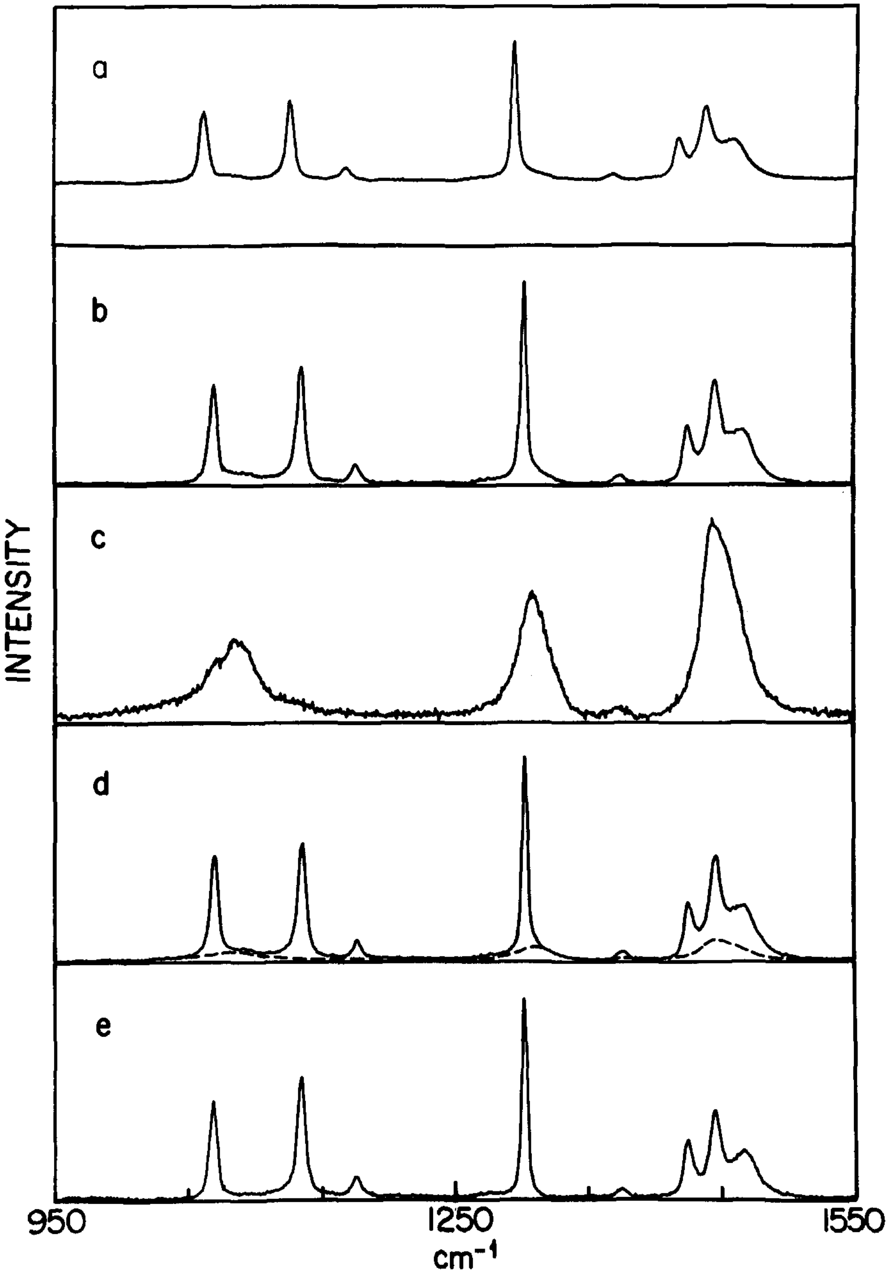

Figure 1 Steps involved in Raman internal mode analysis

determined by integrating from 1400 Δcm^{-1} to the bandhead then doubling the result (7). This area is divided by the original area of the CH_2 twisting region multiplied by a factor of 0.46 (7)(8) to yield the fraction of the sample in the crystalline phase (α_c). The fraction of partially ordered material (α_b) is given by $\alpha_b = 1 - (\alpha_c + \alpha_a)$. The values of α_a, α_b and α_c determined by computer analysis compare favorably (within experimental error) with those determined by deconvolution of the spectra by eye.

Enthalpies of fusion were determined with a Perkin-Elmer DSC-2B scanning calorimeter. Sample masses of about 1-2 mg were scanned from 300-450°K at the heating rate of 10°C min^{-1}. Indium was used as the calibrant for the enthalpy. Peak areas were obtained by planimetry after drawing a straight baseline from the onset of melting to the point at which the sample becomes wholly molten. Crystallinities were calculated using an enthalpy of fusion of 69 calories g^{-1} for a perfect polyethylene crystal (12).

Results and Discussion

The results of the LAM analysis for the isothermally crystallized specimens are given in Table 1 and illustrated in Figure 2. It is readily apparent that these crystallites have relatively narrow size distributions and the ordered sequence lengths are independent of molecular weight. The most probable ordered sequence length is 127 ± 3 Å which is in good agreement with previous results (6)(13). To determine the lamellar core thickness the chain tilt must be known. Two values are available for solution crystals of whole polymers formed close to the temperature used in this study, 25 ±2 from Baltá Calleja *et al* (14) and 30 ± 2° from Folkes *et al* (15). (It is not clear from this paper how the value of the chain tilt was determined.) Using these values, core

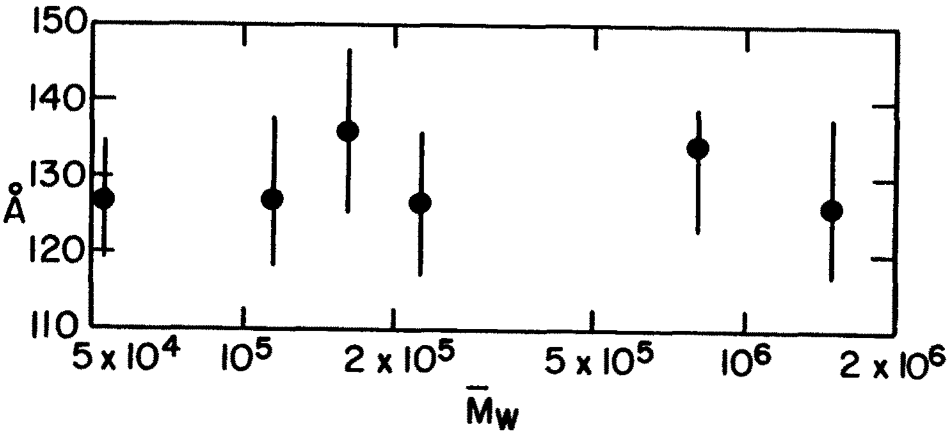

Figure 2 Plot of ordered sequence length from LAM against $\bar{M}_w$. Bars show half height range.

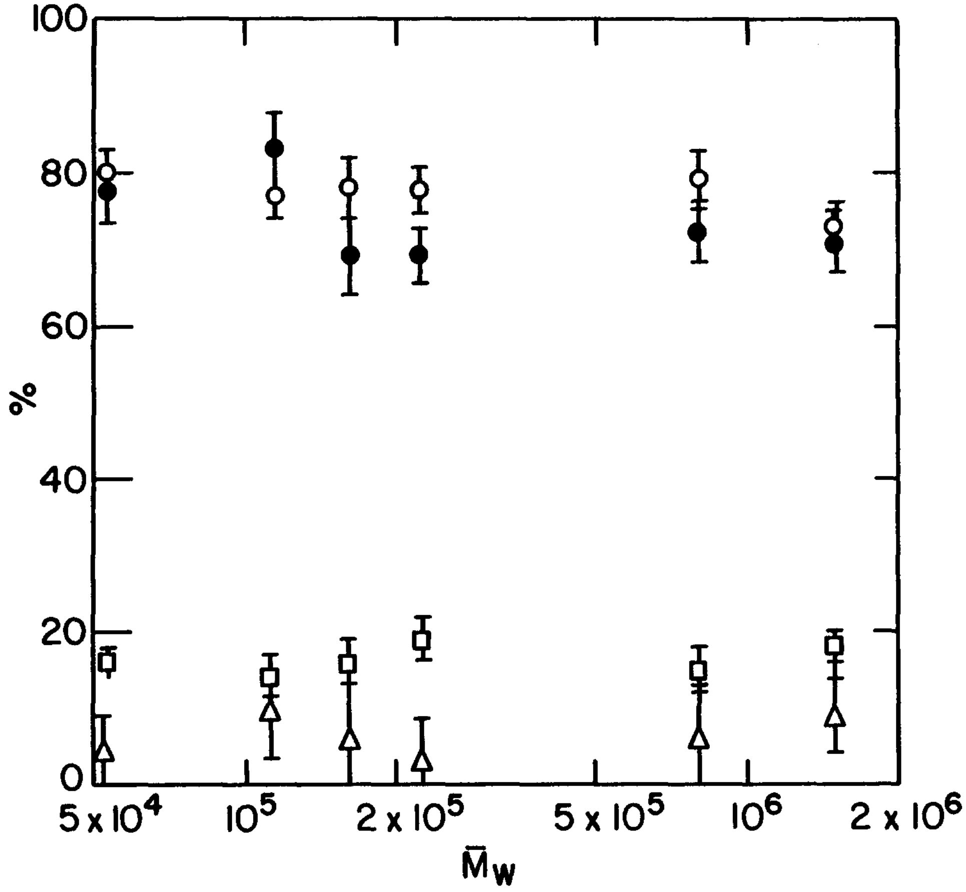

Figure 3 Results of Raman internal mode and DSC analysis. ○ α_c; □ α_a; △ α_b; ● $(1-\lambda)_{\Delta H}$

thicknesses of 115 ± 6 Å and 110 ± 6 Å respectively are obtained. From small angle x-ray scattering studies (5)(9) a periodicity of 133 ± 2 Å is obtained for polyethylene solution crystals formed at 87°C. A comparison of the core thickness with the periodicity indicates that there is an overlayer of 9.5 ± 4 Å or 11.5 ± 4 Å on each side of the lamellar core. The ratio of core thickness to periodicity yields the fraction of crystalline material in the sample which is 0.86 ± 0.05 or 0.83 ± 0.05, depending on the tilt angle.

The Raman internal mode spectra and differential scanning calorimetry give the results of Table 1 and Figure 3. The values of $(1-\lambda)_{\Delta H}$ and α_c, for all the samples, are in close agreement with one another and are about 0.76 ± 0.05. The invariance of $(1-\lambda)_{\Delta H}$ and α_c with molecular weight is in agreement with Glotin et al (13) but contrary to the results of Hamada et al (16)(17). These crystallinity measurements indicate the existence of a substantial amount of disordered material as previously reported by other methods (1)(2)(3). Moreover, the degree of crystallinity calculated from the core thickness and periodicity, for isothermal crystals, agrees with that calculated from internal modes and enthalpy. The small differences may be due to the chain tilt angle. To bring the values into agreement a tilt angle of 37 ± 2° would be required.

The values of the ordered sequence length and degree of crystallinity for the sample quenched to 0°C are lower than for the isothermally crystallized samples. The long period for a similar sample was found to be 103 ± 3 Å (5). To reconcile the periodicity with extended chain length and degree of crystallinity would require a chain tilt of 42 ± 4°. Such an angle would appear to be excessive in the light of the work of Folkes *et al* (15). However, tilt angles of this order have been deduced for low molecular weight linear polyethylene rapidly crystallized from the melt (18).

Both types of Raman spectra demonstrate that the crystallite structure is invariant with molecular weight over the wide range studied. They support similar conclusions reached by other techniques. The rather large non-crystalline overlayer that is found indicates that crystallinity is far from complete. A substantial portion of this overlayer is isotropic; the interfacial region is relatively small for these homopolymers in accord with theoretical expectation (19). When cognizance is taken of chain tilt and level of crystallinity good agreement is obtained between the Raman LAM and the small-angle x-ray periodicity. When these factors are taken into account it is not necessary to develop complex theoretical interpretations for the polyethylene LAM.

Acknowledgments

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