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Order in nascent polyethylene

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Nascent polyethylenes of the high density and linear low density types prepared by gas phase polymerization, together with a series of nascent high density polyethylenes prepared by the slurry process, have been examined by X-ray diffraction, inelastic neutron scattering and Raman spectroscopy. The X-ray diffraction data and inelastic neutron scattering spectra show that the degree of crystallinity is smaller in the nascent samples than is commonly found in melt-crystallized materials. Low frequency Raman spectroscopy shows that the lamellar thickness is also smaller than usual. Melting and resolidification of the nascent, gas phase polymerized polyethylenes result in materials that more closely resemble the melt-crystallized products. The implications of the results are discussed as regards the crystallization process. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The various aspects of the order present in polyethylene have been the subject of a very large number of studies utilizing a wide variety of techniques[1]. Although many of the samples so examined have been prepared using carefully controlled conditions, typified by slow crystallization from dilute solutions, or by the rigorous annealing of melt-crystallized specimens, the polymers in question are usually commercial materials that have previously been subjected to processing operations. These may well impose a prior thermal or mechanical history that is of some consequence. It is clearly of considerable value to examine nascent polyethylene, particularly materials prepared by gas phase or slurry polymerization during which the polymer is always at temperatures significantly below its melting range. This should eliminate a number of largely extraneous factors that may influence the crystallinity and lamellar structure.

Surprisingly, nascent polyethylene samples have attracted little attention, presumably because they are not readily available. Blais and Manley[2] examined nascent polyethylene samples prepared as a slurry in aromatic solvents, such as toluene, at temperatures well below the melting point of the polymer using a Ziegler–Natta-type catalyst. The materials, which were presumably near-linear, were examined by optical and electron microscopy and by X-ray and electron diffraction. The electron microscopic study in particular showed the presence of many fibrils 200–1000 Å (1 Å = 0.1 nm) in width and of indefinite length. These fibrils contained lamellae running perpendicular to their length. Additionally, the X-ray and electron diffraction studies suggest that the molecules are folded within the lamellae, in a manner analogous to conventional single crystals of polyethylene.

Ottani *et al.*[3] investigated a series of nascent polyethylenes prepared by slurry and gas phase routes at 30, 60 and 85°C. Using wide angle X-ray scattering (WAXS), they were able to show that at the lower polymerization temperatures, a small proportion of monoclinic polyethylene was present in addition to the orthorhombic phase.

Previous work has concentrated on the morphology and crystal structure of the polymer. The purpose of the present work is two-fold; to examine high density and linear low density polymers prepared by the gas phase route, and to study several nascent polymers prepared at different polymerization temperatures in a slurry process.

The slurry method of polymerization, from the point of view of polymer structure, has the potential drawback that the polymer morphology may be influenced, to a degree at least, by the fact that monomer molecules are present in the solution phase until they become involved in the polymerization process. It is therefore of particular

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interest to examine polymers prepared by gas phase polymerization, where secondary influencing factors should be substantially absent.

EXPERIMENTAL

The two experimental gas phase polymers were prepared at 85°C. The high density material contained roughly one methyl branch per 1000 carbon atoms, and the linear low density polymer had 18 ethyl branches per 1000 carbon atoms. The four experimental slurry process linear ethylene homopolymers were prepared at 80, 90, 102 and 109°C, respectively.

The X-ray diffraction measurements for crystallinity determinations were made on a Philips vertical X-ray diffractometer using CuKα radiation. The inelastic neutron scattering (INS) spectra of the two gas phase polymers were recorded at 30 K using the high resolution broad band spectrometer TFXA[4] at the ISIS pulsed spallation neutron source at the Rutherford Appleton Laboratory, Chilton, UK. TFXA offers high resolution, $\sim 2\%$ $\Delta E/E$ between 16 and 4000 cm^{-1}. Low frequency Raman spectra (5–100 cm^{-1}) were recorded with an APL 38 spectrometer using the 514.5 nm line from an argon ion laser for excitation. In each case the peak maximum of the longitudinal acoustic mode was corrected by use of the Boltzmann factor $[1 - \exp(-hvc/kT)]$. The lamellar thickness was then derived from the corrected frequency through the equation[5]

$$v = (E_c/\rho)^{1/2}(2cL)^{-1}$$

where v is the corrected frequency, E_c is the Young's modulus (2.9×10^{-11} N m^{-2}), ρ is the density (taken as 970 kg m^{-3} for the high density polymers and 940 kg m^{-3} for the linear low density polymers; these values are correct to 1% and lie within the indicated error bars in *Figure 2*). c is the speed of light and L is the lamellar thickness.

RESULTS AND DISCUSSION

The X-ray diffraction measurements gave a crystallinity value of 53% for the nascent high density polymer, whereas the material in the melt-crystallized form has a crystallinity of about 70–75%. The increase in crystallinity is also supported by the INS spectra. *Figure 1a* shows the spectrum of the nascent polymer, *Figure 1b* the spectrum of the polymer after melting and *Figure 1c* the difference spectrum. The region shown is where the external modes of the polymer occur, i.e. those due to vibrations of the entire chain in the unit cell. The INS spectrum is richer than the infra-red or Raman spectrum because there are no selection rules in INS spectroscopy; hence, both optical and acoustic modes are observed. It can be seen from the difference spectrum (*Figure 1c*) that there is an increase in intensity of the sharp features, as would be expected for an increase in crystallinity. The nascent powder gives a reasonably sharp longitudinal acoustic mode peak, the frequency of which indicates a lamellar thickness of 182 Å. After melting and resolidification of the sample *in-situ*, the lamellar thickness rose to 206 Å.

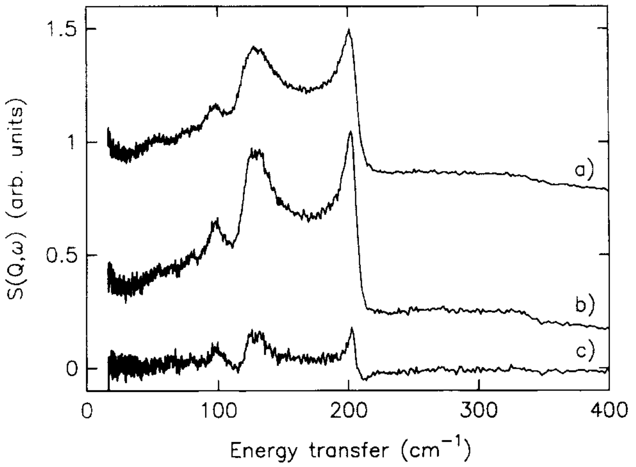

Figure 1 INS spectra of (a) the nascent polymer and (b) the polymer after melting; part (c) shows the difference spectrum. The spectra have been normalized to the same total mass of sample, but the spectrum in (a) is displaced vertically by 0.5 unit for clarity

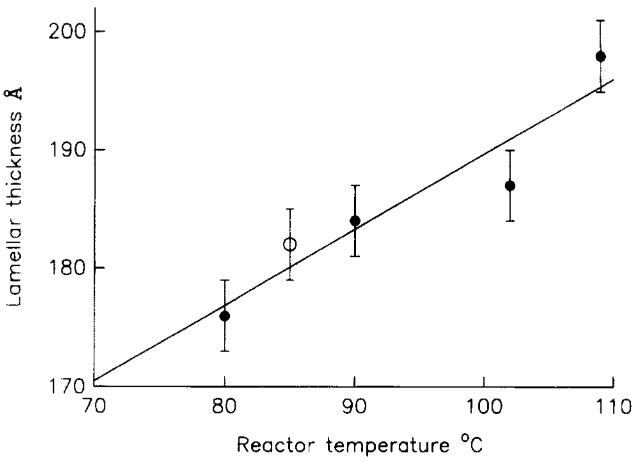

Figure 2 Variation of lamellar thickness with polymerization temperature. The filled circles are for the slurry process polymers and the open circle is for the linear polymer prepared in the gas phase

The results for the nascent linear polymer of low density type prepared in the gas phase showed a similar pattern. The ethyl-branched low density polymer shows a considerable difference between the nascent and melt-crystallized forms. The X-ray diffraction value for the crystallinity of the nascent material is 30%, in contrast to about 45% for the melt-crystallized form. From the low frequency Raman spectrum it is difficult to determine the lamellar thickness better than semiquantitatively, because the longitudinal acoustic mode is extremely broad both for the nascent powder and after *in situ* melting and resolidification. Approximate values in the two cases are 108 and 146 Å, respectively, and the breadth of the two peaks indicates a wide distribution of lamellar thicknesses. The INS spectra were similar to those shown in *Figure 1*, and again showed an increase in the features belonging to the crystalline region.

These results may reasonably be interpreted in terms of the disruptive influence of the ethyl branches, present to the extent of 18 per 1000 carbon atoms. Earlier degradation studies with nitric acid have shown that these branches are not readily accommodated in the crystalline phase[6] when the crystallization process occurs under relatively non-constrained conditions. This should be the case with direct polymerization from the vapour phase. However, if the branches are randomly distributed, it follows that, on average, the distance between consecutive branches will be about 70 Å, and if substantial exclusion from the lamellae occurs a minimum lamellar thickness of this magnitude is to be expected. Crystallization from the melt, with the conditions used during the present work, is a relatively rapid process, leading to constrained conditions, and the incorporation of some branches into the lattice is then quite possible. If chain folding is not constrained by the need to exclude all branches from the lattice, it is easy to envisage that the lamellae will be somewhat thicker, in line with the experimental observations. Furthermore, the conditions used here would allow lamellar thickening of the melt-crystallized samples. All the experimental evidence shows that the nascent polymers are less crystalline and have thinner lamellae than the materials after melting and resolidification, i.e. the conventionally encountered forms.

The measurements on the four nascent polymers prepared in the slurry process also shed light on the crystallization process. The lamellar thicknesses, determined from the Raman longitudinal acoustic mode, are plotted in *Figure 2* with the result from the one gas phase ethylene homopolymer. Despite the very considerable differences in the catalysts used and the molecular weights and molecular weight distributions of the products, there is a very clear trend for lamellar thickness to increase as polymerization temperature is increased, with the result from the one gas phase polymer lying within the experimental scatter. This last result suggests that the parameters that govern chain folding in ethylene homopolymers made at a given temperature may be similar for the gas phase and slurry processes.

The kinetic theory of crystallization[7] predicts that the lamellar thickness should be inversely proportional to the degree of supercooling, and this has been confirmed by Barham *et al.*[8] both in the case of melt and solution crystallization using a fractionated polyethylene with $M_w/M_n = 1.14$. It has been shown[8] that the initial fold length obtained on melt crystallization before any lamellar thickening has taken place is very similar to the fold length found on solution crystallization at the same temperature. If polymerization temperature is regarded as equivalent to crystallization temperature, the present results from the nascent polyethylene (*Figure 2*) follow a similar trend to the results obtained by Barham *et al.*, but the lamellar thicknesses of the nascent powders are typically some 50–70% greater than the initial fold lengths noted by Barham *et al.* for melt-crystallized and solution-crystallized samples. The reasons for these discrepancies are not clear. One possible reason is that the balances of factors which determine the point at which chain folding is energetically favourable differ for the formation of nascent polymer in the gas phase or from solution phase monomer in the slurry process on the one hand and for crystallization from solution or initial crystallization from the melt on the other hand. An alternative explanation is that appreciable lamellar thickening may already have taken place at the temperature of polymerization used for polyethylene in the slurry process and the gas phase.

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REFERENCES

1 *Faraday Discuss. Chem. Soc.* 1979, **68**
2 Blais, P. and Manley, R. St. J. *J. Polym. Sci. (A-1)*, 1968, **6**, 291
3 Ottani, S., Wagner, B. E. and Porter, R. S. *Polym. Commun.* 1990, **31**, 370
4 Penfold, J. and Tomkinson, J.'The ISIS Time Focused Crystal Spectrometer, TFXA', RAL-82-038, Rutherford Appleton Laboratory, 1982
5 Hendra, P. J., Peacock, A. J. and Willis, H. A. *Polymer* 1987, **28**, 705
6 France, C. N., Hendra, P. J., Maddams, W. F. and Willis, H. A. *Polymer* 1987, **28, 710**
7 Hoffman, J. D., Davies, G. T. and Lauritzen, J. L. in 'Treatise on Solid State Chemistry' (Ed. N. R. Hannay), Vol. 3, Plenum Press, New York, 1976, p. 93
8 Barham, P. J., Chivers, R. A., Keller, A., Martinez-Salazar, J. and Organ, S. J. *J. Mater. Sci*, 1985, **20**, 1625