Incorporation of branches into the crystal lattice during the solidification of linear low density polyethylene

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Two linear low density polyethylene (LLDPE) samples containing n-hexyl and iso-butyl branches have been etched with fuming nitric acid and the products of the etching analysed by ^{13}C n.m.r. spectroscopy to determine the concentration of branches. Different weight loss behaviour was observed with the two LLDPEs; the weight of material lost during etching plateaued at 50% with a constant low crystallinity for the iso-butyl material while the n-hexyl continued to lose weight and the residue improve in crystallinity. The residual concentration of branches was 10 and 20% of the initial concentration and clearly the two types of branches were incorporated into the crystalline lattice to different extents. The parent copolymers were fractionated by degree of branching and a comparison made between the two sets of fractions to determine their melting points, degree of crystallinity and unit cell volume. In general it was concluded that more of the hexyl branches are incorporated than the iso-butyl at the same branch content, and that chain flexibility is an important parameter in determining the extent of exclusion of the branches.

(Keywords: linear low density polyethylene; branching; hexyl; iso-butyl; n.m.r.; d.s.c.)

INTRODUCTION

The physical properties of linear low density polyethylene (LLDPE) depend on the chemical nature of the branches, their concentration and the distribution of α-alkene comonomer units along the chain. The α-alkene comonomer produces a uniform short chain branch and this substantially alters the polymer properties from those of high pressure low density material. The location of the branch points after crystallization, i.e. within the crystals or in the amorphous regions, is unclear. Early results have shown[1] that copolymers containing methyl branches alone have significantly higher melting points than those with longer alkyl branches. This must reflect the methyl groups co-crystallizing with the ethylene units. Ethyl branches in turn have been found to be included partially within the crystal lattice[2]. Others[3] have concluded that branches with larger volumes than ethyl, are excluded from the crystalline regions on the basis of the requirement for a close packed structure, yet others[4] have argued that propyl, vinyl acetate and larger branches are included to small extent within the crystal lattice. Conclusions on the extent of inclusion of the co-units also differ considerably with each set of workers. Martinez *et al.*[5] have shown that the amount included within the lattice during isothermal crystallization was as much as 10–20% of the alkyl branch. In contrast, it has been[6] reported that few of the ethyl branches were incorporated into the crystal, and because of the large differences in the volume of the side groups compared to that of the ethylene units they cannot enter the lattice to any measurable extent.

This paper investigates whether bulky side groups, such as n-hexyl and iso-butyl are incorporated into the crystal lattice during the crystallization of LLDPE. Differential scanning calorimetry (d.s.c.), nuclear magnetic resonance spectroscopy (n.m.r.) and wide angle X-ray scattering (WAXS) were used to determine the site of the branches.

EXPERIMENTAL

Two LLDPE samples were used containing octene-1 and 4-methyl-pentene-1 as comonomers. The octene copolymer was obtained from Dow Chemical Co. Ltd as a 4.2 mol% copolymer, density 920 kg m^{-3}, with number- and weight-average molar masses of 16.9 and 207 kg, respectively. The 4-MP copolymer was supplied by Mitsui Petrochemicals as a 1.9 mol% copolymer, density 924 kg m^{-3}, with number- and weight-average molar masses 36.2 and 169 kg respectively. These resins were fractionated by degree of branching using temperature rising elution fractionation, TREF, adopting the procedure outlined before[7].

Fuming nitric acid etching was carried out on film samples prepared by moulding into a flat sheet with a heated hydraulic press, and quenching in iced water. Samples (3 g) were etched in contact with fuming nitric acid at 45°C in sealed containers, the samples being kept below the liquid surface with glass fibre. The reaction products were washed repeatedly with water and then methanol before drying to constant weight.

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Melting and crystallization rate studies were carried out using a Perkin-Elmer differential scanning calorimeter, model 2, interfaced to a BBC Master microprocessor. The calorimeter baseline was stored separately under identical conditions, and subsequently subtracted from the calorimeter response of the samples and displayed heat flow response against temperature of the samples alone. The temperature read-out of the calorimeter was calibrated from the melting point (m.p.) of ultrapure indium, tin and lead and zone-refined stearic acid. Thermal lag corrections were also made by extrapolating m.p.s to zero heating rate. The calorimeter's thermal response was calibrated from the enthalpy of fusion of indium.

WAXS measurements were made using a Picker automated powder diffractometer, and data collection was made using a Phillips PW1710 diffractometer, programmed remotely by a Brother PCAT microcomputer. The data were then transferred to an IBM mainframe computer for further analysis. Flat samples, 20 x 30 x 0.1 mm, were moulded on the hydraulic press and mounted directly into the specimen holder. The diffractometer was calibrated for position by using a quartz standard. The influence of sample transparency on peak position was the same as discussed by Langford and Wilson[8].

^{13}C n.m.r. spectra were measured using a Jeol GX-270 MHz Fourier transform spectrometer at 120°C in o-dichlorobenzene solution with 5% deuterated toluene as an internal lock. Measuring conditions were pulse width 10 μs, pulse interval 15 s, pulse angle 45°, spectra width 25000 Hz and number of scans 36000. Peak assignments and branch concentration calculations were as described by Randall[9].

RESULTS AND DISCUSSION

Etching studies

Fuming nitric acid has been widely used to remove the amorphous regions preferentially and leave the lamellae stems. Unfractionated LLDPE samples were etched at 45°C and the fractional weight change followed with time, see *Figure 1*. Both LLDPE systems initially followed the same rate of loss of material but the iso-butyl continued up to a limit of 50% and then remained constant over the remaining period. The hexyl copolymer continued to lose weight but at a slower rate and this continued over the total etching period of 450 h eventually exceeding the weight loss of the iso-butyl branched material.

The washed solid residue from etching was examined by d.s.c. and the relative change in crystallinity over that of the initial polymer determined by ratioing the enthalpies of fusions. This can be seen in *Figure 2* as a function of etching time. The hexyl branched material continued to increase in apparent crystallinity during the total etching process while that of the iso-butyl branched material plateaued after 100 h following the same trend as weight loss, from which it is apparent that in n-hexyl branched material etching is continuing to remove the less crystalline material at a constant rate to produce a highly crystalline product. In contrast the iso-butyl branched material loses the amorphous content rapidly and the product is poorly crystalline.

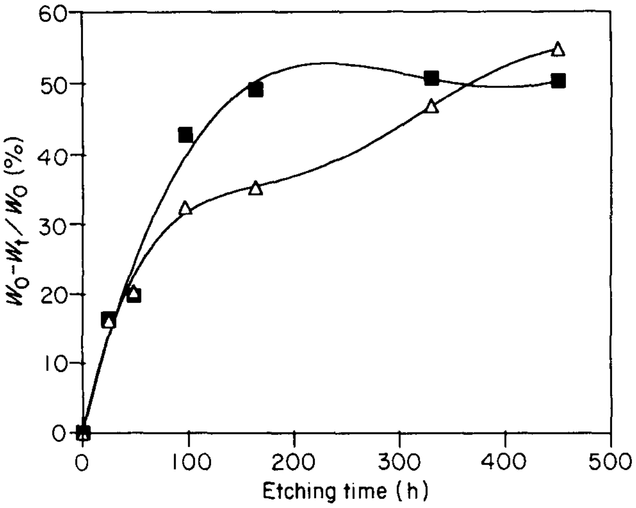

Figure 1 Percentage weight loss of LLDPE with nitric acid etching time: (■) iso-butyl and (△) hexyl branched materials

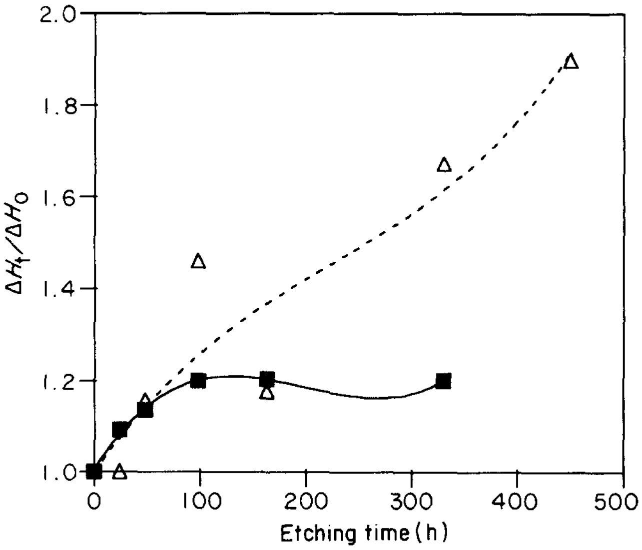

Figure 2 Variation of heat of fusion of the LLDPE samples with etching time: (■) iso-butyl and (△) hexyl branched materials

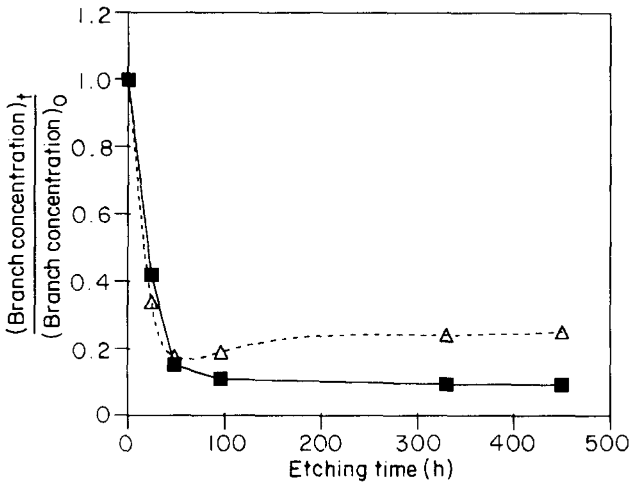

Figure 3 Change in branch content with etching time: (■) iso-butyl and (△) hexyl branched materials

N.m.r. spectroscopic analysis of the products obtained after etching showed (*Figure 3*) that in both systems 80% of the branches are lost within the first 100 h and thereafter the branch content is independent of the extent of etching. This residual content, i.e. 10% in the case of the iso-butyl and 20% in the case of the n-hexyl must be incorporated within the crystalline regions. The reduction in weight on etching the hexyl branched material must be due to progressive attack of the crystalline regions.

Both d.s.c. and ^{13}C n.m.r. spectroscopy show that the two bulky branches are incorporated into the crystal but to different extents. The iso-butyl branches are more readily removed which implies they are more readily accessible to the etchant either in amorphous regions or on the lateral surface of the crystals. This interpretation is, however, complicated by the wide distribution of branches within the polymer chain and also variations in molecular weight distribution. The two systems have different degrees of branching, 4.2 and 1.9 mol% and this will alter lamellar size distribution and ease of attack by nitric acid. Accordingly it was decided to fractionate the two copolymers for degree of branching, and make a comparison of behaviour on branch content alone. However, since etching and subsequent analysis required considerable amounts of material not available from fractionation procedures other test methods were adopted in characterizing the fractions.

Melting studies

The unfractionated LLDPE samples were characterized by complex melting behaviour with multiple endotherms. The heterogeneity in branch distribution and also molecular weight determines the lamellae thickness distribution and subsequent thermal behaviour. If the branches are excluded from the crystalline regions, the highest melting endotherm can be attributed to the thicker lamellae and the lower to the thinner lamellae, both limited by the ethylene sequences between branches. If the branches are incorporated within the crystals then the melting profile reflects increasing disorder within the lamellae. In contrast fractionated samples exhibit a much narrower melting region, which increases to higher temperature with decreasing branch concentration, and also a single peak endotherm (*Figure 4*).

The crystallinity of the TREF samples was measured from the enthalpy of fusion, assuming 290 J g^{-1} for the totally crystalline polyethylene. For the same branch content, the hexyl and iso-butyl branched material had similar degrees of crystallinity but these were very much lower than the corresponding ethyl branched material. The differences in crystallinity between the hexyl and iso-butyl samples are not marked (*Figure 5*).

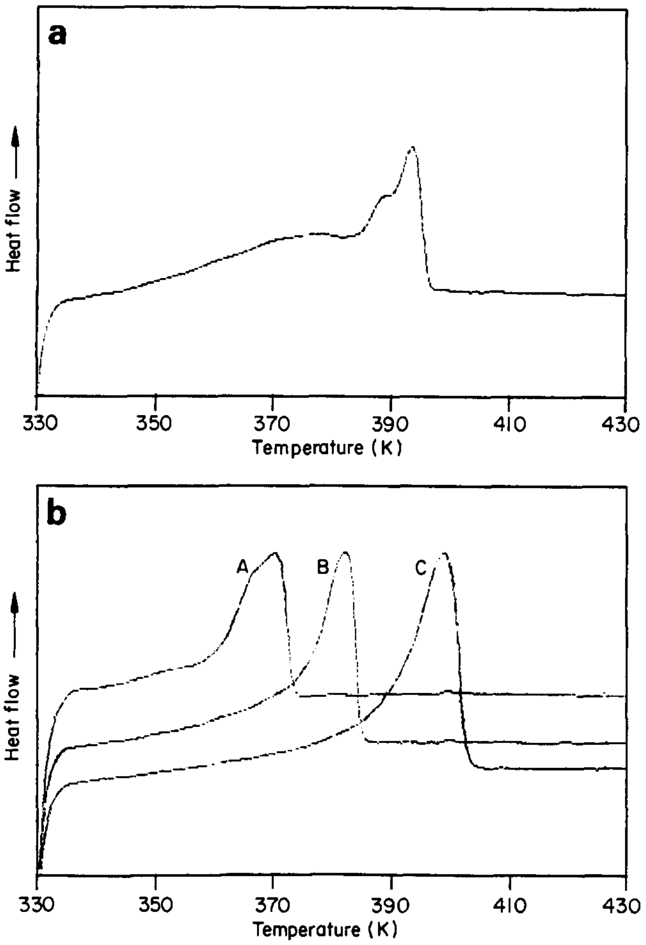

Figure 4 D.s.c. melting endotherms: (a) unfractionated bulk hexyl branched polymer and (b) fractions eluted at (A) 55°C, (B) 75°C and (C) 120°C

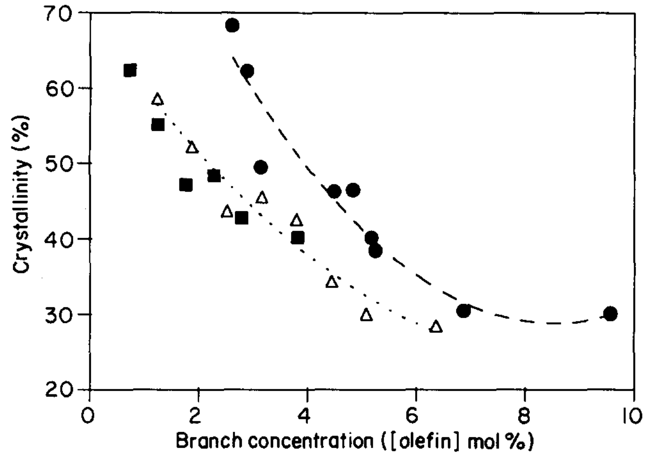

Figure 5 Variation of the per cent crystallinity with branch concentration: (△) hexyl, (■) iso-butyl and (●) ethyl branched samples

The melting temperature of the copolymers is related to the extent of comonomer units incorporated into the crystal lattice. If the mole fraction of defects within the crystal is x, the m.p. of the crystal, T_m, is given by [10]:

$$1/T_m - 1/T_m^0 = (R/\Delta H)(\sigma_e \beta x / R T^0_{m(x)}) + (1-\beta x)\ln[(1-\beta x)/(1-x)] + \beta x \ln(\beta) \tag{1}$$

By expanding the logarithm and setting $x \ll 1$ for the LLDPE samples, equation (1) reduces to:

$$1/T_m - 1/T_m^0 = R/\Delta H \zeta x \tag{2}$$

in which:

$$\zeta = \sigma_e \beta / R T^0_{m(x)} + (1-\beta) + \beta \ln(\beta) \tag{3}$$

where: $T^0_{m(x)}$ and T^0_m are the equilibrium melting points of the defect and perfect crystals, respectively; σ_e is the excess lateral surface free energy associated with the defect crystal; ΔH is the enthalpy of fusion of an infinite crystal with $x=0$; x is the mole fraction of non-crystallizable units; and β is a parameter which characterizes the degree of incorporation of the branches into the crystal, clearly $0 < \beta < 1.0$.

Using values of σ_e and T^0_m separately determined, the plots of m.p. depression against mole fraction of branches for hexyl and iso-butyl groups in LLDPE fractions are shown in *Figure 6*. Linear relationships were obtained consistent with equation (2). The slopes and the β values are listed in *Table 1*. The corresponding dependence for both the Flory exclusion, $\beta = 0$, and the uniform inclusion models, $\beta = 1.0$, are included for

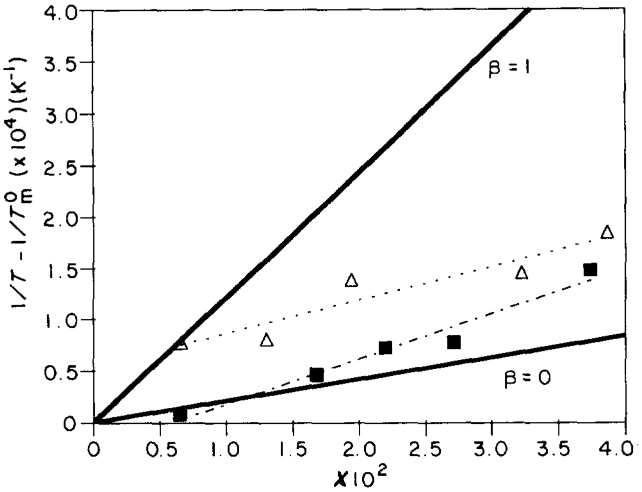

Figure 6 Depression of the equilibrium melting point as a function of mole fraction of branches: (△) hexyl and (■) iso-butyl branched. $\gamma = 83.6$ kJ mol^{-1} in the case of $\beta = 1.0$

Table 1 β and τ_1 values for the branch types

Type	iso-Butyl	n-Hexyl
β	0.34	0.42
τ_1 $(s^{-1})^a$	2.96	8.53

[a] τ_1 is the ^{13}C n.m.r. spin-lattice relaxation time for the methyl C atom on the branch

comparison. It is apparent that both branch types show some incorporation into the crystal lattice but to a different extent. Associated with the incorporation of branch sites are lattice distortions and an increase in the average unit cell dimension, as well as a decrease in enthalpy and a reduction in the m.p.

A proportion of the branches are excluded from the crystal lattice. More of the iso-butyl branches are excluded from the crystal lattice than the n-hexyl, as seen from their relative β values, 0.34 for iso-butyl and 0.42 for hexyl and this is consistent with iso-butyl being a bulky group while the n-hexyl is flexible rather than bulky.

Studies were also carried out by WAXS on the unit cell dimensions of the LLDPE fractions, and the cell volume showed that the incorporation of the bulkier iso-butyl groups produces an apparently larger change than the hexyl group particularly if allowances are made for the smaller fraction incorporated into the lattice, as shown by the depression of the m.p. The hexyl branch has little effect in altering the unit cell volume. This must reflect its closer similarity to the polyethylene units than the iso-butyl unit such that it can be incorporated into the lattice with little distortion. The WAXS results are consistent with the progressive incorporation of branch sites into the crystal lattice.

According to Alamo *et al.*[2] the dominant factor controlling the exclusion of the branch from the crystal lattice during solidification is the molecular volume of the group. The results of the present study rather suggest that the flexibility of the branch must also be taken into account. The more flexible n-alkane units can change conformation by rotation around C–C bonds and adopt the planar zig-zag of the polyethylene molecule in the crystal with little disruption except at the branch C atom. The bulkier, iso-butyl branch, however, cannot avoid the increased interaction energy if incorporated into the lattice. Although iso-butyl has a lower molecular volume than the n-hexyl unit, the solution n.m.r. spectra shows that the spin lattice relaxation time, τ_1, of the methyl groups of the branch is smaller for the iso-butyl group than the hexyl (*Table 1*). The terminal methyl group on a linear chain is known to be even longer. This implies that the hexyl branches have a higher degree of freedom than the iso-butyl and that chain flexibility is an important parameter in determining the extent of exclusion of the branch.

It should be appreciated that these conclusions are only relevant for the conditions chosen, i.e. quenched crystallization. The amount of branches incorporated within the crystal lattice will be substantially altered if crystallization occurred at a higher temperature and at a slower rate, so closer to equilibrium conditions. Under equilibrium conditions the branches may be essentially excluded from the crystalline regions.

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