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X-Ray diffraction study of lattice distortions in branched polyethylene rapidly quenched from the melt

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SUMMARY

Unit cell expansion data for branched polyethylene (PE) rapidly quenched from the melt are examined with reference to the level of chain defects incorporated within the crystal lattice. The data presented here complement earlier studies and show that the incorporation of defects, ε_c, after quenching is twice as large as the penetration obtained for slowly cooled samples. The parallel increase of the K-distortions parameter with ε_c is in direct support of the inclusion of a large fraction (40%) of bulky defects (butyl or larger) within the polyethylene lattice.

INTRODUCTION

Previous X-ray diffraction studies, carried out in branched PE containing butyl or longer side groups slowly cooled from the melt, indicate that only a relatively small fraction of these defects (~15-20%) can be accommodated within the crystal lattice (BALTA CALLEJA, GONZALEZ ORTEGA, MARTINEZ SALAZAR, 1978). The interpretation of the expansion of the unit cell with increasing defect penetration was based on the assumption of inclusion of branches within the crystals around 2g1 kinks. The levels of defect incorporation into the lattice were further confirmed from statistical calculations involving a relation between crystallinity and defect content times crystal thicknes (MARTINEZ SALAZAR, BALTA CALLEJA, 1980) and from the increasing level of paracrystalline lattice distortions (MARTINEZ SALAZAR, BALTA CALLEJA, 1980). The number of defects has been further verified from the IR evaluation of the side groups occluded in the crystals after selective chemical removal of the non-crystalline regions (CAGIAO, BALTA CALLEJA, 1982). A recent application of Sanchez and Eby's simplified kinetic approach to equilibrium melting data of these samples similarly led to inclusion values of 10-20% (MARTINEZ SALAZAR, SANCHEZ, BALTA CALLEJA, in press)

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The purpose of the present study is firstly to investigate whether the rate of crystallization may affect substantially the penetration level of these bulky groups within the crystals. For this reason a fast quenching of the samples was adopted in this study(see below) . Secondly we wish to examine to what extent the increasing level of defects in the crystal may affect the degree of lattice distortions as derived from Ruland's method (RULAND, 1961)

EXPERIMENTAL

Materials

A series of PE commercial samples with varying number of side groups (butyl or larger) were investigated in this study. The number of side groups per 100 atoms and the molecular weight, M_w, are presented in Table I. Homogeneization of the samples was carried out by dissolving the polymer pellets in hot p-xylene and subsequent acetone precipitation. The filtered polymer was dried in a vacuum oven at 60°C. The samples were rapidly quenched at -25°C from the melt (160°C) in the form of 300 μm thin films. This fast quenching mode gives rise to well defined single peak melting endotherms (MARTINEZ SALAZAR, SANCHEZ, BALTA CALLEJA, in press)

TABLE I

	sample	$M_w \times 10^{-3}$	ε(%)	ε_c(%)	α(%)	K
1	Lupolen 6011 L	100	0.00	0.00	65	0.65
2	Hostalen GC	50	0.28	0.08	66	0.63
3	Hostalen GF	120	0.70	0.17	63	0.43
4	Epolene C-11	10	1.21	0.54	56	1.04
5	Lupolen KR-1051	51	1.76	0.83	50	1.05
6	Lupolen KR-1032	53	2.53	0.92	47	1.62
7	Lupolen 1810 H	54	3.04	1.12	45	1.44

Techniques

Wide angle X-ray diffractograms were obtained at room temperature (20°C) using Ni filtered CuKα radiation from a tube operating at 40kV and 40mA. The $\underline{a}$ and $\underline{b}$ unit cell parameters were determined from measurements of the 110, 200 and 020 peak positions using a Rigaku powder diffractometer. Si powder was used as a standard. The standard errors in the cell dimensions were about ±0.005 Å.

To calculate the crystallinity, α, and the K-Ruland factor scans between 8-150°2θ, were carried out in the step mode, using 2700 points for each scan. Owing to the very thin samples studied identical divergence and antiscattering slits of 1/2°, 1° and 2° were respectively used in the ranges 8-35°, 30-60° and 55-150°(2θ). The corresponding loss of intensity, increasing with scattering angle, was corrected according to the expression:

$$I_\infty/I_t = 1 - \exp\left(- \frac{2\mu t}{\cos\theta}\right) \qquad |1|$$

where I_∞ represents the maximum intensity for the optimum sample thickness. Monochromatization of the beam was performed by the double Ross filter method (Ni,Co). Analysis of the X-ray profiles was carried out with help of the computer program FF-CRYST described by Vonk, 1973. The program was adapted for its use in a IBM microcomputer. Sample 4 shows a faint b-axis orientation on the film plane. In this case a correction factor for the 110 and 020 reflections was taken into account. The rest of the samples show isotropic X-ray diffraction patterns. Fig. 1 illustrates the plots of R vs S_p^2 for all the investigated samples. Here R is the ratio of the total coherent sccattered intensity to the crystalline intensity measured between the lower limit $s_o = 0.09$ Å^{-1} and the upper integration limit s_p. The intercept of these curves provides the reciprocal value of the crystallinity α and the slope at the origin for the second degree curve fitting gives the value for the K-distortion parameter.

RESULTS AND DISCUSSION

Fig. 2 illustrates the parallel increase of the a and b-axes of the PE unit cell with the overall defect concentration ε. All these bulky defects can be accommodated into the lattice by expansion, mainly, along the a-axis. It is

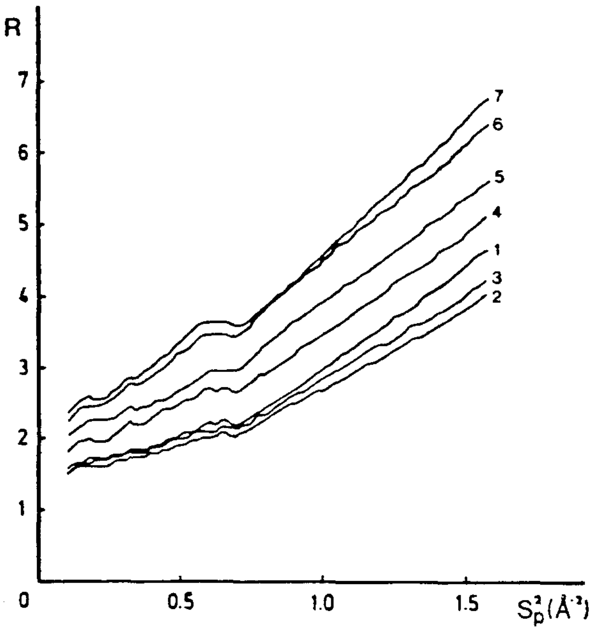

Fig. 1. Plot of R versus Sp^2 for the quenched PE samples with increasing number of defects (see Table I).

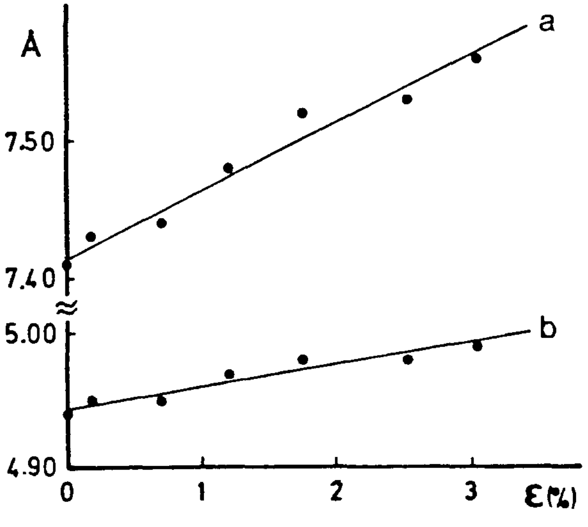

Fig. 2. Expansion of the unit cell dimensions a and b for polyethylene samples quenched at -25°C, as a function of the overall defect concentration.

convenient to define at this point the defect expansion coefficient (similarly to the thermal expansion coefficient) as the rate change in the unit cell parameter with respect to the parameter specified for $\varepsilon=0$:

$$\beta_a = \frac{\Delta a}{\Delta\varepsilon . a_o} \qquad |2|$$

This coefficient defines evidently the capability of a specific type of defect to expand the lattice.

TABLE II

Defect expansion coefficient (β_ax10^{-3})for different groups

side group	slowly cooled	rapidly quenched
methyl, ethyl	10	10
butyl & longer	3.0	6.0
carboxyl	2.6	5.5
ester	2.0	3.5

Table II illustrates comparatively values of β_a for different side groups and two modes of crystallization. In our case (Fig. 2) the expansion of the lattice yields a β_a value of 6x10^{-3}. This means a lattice expansion of 0.6 percent per defect every 100 carbon atoms. It is noteworthy that this rapid mode of crystallization yields an expansion which is twice as that measured when samples are slowly cooled (BALTA CALLEJA, GONZALEZ ORTEGA, MARTINEZ SALAZAR, 1978). Data obtained from the literature for other side-groups such as esters or carboxyl groups (KORTLEVE, TUIJMAN, VONK, 1973) lead to an analogous behaviour showing a larger a-axis expansion for the quenched materials. Only in case of methyl side-groups the rate of crystallization does not affect the defect expansion coefficient (BAKER, MANDELKERN, 1966). However, the small size of these defects induces the largest β_a value, implying the highest level of defect accommodation within the lattice.

In order to offer a quantitative estimate about the level of defects incorporated within the PE lattice we make use of a preceding approach using the concept of defect accommodation within the lattice through generation of 2g1 kinks (BALTA CALLEJA, GONZALEZ ORTEGA, MARTINEZ SALAZAR, 1978). Accordingly the concentration of ε_c defects per 100 carbon atoms incorporated in the lattice is given by: $\varepsilon_c = (V_\varepsilon - V_o) / 4\Delta V$ |3| where V_o and V_ε are the unit cell volumes for the undisturbed lattice ($\varepsilon=0$) and for the lattice with ε defects respectively and $\Delta V = 60$ Å^3 represents the excess volume per kink associated to a CH_2 group in the crystal. Fig. 3 illustrates the notorious increase of ε_c as function of ε for the rapidly quenched samples as compared with data obtained for the PE samples slowly cooled at a rate of 1°C/min. It is clearly seen that the penetration of defects after quenching ($\varepsilon_c/\varepsilon \sim 0.4$), in accordance with kinetic predictions HELFAND and LAURITZEN, 1973), is much larger (twice) than the penetration reached in case of the slowly cooled samples ($\varepsilon_c/\varepsilon \sim 0.2$).

The above interpretation concerning the lattice expansion in terms of a defect penetration within the crystals lies between two extremes: a uniform inclusion of defects, on the one hand, and a complete exclusion of these chain irregularities on the other (BALTA CALLEJA, 1986). If the observed lattice expansion in

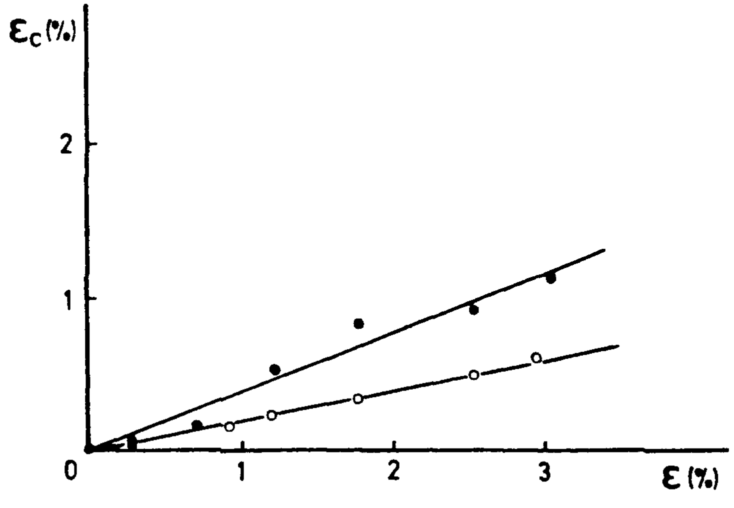

Fig. 3. Defect concentration within the crystals, ε_c, from eq. 3 for the quenched samples (solid symbols) as compared with values obtained for the slowly cooled materials (1°C/min) (open symbols).

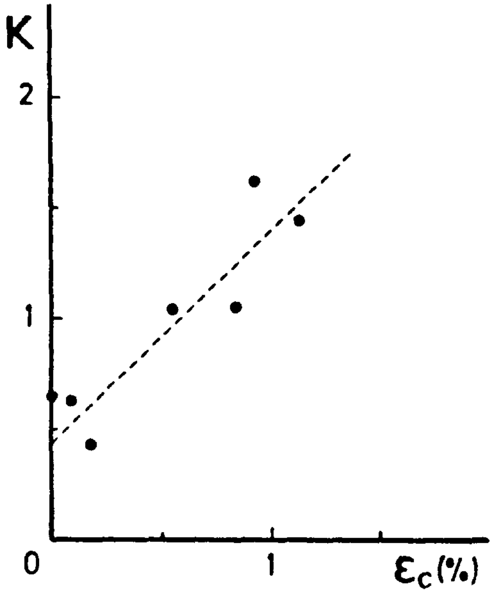

Fig. 4. Correlation of the K-distortion parameter, derived from Fig. 1, with ε_c (eq. 3), for the PE samples quenched at -25°C.

Fig. 2 is connected with the penetration of defects in the crystals one could expect a parallel increase in the emerging lattice distortions. The data of Fig. 1 indicate that the crystallinity α gradually decreases and that the slope of the plot (proportional to K) concurrently increases with increasing number of defects (see Table I). The plot of Fig. 4 supports, indeed, the existing relationship between the derived concentration of incorporated defects within the lattice ε_c and the increasing K-disorder lattice parameter. A similar parallel increase of ε_c and the level of paracrystalline lattice distortions has been previously pointed out (MARTINEZ SALAZAR, BALTA CALLEJA, 1980). The intercept of the plot of Fig. 4 at ε_c=0 yields a value for K close to 0.4, which could be related to the remnant level of kinks within the crystals (PECHHOLD, 1968) with no branches.

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REFERENCES

BALTA CALLEJA, F.J., GONZALEZ ORTEGA, J.C. and MARTINEZ SALAZAR, J.: Polymer 19, 1044 (1978)

BALTA CALLEJA, F.J., in "Morphology of Polymers", W. de Gruyter, Berlin, New York, p. 27 (1986)

BAKER, C.H., MANDELKERN, L.: Polymer 7, 11 (1966)

CAGIAO, M.E., BALTA CALLEJA, F.J.: Macromol. Sci. Phys. B21, 519 (1982)

HELFAND, E. and LAURITZEN Jr. J.I.: Macromolecules, 6, 631 (1973)

KORTLEVE, G., TUIJMAN, A.F. and VONK, C.G.: J. Polymer Sci. A2, 10, 123 (1972)

MARTINEZ SALAZAR, J. and BALTA CALLEJA, F.J.: J. Crystal Growth, 48, 283 (1980)

MARTINEZ SALAZAR, J. and BALTA CALLEJA, F.J.: Polymer Bulletin, 2, 163 (1980)

MARTINEZ SALAZAR, J., SANCHEZ CUESTA, M., BALTA CALLEJA, F.J.: Colloid and Polymer Sci. (in press)

PECHHOLD, W.: Kolloid z.z. Polymere, 228, 1 (1968)

RULAND, W.: Acta Cryst., 14, 1180 (1961)

VONK, C.G.: J. Appl. Cryst., 6, 148 (1973)

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