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On the Inclusion of Chain Defects in the Polyethylene Lattice
A Statistical Approach

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Summary

A simple statistical calculation leads to a relation between crystallinity and concentration of defects (ε) times crystallite thickness yielding the average inclusion of chain defects per crystalline chain segment as an independent parameter. Comparison of X ray crystallinity data for branched isothermically crystallized polyethylene (PE) with buthyl or longer side sequences with our statistical predictions confirms inclusion of up to one defect per 100 carbon atoms (depending on ε) within the crystal lattice. These results are in good agreement with values derived from unit cell expansion measurements.

Introduction

In a previous paper (BALTA CALLEJA, GONZALEZ ORTEGA, MARTINEZ SALAZAR, 1978) we have described a X-ray diffraction study of a series of polyethylenes (PE) with a wide range of chain defect concentrations, ε, (mainly butyl or larger methylene sequences) crystallized from the melt. The obtained concurrent expansion of the lattice unit cell and long period decrease with increasing defect concentration was interpreted in terms of a model which assumes inclusion of a fraction of defects within the lattice, by means of a generation of 2gl kinks. It was concluded that the concentration of defects, ε, within the crystal lattice gradually increases from ~0.05% for ε=0.2% up to ~1% for ε=6.9%. Furthermore the fraction of defects rejected from the lattice is larger than 20% of the total number of defects. These results were also shown to apply quatitatively for the isothermally crystallized PE samples (MARTINEZ SALAZAR and BALTA CALLEJA, 1979). In addition, the increase of lattice distorsions with ε involves the formation of an equilibrium shape of the microparacrystals (HOSEMANN and BALTA CALLEJA, 1979).

In order to verify the validity of our conclusions with regard to the quantitative estimate of the inclusion of defects in the PE lattice, we wish to report a statistical approach which leads to a relationship between crys-

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tallinity and branching ratio times crystal thickness and which depends upon the average number of chain defects per crystalline chain segment. By comparison of X-ray crystallinity data with the crystallinity predicted on the basis of statistical considerations a value for the degree of defect inclusion can be derived.

Experimental

The PE's used in this study, mostly of the low density type, were isothermally crystallized from the melt at $\Delta T \sim 10°C$ following a procedure described in a recent work (MARTINEZ SALAZAR and BALTA CALLEJA 1979). The X-ray diffraction method described by Vonk (1973) was used to determine the percent crystallinity α. The crystal thickness, l, was derived from the X-ray long period, L, assuming the two phase concept $l = L\alpha\rho/\rho_c$ (where ρ and ρ_c are the macroscopic and unit cell densities respectively). The length, L, was obtained from the 1st SAXS maximum using a Rigaku camera with point collimation and Ni filtered Cu Kα radiation. The values of ε, α, l, ρ and ρ_c are collected in Table I.

TABLE I

Sample	ε%	α(%)	l(Å)	ρ(g cm^{-3}) ±0.0005	ρ_c(g cm^{-3})
1	0.19	75.9±0.3	245±8	0.9830	0.9870±0.0005
2	0.70	62.0±1.4	234±6	0.9602	0.9823±0.0005
3	1.76	51.1±0.8	111±7	0.9311	0.976 ±0.001
4	2.63	44.8±1.6	109±4	0.9402	0.9759±0.0007
5	3.04	40.9±0.6	96±8	0.9165	0.971 ±0.001
6	3.61	36.2±0.8	92±4	0.9123	0.975 ±0.002
7	4.77	30.0±3.0	69±3	0.9038	0.970 ±0.001
8	5.34	35.6±0.7	67±4	0.9102	0.970 ±0.001
9	6.90	21.6±3.6	51±3	0.8900	0.964 ±0.001

According to the infrared analysis the chain defects are butyl or longer methylene sequences (RUEDA, BALTA-CALLEJA, HIDALGO 1979). The level of unsaturations is, on the other hand, manifestly lower than that of chain branching (RUEDA, BALTA-CALLEJA and HIDALGO 1974).

Statistical Models

Let $1-\varepsilon$ be the concentration of A crystallizable (CH_2) units and ε the concentration of B non crystallizable units within the polymer chains. Let us further call ν the average number of A and/or B units within a crystalline chain segment. Since the probability that j units in a stem of ν units within the crystal will be B units is given by a binomial distribution,

$$P(j) = \binom{\nu}{j} \varepsilon^{j} (1-\varepsilon)^{\nu-j} \qquad (1)$$

we may define the weight fraction of crystallized polymer segments (crystallinity) as follows: Let us allow all chain segments containing defects up to a certain limiting number of them - say, from zero defects up to a maximum number i - to crystallize. The crystallinity can, then, be defined as the sum:

$$\alpha^{i} = \sum_{j=0}^{i} \alpha_j \quad (2) \quad \text{where} \quad \alpha_j = \frac{P(j)}{\sum_{j=0}^{\nu} (P_j)} \qquad (3)$$

with the normalization condition $\sum_{j=0}^{\nu} P(j) = 1$

Here each α_j value represents the single probability to find a crystalline stem with 0,1,2... or j defects. Since we are dealing with samples isothermally crystallized at low supercooling, we may impose the additional condition that for a given concentration of B units within the crystal α_j assumes a maximum value. Since the different values may not present the same probability to occur,

$$\text{in general,} \quad \alpha^{i} = \sum_{j=0}^{i} \mu_j \alpha_j \quad \text{and} \quad 0 \leq \mu_j \leq 1 \qquad (4)$$

where μ_j is a parameter which can depend upon factors such as crystallization conditions, mechanical treat - ment, etc. For simplicity we shall take here $\mu_j=1$

The fully exclusion of the B units from the crystals represents a particularly simple example (Fig. 1a). In this case the crystalline phase is composed entirely of A units, and eq. 2 takes the form:

$$\alpha^{0} = (1-\varepsilon)^{\nu} = e^{\nu \ln(1-\varepsilon)} \quad \text{and since} \quad \varepsilon \ll 1 \; ; \; \ln(1-\varepsilon) \simeq -\varepsilon$$

$$\alpha^{0} \simeq e^{-\nu\varepsilon} \qquad (5)$$

This expression coincides, in fact, with the theoretical model of H. Cackovič et al (1974) based on the assumption of a random distribution of defects along the chains and a fully exclusion of branches from the crystals. If we further let crystallize not only chain sequences which are free from defects but also sequences having just one defect (Fig. 1b) then the crystallinity will take the form:

$$\alpha^1=(1-\varepsilon)^{\nu}+\nu\varepsilon(1-\varepsilon)^{\nu-1}\simeq e^{-\nu\varepsilon}(1+\nu\varepsilon) \quad (6)$$

This model demands on the average 0.5 defects per crystalline chain segment. If, in addition, also the chain sequences with two defects are allowed to crystallize (Fig. 1c) the crystallinity will be:

$$\alpha^2\simeq e^{-\nu\varepsilon}\left(1+\nu\varepsilon+\frac{(\nu\varepsilon)^2}{2}\right) \quad (7)$$

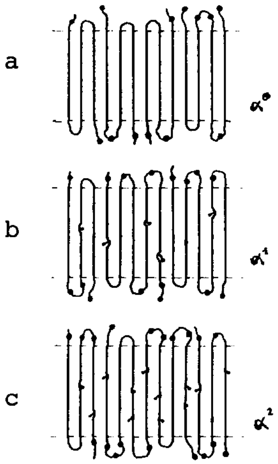

Fig. 1. Inclusion models according to eqs. (5), (6) and (7)

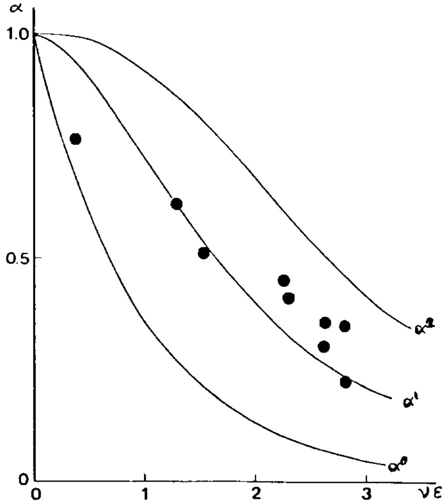

Fig. 2. Plot of experimental α v.s. $\nu\varepsilon$. Curve α^0 corresponds to an exclusion of defects and α^1 and α^2 to an average inclusion of 0.5 and 1 defect per crystalline stem, respectively.

In this case, on the average, there should be one defect per crystalline chain segment. Fig. 2 illustrates the theoretically obtained decreasing variation of α with $\nu\varepsilon$ according to the three models described by equations 5,6,7, i.e. average inclusions of zero, half and one defect per crystalline stem.

Discussion

Our data of X-ray crystallinity for the isothermally crystallized samples lie between the curves α^0 and α^2. A larger inclusion of defects within the lattice seems for the present samples unrealistic and will not be considered here. The experimental data show, indeed, that in all cases an inclusion of chain defects within the crystals takes place. This defect inclusion conspicuously increases with ε. Thus, the proportion of crystalline stems containing one defect varies from 15% for $\varepsilon \sim 0.2\%$ up to 75% for $\varepsilon \simeq 6\%$. These values are consistent with a concentration of defects within the lattice which does not exceed a 1% of branches per 100 carbon atoms, in accordance with our previous calculations based on the expansion of the lattice unit cell (BALTA CALLEJA, GONZALEZ ORTEGA and MARTINEZ SALAZAR 1978). It is worth pointing out that the level of defect inclusion will be admittedly larger in the case of smaller defects such as methyl or ethyl side groups (PREEDY, J.E. 1973)

In conclusion the present statistical approach not only offers an optional route for the calculation of the concentration of defects within crystals based on crystallinity and thickness data but also furnishes values which are comparable to those derived assuming an in - clusion of chain defects in the lattice through generation of 2g1 kink isomers. In addition the present approach offers the advantage that does not rely on any specific model of defect accommodation in the crystal lattice. Hence, the present statistical approach seems to be applicable to any polymer system having a random distribution of defects (comonomer units).

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