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Long Periods in Melt Crystallized Polyethylene Two Coexisting Structures?

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Summary

New small angle X-ray diffraction data of a series of mostly low density PE samples isothermally crystallized from the melt are reported to discern between the existing ambiguities concerning the alternative of one or two lamellar periodicities. The ratio of X-ray spacings turns out to be dependent on the supercooling of the samples. This result together with the analysis of the 1st and 2nd diffraction peaks during and after heat treatments reveals that the two scattering maxima in the samples investigated most probably originate from the coexistence of two different lamellar periodicities.

Introduction

The presence of two small angle X-ray diffraction (SAXD) maxima, observed for many semicrystalline polymers, still entails uncertainties in connection with the values which are derived for the lamellar thickness (GEIL, 1965; BLAIS et al., 1967; DAVIS et al., 1974). Indeed, when more than one SAXD maximum is observed the question arises as whether the lamellar spacings may be due either to higher orders of diffraction from a single lamellar periodicity or to two independent stacking periodicities. In the latter case there is, in addition, controversy about which one is the lamellar spacing observed (BROWN and EBY, 1964; ILLERS and HENDUS, 1967). Deviations of the ratio of spacings from the 2:1 value for linear polyethylene (PE) have been explained as due to "smearing" effects when slit collimation was used (KORTLEVE and VONK, 1968) or to the influence of skewed paracrystalline lattice statistics (CRIST and MOROSOFF, 1973). These results would favour the interpretation of a single lamellar periodicity. Support for the alternative concept of two independent first orders of diffraction corresponding to two different periodicities has been found using electron microscopy (ANDERSON, 1964).

The present work attempts to throw light on some of the ambiguities concerning the interpretation of the two SAXD maxima occurring in melt crystallized PE. The wider implications of this study are focused in the

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steering of the properties - structure relationship of low density PE prepared by crystallization from the melt (BALTA-CALLEJA et al., 1980).

Experimental

A series of commercial PE samples with a wide range of branching concentrations (ε) (Table I) were crystallized isothermally from the melt at $\Delta T \sim 10°$ and 68°C respectively. Details of sample characterization and preparation have been given elsewhere (MARTINEZ-SALAZAR and BALTA-CALLEJA, 1980). The SAXD photographs were taken on a Rigaku Camera using 0.5/0.3 and 0.3/0.2 mm pairs of pinhole collimators and a 12 KW-Cu rotating anode generator with Ni filter. The primary beam width at half maximum intensity was $1\text{-}2 \times 10^{-3}$ radians. Densitometer traces of the X-ray films were recorded using a Joyce-Loebl two beam microdensitometer. After subtracting the background scatter two Gauss symmetrical components were fitted into the shoulders of the SAXD pattern using a curve-resolver. Since the condition of large lateral dimensions is not met in our crystals the maxima were not corrected with the usual θ^2 Lorentz factor. Bragg's law was applied to the maxima to determine the long spacings. We shall call L_1 the larger spacing and L_2 the smaller one.

Results and Discussion

Fig. 1 illustrates the dependence of the SAXD pattern on the supercooling for three different PE samples. The SAXD patterns for $\Delta T \sim 10°C$ show two distint rings with no tangential intensity variation. For higher branching concentrations ($\varepsilon > 3\%$) the rings tend to be obscured by the intense continuous scattering. For $\Delta T \sim 68°C$ the intensity increase of the SAXS maxima, which is concurrent with the increase of background scatter, indicates a larger electron density difference between the crystal lattice and interlamellar regions together with a worsening in the lamellar stacking. The values of L_1 and L_2 are plotted as a function of ε for the samples investigated in Fig. 2. The L_1 values are larger for $\Delta T = 10°C$ than for $\Delta T = 68°C$. The L_2 values are, on the contrary, nearly indistinguishable from each other, for both supercoolings. The dependence of L_1 on ε, has been interpreted as supporting the concept of a major exclusion of chain defects from the crystals (MARTINEZ-SALAZAR and BALTA-CALLEJA, 1980). The ratio L_1/L_2 is, in addition, nearly equal or larger than 2 for $\Delta T = 10°C$, whereas it shows values around 1.6 for $\Delta T = 68°C$. The reduced width values of the first scattering peak, $\Delta_1/2\theta_1$ (where Δ_1 is the peak width at half height and $2\theta_1$ the angular position of the first peak) are in reasonable agreement with the results quoted by CRIST and MOROSOFF, 1973) (0.50-0.52) for quenched material. These values sustain the adopted

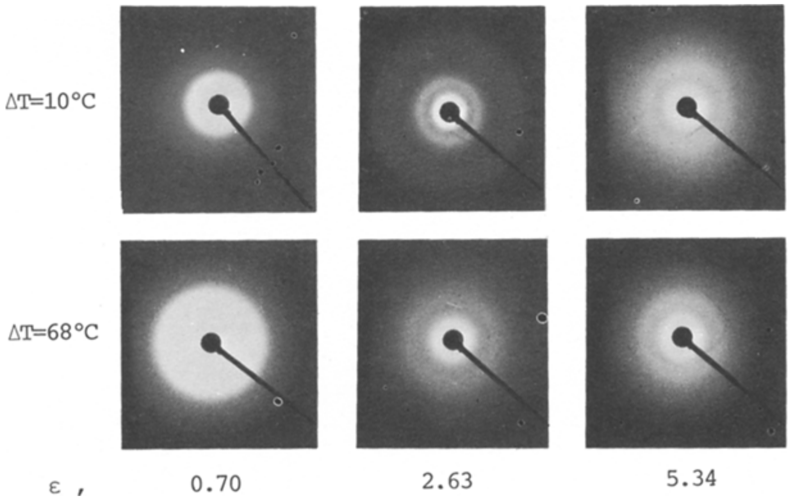

Fig. 1. SAXD patterns of PE with various branching ratios (ε) at 2 different supercoolings.

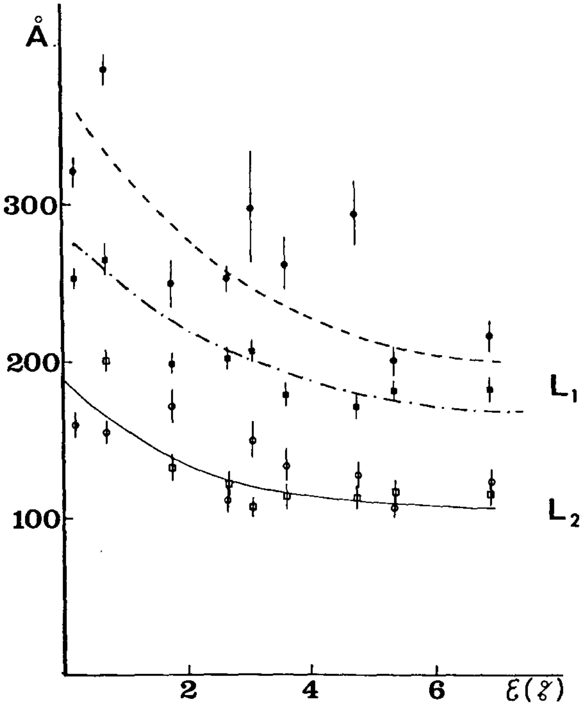

Fig. 2. Plot of L_1 and L_2 vs. ε: (●,0) ΔT=10°C ; (■,□) ΔT=68°C .

separation procedure for the 1st and 2nd peaks in the SAXD patterns.

TABLE I

		ΔT=10°C		ΔT=68°C	
Samples	ε (%)	L_1/L_2	$\Delta_1/2\theta_1$	L_1/L_2	$\Delta_1/2\theta_1$
1	0.19	2.03±0.13	0.74	2.36±0.13	0.49
2	0.70	2.51±0.18	0.53	1.34±0.08	0.45
3	1.76	1.46±0.17	0.57	1.50±0.09	0.51
4	2.63	2.26±0.12	0.44	1.64±0.13	0.54
5	3.04	1.98±0.42	0.45	1.92±0.12	0.71
6	3.61	1.95±0.27	0.76	1.56±0.12	0.57
7	4.77	2.31±0.32	0.45	1.51±0.13	0.57
8	5.34	1.86±0.09	0.65	1.56±0.13	0.50
9	6.90	1.75±0.17	0.63	1.57±0.14	0.50

The fact that L_1 (and L_1/L_2) for the samples investigated depends on ΔT while L_2 is practically independent on ΔT strongly suggests that the two long spacings derived cannot be simply associated to two orders of diffraction from a single lamellar periodicity.

To test our premonition that the two SAXD maxima possibly are two independent first orders of diffraction related to two different lamellar periodicities sample Nr. 4 was quenched from the melt (170°C) into liquid nitrogen and subsequently annealed for periods of 30min. in the range of 20-100°C. The X-ray measurements were made at room temperature. The main observations, reported in Fig. 3, are: a) The X-ray spacing corresponding to peak 1 increases as a function of annealing temperature from 170 Å at 20°C up to 213 Å at 100°C. The lamellae structure is known to be initially not present on quenching at cryogenic temperatures but it develops above -100°C (HENDRA et al., 1975); b) The spacing corresponding to peak 2 is independent of the annealing temperature. The value is in the range of 112-119 Å. From these results we contend that L_1 corresponds to stacks of lamellae which recrystallize isothermally at the temperature of the oil bath with a larger fold period, and that L_2 could be correlated to material non-crystallized during the crystallization process and crystallized while the sample was cooled down to room temperature. The striking constancy of the second maxima L_2 even for long annealing times (~ 6 days at 100°C), while L_1 further increased up to 260 Å, could explain the contribution to the stacking of thinner lamellae, of lower molecular weight components which

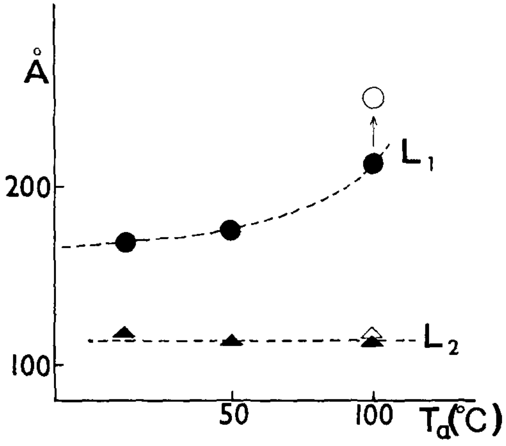

Fig. 3. Values of L_1 and L_2 (sample 4) as a function of annealing temperature. Annealing time: 30 min. Open symbols: 6 days.

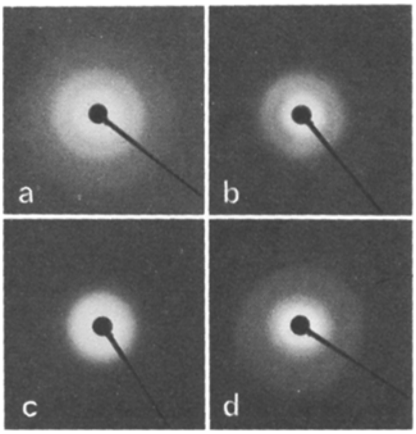

Fig. 4. SAXD patterns of sample 4 taken at :
a) 22°C ;b) 80°C ;c) 100°C ;d) 22°C

were fractionated during crystallization. Reports on molecular fractionation during crystallization from the melt have been given previously (DUGLOSZ et al.,1976).

To demonstrate in a conclusive manner the different origin of the two diffraction maxima various diffraction exposures were carried out at high temperature using a heated sample holder. Sample Nr. 4 was crystallized from the melt at 22°C in a sealed glass capillary. The SAXD photographs are illustrated in Fig. 4. The initial X-ray spacings recorded corresponded to L_1=170 Å and L_2=112 Å respectively. The sample temperature was increased at 80°C (1h). At this temperature the observed maximum L_1 was at 170 Å while L_2 had totally vanished. The temperature was further increased up to 100°C (24h) (~10°C below the macroscopic melting point) with a consequent increase of L_1 up to 250 Å. The temperature was then reduced to 22°C and the spacing of 112 Å corresponding to peak 2 was again detected. These experiments suggest that the stacks of thinner lamellae 'melted' selectively above ~80°C, recrystallizing again below this temperature with the same original spacing of 112 Å. On the other hand, the stacks of thicker lamellae recrystallized, above 80°C with a larger long period. From these observations we conclude that the two maxima in the PE sample investigated originate from the coexistence of two different lamellar structures. This conclusion should be confirmed for the other samples of table I when experiments to observe lamellar changes during annealing at high temperature are completed.

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