Factors affecting the nascent structure and morphology of polyethylene obtained by heterogeneous Ziegler—Natta catalysts:
2. Crystallinity and melting behaviour

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Following studies of the factors affecting the structures and morphologies of nascent polyethylene crystals, density, heat of fusion, crystallinity and melting behaviour of the samples as-polymerized and also after nitric acid oxidation and annealing, were determined by density gradient column, X-ray diffraction and differential scanning calorimetry. The results show that the polymerization temperature is the most important factor controlling the crystal structure. The highest density, crystallinity and crystal quality were found for polymerization temperatures under 100°C, where the growth of the crystals was controlled by a successive polymerization and crystallization mechanism. For this range of polymerization temperatures, density and crystallinity decrease as the polymerization temperature and time increase. When the polymerization temperature is higher than 100°C, near the polyethylene solubility, the crystal grows without any polymerization control, according to a separate polymerization and crystallization mechanism. In this case, density and crystallinity increase with polymerization temperature and time, as with crystallization from melt and solution. The density and crystallinity values of all nascent polyethylene crystals are in the typical range of folded-chain drawn polyethylene or crystallized from the melt. Furthermore, no as-polymerized crystals exhibit a superheating effect suggesting a folded-chain macroconformation. From the melting depression for folded-chain crystals and extended-chain paraffin crystals with finite dimensions, and also from the molecular weight after nitric acid oxidation, the crystal thickness could be calculated. The values are within the range of folded-chain melt crystallized polyethylenes. The results indicate that the crystal thickness of the samples polymerized at below 100°C increases as the polymerization temperature decreases. For the samples polymerized at above 100°C, the crystal thickness increases with the polymerization temperature.

INTRODUCTION

In the past few decades a large amount of information on crystal nucleation, growth mechanisms, morphology, crystal habit and structure of polyethylene, crystallized from solvent and metl has been obtained[1–5]. Data concerning density, crystallinity, melting behaviour, crystal order—disorder and macroconformation of the chain could easily be acquired, employing flotation or density gradient column methods, differential scanning calorimetry (d.s.c.) and X-ray diffraction[6–8]. Furthermore, by annealing of the metastable crystals, as well as by nitric acid oxidation techniques, very useful information could be obtained on the crystal structure details[9,10].

On the other hand, relatively little is known at present concerning the crystallization features of polyethylene obtained immediately after it has been polymerized from the monomer. In the majority of investigations reported, information about the morphology and structure of nascent polyethylene was obtained using mainly electron microscopy together with small-angle X-ray scattering, in order to determine how polymer crystal nucleation and growth mechanism occur[11–22]. Very few works leading to an understanding of the crystallization mechanism during polymerization give results on the melting behaviour of the as-polymerized polyethylene crystals[23–26], although significant information can be deduced by this means. Thermal analysis carried out by d.s.c. has already been found useful up to a certain degree to differentiate between polymer crystals with extended and folded-chain macroconformation, and also for determination of the crystallinity degree[24–27]. From a high melting point and superheating effect an extended-chain conformation may be inferred[28,29]. Finally, there appear to be only three publications reporting crystallinity data of nascent polyethylene crystals obtained by Ziegler—Natta catalysts[24,25,30], although one of the most useful and practical methods for the characterization of semicrystalline polymers is the degree of crystallinity[8]. Therefore, the re-

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search described in this paper deals mainly with the characterization of polyethylene crystals as produced by polymerization with a $TiCl_3/AlEt_2$ heterogeneous catalyst system and after annealing, recrystallization and also after etching with fuming nitric acid. In the same way, some results obtained with a high activity supported heterogeneous Ziegler catalyst prepared by deposition of $TiCl_4$ on modified SiO_2 silical gel with $ZnCl_2$, were also included. Data have been gathered on crystallinity and melting point as determined from density, wide-angle X-ray diffraction and d.s.c. The results are interpreted by comparison with the properties of folded- and extended-chain polyethylene obtained by crystallization of the finished polymer from quiescent and sheared solution[31,32], from melt at atmospheric and high pressure[33], and also with drawn polyethylene[34–36]. Finally, in order to understand the crystal growth mechanism, attempts were made to correlate these results with polymerization conditions, presented in the first part of this series[37], and which affect the polymerization rates, molecular weight and number of growing polymer chains. Conclusions are obtained on how the polymerization variables such as pressure, temperature and stirring, control the structure of the as-polymerized polyethylene crystals.

EXPERIMENTAL

Preparation of the nascent polyethylene samples

Sample preparation under very different experimental conditions, withdrawal from the reactor at different polymerization times, handling and characterization according to average viscosity molecular weight, has already been described[37]. The same run numbers, employed in the first part of this series to identify the experimental conditions such as pressure (1–10 atm), temperature (0°–120°C) and stirring speed (10–1000 rpm) are also used in this work. When necessary, the samples are referenced with two numbers; the first one indicates the run and the second the polymerization time, e.g. sample 5–45 means the sample obtained under the polymerization conditions given for run 5 and 45 min polymerization time.

Annealing

In order to examine the change of the nascent polyethylene samples by annealing, about 0.2 g of the samples were wrapped in aluminium foil and placed in glass ampoules. The ampoules were vacuum-sealed and immersed in a silicone bath at the desired temperature controlled to ± 0.1°C. After the annealing period, the samples were quenched and the glass ampoules opened. The annealed samples were then examined by d.s.c.

Crystallization from paraffin solvent

Due to the fact that the ethylene polymerization was carried out in n-paraffin viscous medium as solvent[37], some samples of nascent polyethylene were dissolved at 140°C in the same solvent and then immersed in a thermostated silicone oil bath at the same respective polymerization temperatures as for crystallization. After the crystallization time, the samples were filtered with a sintered glass filter and washed several times with chloroform, water and acetone in order to remove the residual paraffin. The polymer crystals were then dried at 50°C under vacuum and examined by differential scanning calorimetry and X-ray diffraction. The data were compared with similar measurements made on the original nascent polymer samples.

Fuming nitric acid treatment

In order to examine the oxidation effect of fuming nitric acid on nascent polyethylene, some samples were treated with excess fuming nitric acid in sealed glass tubes. The acid used was an analytical grade containing greater than 95% HNO_3 and using about 1% w/v of sample/acid. In order to increase the oxidative effect, the tubes were immersed in an oil-thermostated bath maintained at 70° ± 0.1°C for times ranging from 2–34 h. The temperature was chosen on the basis of the experiments reported in the literature[9–24]. After the desired treatment, the tubes were opened and the oxidized material left for 24 h in distilled water. It was then filtered with a sintered glass filter and washed with an excess of distilled water until the acid was eliminated. Finally, it was washed wtih acetone and dried at 50°C under vacuum. After drying, the samples were weighed and the percentage weight loss calculated.

Thermal analysis

The thermal analysis carried out on polyethylene samples, before and after nitric acid oxidation, included the measurement of the melting peak temperatures and heats of fusion (using a constant heating rate of 10°C/min), and also a study of the effects of the heating rate on the melting characteristics. A Du Pont thermal analysis apparatus model 990 was employed together with a Differential Scanning Calorimeter (d.s.c.) cell. The instrument was operated with a sensitivity range set at 2 mcal/sec in. The temperature scale was calibrated with pure compounds of known transition temperature such as indium, benzoic acid, benzamide, acetanilide and phenacetin, at the same heating rate. Calibration of the power input into the sample was made by measurement of the heat of fusion of indium. The calibration was repeated sufficiently, finding that the imprecision is due mostly to errors in planimetry measurements of the area under the melting curve. The precision was better than 5%.

All measurements were carried out under a nitrogen stream in closed capsules containing between 2 and 5 mg of polymer measured with a 2% accuracy on a Mettler H-54 electrobalance. If, after the first melting, a second scan melting curve was desired, the samples were heated above the exothermic peak, stopping the heating mode, and allowed to cool slowly inside the instrument well below the exothermic peak. A second thermogram of the recrystallized samples was then performed.

Density and crystallinity measurements

Density and crystallinity were measured on the dried polymer samples employing the density gradient column technique. This method together with the heats of fusion have been the simplest and most convenient for characterizing the crystallinity in melt-crystallized polymers[7]. The flotation liquid for the density gradient column was a mixture of monochlorobenzene and toluene. The density gradient column was prepared according to the ASTM-D1505-62 method[38]. In order to avoid air bubbles from the dry samples, these were evacuated for at least 8 h and then immersed under vacuum in a liquid mixture having a density close to that of the crystals. After further pumping, the wet samples of polymer were transferred to the density gradient column. All measurements were carried out at 23°C. The column was calibrated by a series of glass beads whose density was known to within ± 0.0001 g%cm^3. The density values showed only little variation, being in the range of ± 0.0003 g cm^{-3}. In order to convert the density values to degree of crystallinity, it is assumed that a two phase system exists and that the contributions to the specific volume from the amorphous and crystalline phase are additive. The following relation was used:

$$\text{Crystallinity (\%)} = \frac{\rho_c}{\rho}\,\frac{\rho - \rho_a}{\rho_c\,\rho_a} \times 100 \qquad (1)$$

where ρ is the density of the sample, ρ_a and ρ_c are the density of the amorphous and crystalline phases, which are taken as 0.854 g cm^{-3} [38] and 1.005 g cm^{-3} [39], respectively. From the heat of fusion values, the percentage crystallinity of the polyethylene samples may also be calculated, utilizing the relation:

$$\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_f^*} \times 100 \qquad (2)$$

where ΔH_f is the heat of fusion of the sample as determined from the d.s.c. curves, and ΔH_f^* is the thermodynamic heat of fusion of folded-chain polyethylene crystals, which is taken as 66 cal g^{-1} [40]. Finally, the crystallinity was also measured by wide-angle X-ray diffraction employing a North American Phillips apparatus. An iron target working at 36 kV/20 mA supplied the necessary radiation, which was filtered through a thin Mn foil. The intensity measurements were made with a Norelco wide range goniometer by means of a Geiger detector coupled to a recorder. An Si standard was used to calibrate the scale. Two crystalline reflections are recorded in this range corresponding to (110) and (200) planes, representing interferences due to the principal side spacing in the polyethylene structure. The shoulder on the low-angle side of the 110 peak is part of the broad diffraction band characteristic of the amorphous phase. The method used to resolve the peaks is based on its symmetrical character. The background correction is the main source of errors, this being the cause of the different results obtained by various researchers. The three areas were planimetered and corrected for atomic scattering factors, absorption, temperature and diffraction angle. The percentage crystallinity was then calcualted by the relation[41]:

$$\text{Crystallinity (\%)} = \frac{I_{110} + I_{200}}{I_a + (I_{110} + I_{200})} \times 100 = \frac{b + 1.43c}{0.69a + (b + 1.43c)} \times 100$$

where I_a, I_{110} and I_{200} are the relative intensities, reflection of the amorphous and crystalline phases, respectively; *a, b* and *c* are the areas under the respective peaks.

RESULTS AND DISCUSSION

Crystallinity of the nascent samples

All wide-angle X-ray diffraction experiments indicated the most stable and normal orthorhombic crystal structure for nascent polyethylene. The same crystal structure is found in all normal crystallization experiments of polyethylene from the melt or from solution[4]. The degree of crystallinity of all nascent polyethylene samples obtained at different polymerization conditions are given in *Table 1.* It can be seen that, in the analysed temperature range, the polymerization temperature had a strong influence on the crystallinity. On the contrary, the crystallinity depends very little on the polymerization time, pressure and stirring speed. The higher degree of crystallinity was obtained at low polymerization temperatures such as 0°C (runs 5, 6, 7 and 8); the highest value found was 85.5% from density (run 7 at 5 min polymerization time). By increasing the polymerization temperature to 70°C, the crystallinity decreases a little, ranging from about 3 to 5%. A larger reduction in the degree of crystallinity is observed by further increases of the temperature above 70°C, e.g. 100°, 115° and 120°C. At these high temperatures the crystallinity relation with the polymerizatio time is inverted in comparison with the runs carried out at 0° and 70°C. For all experiments performed at 0° and 70°C the degree of crystallinity decreases with the polymerization time. These results agree with those reported by Chanzy *et al.*[25] for ethylene polymerization with VCl_3 at room temperature in n-heptane as solvent. On the contrary, at higher polymerization temperatures the crystallinity increases with polymerization time. From the large amount of crystallinity data given in *Table 1,* it can also be concluded that the pressure reduction and increase in stirring improve slightly the crystallinity. Finally, very similar results were obtained in the experiments using the high activity Ziegler catalyst (runs 12, 13).

The above results can be explained according to the Wunderlich's principles of crystallization during polymerization. Under conditions where polymerization rate is identical with crystallization rate, a simultaneous polymerization and crystallization mechanism can be expected, giving rise to a fibrillar morphology with extended-chain macroconformation. This mechanism is easy to identify from the morphology and structure of the as-polymerized polymers. However, when polymerization and crystallization are two events more or less simultaneous a separate or successive polymerization and crystallization mechanism occurs. The resulting crystal morphology and macroconformation of the polymer chain will now depend upon the length of the polymerizing chain segment before crystallization takes place. This mechanism is more difficult to elucidate from the morphology. This can be strongly affected by the polymerization conditions, such as temperature and solvent, giving rise to a folded-chain macroconformation. The folded-chain length and the morphology characteristics depend on the continuous transition from successive polymerization and crystallization to separate polymerization and crystallization mechanisms[5].

As can be deduced from *Table 1,* when the polymerization temperature is low enough (0° and 70°C), the polymerization is most likely controlled by a successive polymerization and crystallization mechanism. This is due to the fact that under these supercooling conditions, the crystallization rate is enhanced, and at the same time, the polymerization rate is reduced so that the polymerization and crystallization are brought together and take place very closely, giving rise to the higher crystallinity values. Similarly, the pressure effect on the crystallinity can be explained. In the viscous polymerization medium employed the pressure drops from 10 to 1 atm, hinders the monomer diffusion to the polymerization sites, and so delays the polymerization rate. Under such conditions, the successive polymerization and crystallization mechanism is more likely. On the other hand, the crystallinity increases observed with changes in the stirring speed

Table 1 Influence of the experimental conditions on the density, crystallinity, heat of fusion and melting peak temperature of nascent polyethylene

	Experimental conditions							Crystallinity (%)			
Run	Pressure (atm)	Temp. (°C)	Stirring (rpm)	Polym. time (min)	Molecular weight $M_v \times 10^{-4}$	Density (23°C) (g cm^{-3})	Heat of fusion ΔH_f (cal g^{-1})	From density	From X-ray	From d.s.c.	Melting temp. (°C)
1	10	70	1000	5	36.5	0.9674	52.00	78.0	75.0	78.8	131.3
				20	48.5	0.9610	46.60	74.1	72.6	70.6	132.0
				45	60.0	0.9578	45.70	72.1	71.0	69.2	133.0
				150	78.4	0.9547	44.60	70.2	68.0	67.5	133.0
2	10	70	10	5	35.0	0.9626	46.10	75.2	73.2	69.8	126.0
				20	43.0	0.9584	44.60	72.5	70.6	67.5	132.0
				45	52.0	0.9547	43.60	79.2	69.3	66.0	132.4
				150	66.0	0.9515	42.20	68.2	67.5	64.0	132.5
3	1	70	1000	5	35.0	0.9680	48.20	78.4	75.8	73.0	131.0
				20	44.0	0.9630	47.40	75.3	74.0	71.8	132.2
				45	54.0	0.9594	46.40	73.1	72.5	70.3	133.5
				150	68.0	0.9562	44.70	74.0	68.6	67.8	133.7
4	1	70	10	5	—	0.9642	45.30	76.0	—	68.6	128.5
				20	—	0.9610	43.80	74.1	71.5	66.4	128.7
				45	—	0.9562	42.00	71.1	69.0	63.6	129.5
				150	—	0.9546	40.90	72.4	66.7	62.0	129.0
5	10	0	1000	5	69.3	0.9732	51.70	81.5	81.0	78.3	132.5
				20	110.8	0.9690	50.40	79.0	78.8	76.4	134.8
				45	142.6	0.9660	48.60	76.9	77.6	73.7	134.5
				150	190.4	0.9654	47.50	76.8	75.4	72.0	135.0
6	10	0	10	5	43.0	0.9732	50.40	81.5	77.9	76.3	131.0
				20	72.3	0.9682	48.50	78.5	76.4	73.5	131.8
				45	106.0	0.9642	46.90	76.0	74.2	71.0	132.3
				150	146.0	0.9600	45.90	73.5	72.0	69.6	134.5
7	1	0	1000	5	—	0.9799	52.10	85.5	—	79.0	131.5
				20	—	0.9754	50.40	82.8	80.6	76.4	131.9
				45	—	0.9694	49.20	79.2	78.4	74.5	135.1
				150	—	0.9607	48.20	73.9	76.3	73.0	133.8
8	1	0	10	5	—	0.9706	—	80.0	—	—	—
				20	—	0.9701	—	79.6	—	—	—
				45	—	0.9657	—	77.0	74.3	—	—
				150	—	0.9614	—	74.3	72.7	—	—
9	10	100	1000	5	33.4	—	37.10	—	60.0	56.2	126.5
				20	41.0	—	37.60	—	61.6	57.0	131.0
				45	48.0	—	38.60	—	62.8	58.5	129.4
				150	56.0	—	39,20	—	64.0	59.3	132.7
10	10	115	1000	5	29.7	—	35.20	—	57.0	53.3	125.0
				20	32.0	—	35.60	—	58.0	54.0	126.6
				45	37.0	—	36.30	—	59.0	55.0	131.0
				150	41.4	—	36.80	—	59.5	55.8	130.5
11	10	120	1000	5	21.5	—	33.80	—	55.0	51.2	124.3
				20	23.8	—	34.30	—	56.3	52.0	125.0
				45	29.2	—	34.80	—	56.8	52.7	128.5
				150	31.7	—	35.30	—	57.5	53.5	129.0
12	10	70	1000	5	38.4	0.9674	48.80	78.1	76.3	74.0	—
				20	52.0	0.9637	47.70	75.8	74.3	72.3	—
				45	58.0	0.9690	46.90	73.7	72.4	71.0	—
				150	80.0	0.9578	45.30	72.2	71.0	68.6	—
13	10	0	1000	5	71.2	0.9755	52.40	83.0	82.0	79.4	—
				20	102.4	0.9706	51.00	80.0	79.8	77.2	—
				45	103.4	0.9687	49.50	78.9	77.5	75.0	—
				150	106.7	0.9648	48.50	76.5	75.0	73.5	—

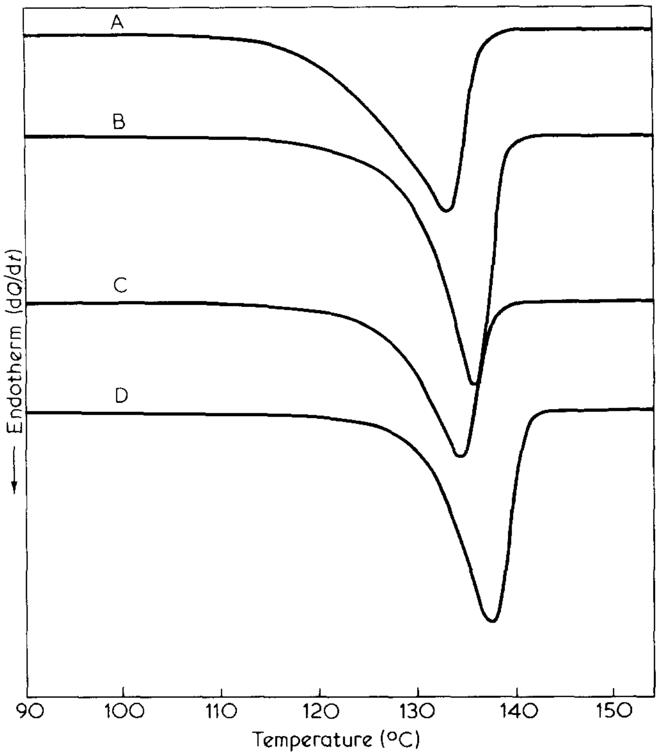

Figure 1 D.s.c. thermograms of typical as-polymerized polyethylene at different polymerization times. Polymerization conditions: temperature, 0°C; pressure, 10 atm; stirring speed 100 rpm A, Polymerization time, 5 min; B, 20 min; C, 45 min; D, 150 min

are due to the orientation effect induced during the crystallization of the already polymerized chain segment. The decrease in crystallinity with polymerization time under these polymerization conditions can be attributed to the disruption and deformation of the already well preformed crystals by the yield increase[25,43]. For polymerization temperatures above 70°C, near the solution temperature of the polyethylene crystals, a separate polymerization and crystallization mechanism takes place. The polymerization has practically no control on the crystal structure of the nascent polymer. In this case, the crystallinity falls markedly and also increases with the polymerization temperature and time, due to an annealing effect, as it appears in the widely studied crystallization from melt and solution. In an effort to obtain a better understanding of these results, sample 5 at 45 min polymerization time was dissolved in paraffin at 140°C and afterwards crystallized at 100°C over 96 h. A degree of crystallinity of 50% was found by d.s.c. Furthermore, by comparison of the density and crystallinity values from *Table 1* with those reported in the literature for different crystal structures, additional conclusions can be obtained about the more likely macroconformation of the as-polymerized crystals. The density values of drawn polyethylene before and after annealing have been reported as 0.962 and 0.973 g cm^{-3} [35,36] showing good agreement.

The drawn fibre morphology has a folded-chain macroconformation, although it shows a great superficial resemblance to extended-chain fibrillar crystals. The density for polyethylene crystallized under pressure below 1.500 kg cm^{-2} has been reported as 0.9658–0.9702 g cm^{-3} and the crystallinity as 80.0–81.9%, respectively[33]. These values are also similar to those given in *Table 1*. The polyethylene crystallized in the low pressure region presents similarly a typical folded-chain lamellar structure. On the contrary, typical extended-chain polyethylene crystals show much higher values for density and crystallinity, being in the ranges 0.9860–0.9922 g cm^{-3} and 92.3–96.0%, respectively[5,33].

Finally, it is noteworthy to point out the good agreement between the degree of crystallinity obtained by the three different methods. The calorimetry gives the lowest values. Although the difference between crystallinities from the heats of fusion and from X-ray data is nearly within experimental error, these results suggest a range of crystallite sizes and a diversity of structural defects[44]. The same conclusion can also be inferred from the melting behaviour.

Melting behaviour

D.s.c. curves for as-polymerized polyethylene samples obtained at polymerization temperatures below 100°C, show a single and relatively broad melting peak indicating no appreciable molecular reorganization during the heat treatment (*Figure 1*). At higher polymerization temperatures a shoulder on the low melting temperature could occasionally be observed (*Figure 2*). This melting behaviour points to differences in polymer macroconformation and morphology for the samples obtained at the highest polymerization temperatures. The melting peak temperatures at 10°C/min together with the melting peak sharpness can be used as indicators for the crystal perfection[28]. From *Table 1* and *Figure 2* it can be concluded that the crystal perfection greatly decreases with increasing polymerization temperature.

From the melting points of the as-polymerized sample and with the aid of the well known Thomson–Gibbs equation:

$$T_m = T_m^0 - \frac{2\sigma_e T_m^0}{\Delta H_f \rho} \times \frac{1}{\bar{l}} \qquad (4)$$

the average crystal thickness $\bar{l}$ can be obtained. T_m represents the melting point temperatures of the folded-chain crystals with finite dimensions. ΔH_f and ρ are the heat of fusion and density. T_m^0 is the equilibrium melting point and σ_e the lamellar surface free-energy determined for linear

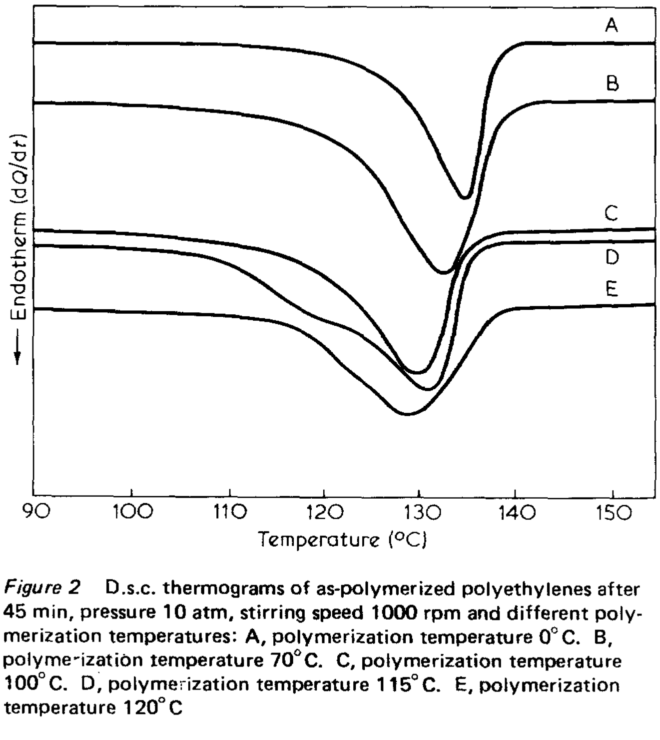

Figure 2 D.s.c. thermograms of as-polymerized polyethylenes after 45 min, pressure 10 atm, stirring speed 1000 rpm and different polymerization temperatures: A, polymerization temperature 0°C. B, polymerization temperature 70°C. C, polymerization temperature 100°C. D, polymerization temperature 115°C. E, polymerization temperature 120°C

Table 2 Average crystal thickness for as-polymerized polyethylene

Sample Nr	Average crystal thickness $\bar{l}$ (Å) obtained equation (4)	equation (5)	from mol. weight
1–45	273	220	212
2–45	276	228	221
3–45	316	226	218
4–45	206	2 5	216
5–45	365	236	236
6–45	273	236	239
7–45	300	240	241
9–45	–	190	186
10–45	–	205	199
11–45	–	210	209

polyethylene as 141° ± 0.5°C and 79.5 ± 2.5 ergs cm^{-2} [45]. The results are given in *Table 2*. Although there are disadvantages in the use of equation (4), such as the annealing of the unstable thin lamellae when heated to the melting temperature so that only the higher melting temperature of the most perfect crystals are obtained, it can be seen that the crystal thickness corresponds in approximately the same order of magnitude as found for melt-crystallized polyethylene[35].

Finally, the melting behaviour of all as-polymerized polyethylene samples was investigated for the superheating effect by variation of the melting point with the heating rate. The superheating effect observed in polymer materials is attributed to different reasons, including extended-chain macroconformation, lateral crystal dimensions, stiffness and motion restrictions of the polymer chain due to loops and tie molecules[46]. No superheating effect was found in the samples. These results excluded the existence of crystals with extended-chain macroconformation. For samples obtained at high polymerization temperatures (e.g. 100°, 115° and 120°C), a typical reorganization similar to those found for folded-chain lamellae of polyethylene, crystallized at low temperatures from melt and solution, was observed to a certain degree (*Figure 3*). At high heating rate the molecular reorganization does not occur and the high temperature peak represents the melting temperature of the nascent polymer crystal. This behaviour deserves more consideration so that after melting the polymer was recrystallized in the calorimeter and subsequently remelted; the second scan peak lies between the two original peaks (*Figures 3b* and *3c*). The foregoing observations indicate once again that the nascent polymer is composed of folded-chain crystals and also that the polymerization temperature is the main factor controlling the nascent crystal characteristics[43].

Nitric acid oxidation and annealing

In order to analyse the structure of the nascent polymer in greater detail, as-polymerized samples were submitted to the nitric acid action. Nitric acid cuts the polymer chains first in the disordered amorphous regions of the crystals before erosion continues on the outer surfaces[49]. The weight loss as a function of time of exposure to nitric acid is shown in *Figure 4*, for two representative samples of nascent polyethylene. These results are very similar to those found in cases of lamellar single crystals of polyethylene, crystallized from the solution[50], and also to those obtained by Georgiadis and Manley for nascent polyethylene prepared using a soluble

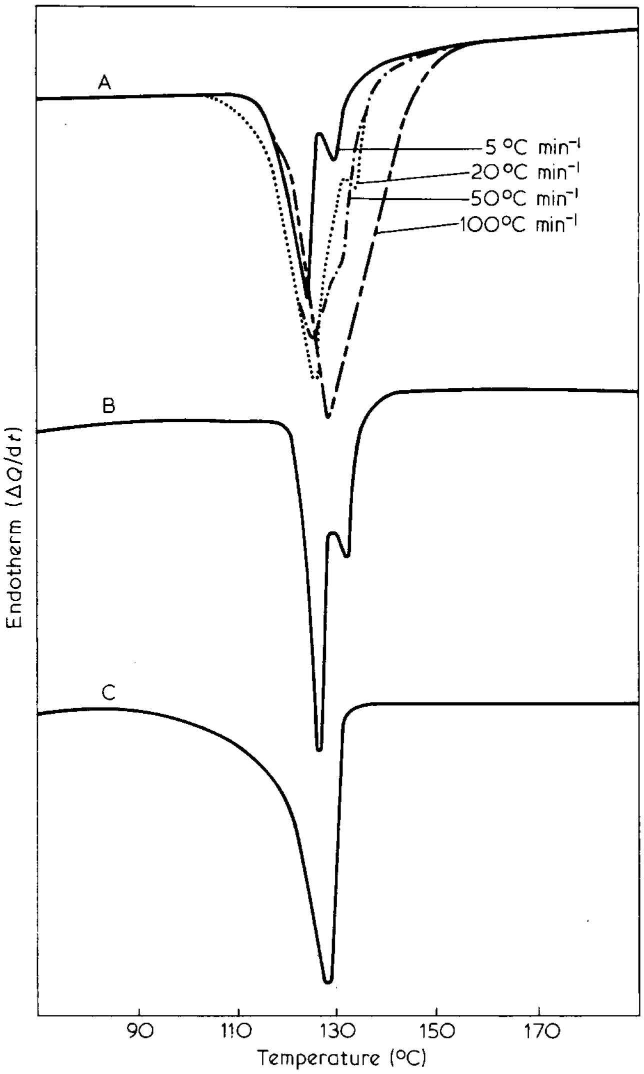

Figure 3 D.s.c. thermograms of as-polymerized polyethylene obtained at 120°C polymerization temperature (sample 11). A, different heating rates; B, first melting curve of the original sample at 10°C/min. heating rate. C, second melting curve after recrystallization from the melt

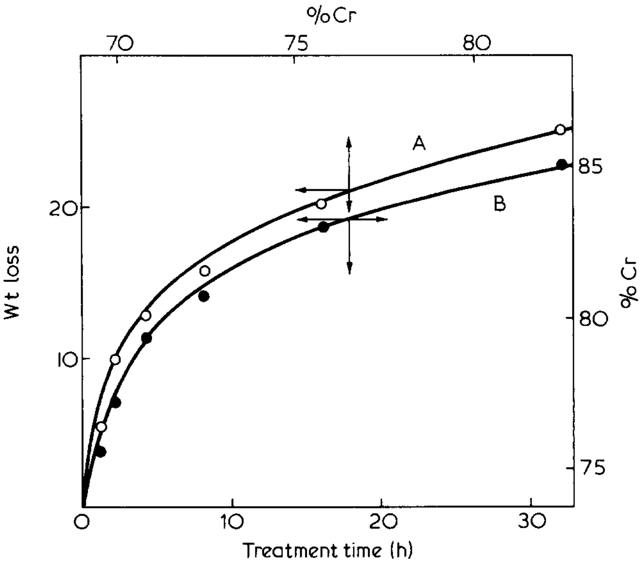

Figure 4 Weight loss (%) as a function of time of treatment for two typical samples of as-polymerized polyethylenes with fuming nitric acid at 70°C. A, 1–45; B, 5–45

Table 3 Annealing and nitric acid oxidation effects on the density, heat of fusion, crystallinity and average crystal thickness

Sample	Annealing time (h)	Density (23°C) (g cm^{-3})	Heat of fusion ΔH_f (cal g^{-1})	Crystallinity (%)		Melting temp. (°C)	Crystal thickness $\bar{l}$ (Å)
				Density	d.s.c.		
1–45	00	0.9578	45.7	72.1	69.2	132.3	273[a]
1–45	24	0.9672	45.80	78.1	69.4	134.3	354
1–45	72	0.9710	46.80	80.20	71.0	135.0	395
5–45	0	0.9660	48.60	76.90	73.7	134.5	365
5–45	24	0.9685	49.00	76.70	74.2	135.2	409
5–45	72	0.9725	51.9	81.9	78.6	136.0	474
After nitric acid oxidation during 16 hr at 70°C							
1–45	24	1.0060	57.20	–	86.7	131.0	330[b]
1–45	72	1.0090	60.40	–	91.5	132.2	375
5–45	24	1.0065	56.00	–	84.9	132.3	382
5–45	72	1.0085	59.30	–	89.8	132.9	410

[a] Calculated using equation (4)
[b] Calculated using equation (5)

Ziegler–Natta catalyst, exhibiting a folded-chain macroconformation[24]. From *Figure 4* it can also be seen that both samples behave similarly on nitric acid attack. The only difference observed is due to the fact that the sample 5-45 has a greater crystallinity and therefore the weight loss is lower than the sample 1–45. The melting behaviour of the oxidized samples was also examined using d.s.c. In both cases, the melting region is sharpened and moved to lower temperature as oxidation progresses. This is due to the formation of more regular crystals with lower molecular weight. Furthermore, only a single melting peak was found. The second scan curves of melted and crystallized samples show, however, two melting peaks corresponding to the melting of crystals formed by the low molecular weight paraffinic segments arising from folded cutting, and whose length corresponds to the origin crystal thickness, also to the crystals formed by the higher molecular weight unetched polyethylene chains. Both crystal types are originated by separate crystallization, due to a fractionation process occurring during crystallization from the melt. These results are similar to those reported by Giorgiadis and Manley[24] for nascent chain-folded polyethylene crystals. The melting point of the etched as-polymerized samples, after 16 h treatment time, can be used, in order to calculate the average crystal thickness by Broadhurst's equation for stable fully extended-chain lamellae of paraffins[49]:

$$T_m = 414.3 \frac{X - 1.5}{X + 0.5} \qquad (5)$$

where X is the number of $-CH_2-$ groups with a length of 1.273 Å.

The results are given in *Table 2.* As was predicted the average crystal thickness obtained by equation (4) is larger than that calculated by equation (5), due to the fast thickening of the unstable thin lamellae during the heating process.

Finally, the average crystal thickness calculated from the average viscosity molecular weight of the samples etched for 16 h are also included in *Table 2.* A reasonable agreement between these results and those calculated by equation (5) were obtained.

The crystal thickness of the samples polymerized below 100°C increases as the polymerization temperature decreases. On the contrary, for the samples polymerized over 100°C, the crystal thickness increases with the polymerization temperature.

Since many polymers crystallize from the melt and solution as metastable crystals, due to size, shape and defects being in non-thermodynamic equilibrium, they are susceptible to change on annealing, giving rise to larger and more perfect crystals. The term annealing implies, in a narrow sense, the release of the metastable state by heat treatment without large-scale melting. If a partial melt occurs and crystallization takes place on the remaining crystal parts as substrate, the term recrystallization should then be used[5]. Because of this, great care was taken in order to select the appropriate annealing temperature, without recrystallization occurring. The representative samples 1–45 and 5–45 were heated at 130°C for 24 and 72 h. This temperature is about 2° to 4°C under the respective melting peak temperatures. These experimental conditions are different to those reported by Chanzy *et al.*[25], used to study the annealing effect on as-polymerized polyethylene crystals obtained by heterogeneous Ziegler–Natta catalyst. The temperatures selected by these authors are some degrees higher than the melting peak temperatures, so that melting and recrystallization takes place, with complete loss of the original morphology.

From *Table 3*, the annealing effect on the density, crystallinity and growth of the crystal thickness, can be observed in two representative samples.

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