Crystallinity and Lateral Crystallite Size of Different UHMW PE Materials

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SYNOPSIS

Nascent high-molecular-weight (UHMW) polyethylene (PE) samples of different origins show a rather high crystallinity of about 70–75% and contain both a major portion of orthorhombic extended chain crystallites and a minor portion of triclinic crystallites. The triclinic content is greater the higher the molecular weight of the sample and the higher the activity of the used catalyser. A melting/recooling treatment results in a reduction of crystallinity by about 15–25% and disappearance of the triclinic phase. Further, an irreversible conversion of nascent orthorhombic extended chain crystallites to orthorhombic folded chain crystallites of increased lateral dimensions and crystalline perfections takes place during the melting/recooling treatment. The results are compared to those obtained for lower-molecular-weight PE samples and for high-strength/modulus PE fibers of different origins.

INTRODUCTION

Wang and Salovey[1] recently published a paper dealing with DSC investigations on the melting behavior of nascent high-molecular-weight (UHMW) polyethylenes (PE). Most notably, the irreversible conversion of nascent to folded chain crystals could be observed. The aim of our study was the characterization of supermolecular structure of different UHMW starting materials for the preparation of high-modulus/strength PE fibers. For this end the crystallinities, disorder parameters and lateral dimensions of crystallites were determined for a number of UHMW PE samples of different molecular weights after polymerization (nascent state) and after an additional melting treatment. Further, the melting behavior of these materials was investigated via DSC.

EXPERIMENTAL

Samples

The weight average molecular weights M_w of the investigated samples are shown in Table I. A second sample (1a, 2a, etc.) was obtained in all cases via a 10-min melting treatment at $T = 435°K$.

WAXS Measurements and Data Treatment

A horizontal X-ray counter goniometer HZG-4A (Freiberger Präzisionsmechanik, Freiberg/Sa., GDR) was used in symmetric transmission mode employing Ni-filtered CuK_α radiation ($\lambda = 0.15418$ nm) and an impulse height analyser with stepwise recording $4° < 2\Theta < 104°$ at a step width of 0.1°. The diffraction profiles were corrected for parasitic scattering, absorption, and polarization. The background elimination was done according to Vonk[2] and separation of overlapping reflections was performed with a Pearson-VII function fit program.

Table I Investigated Samples

No.	Material	M_w	Catalyser
1	Lab product	2.7×10^6 g/mol	Very active/relatively high temperature in the zone of macromolecular growth T_{mg}, Ti catalyser;
2	Hostalen Gur	1.5×10^6 g/mol	Less active
3	Lab product	0.96×10^6 g/mol	As for sample 1
4	Lab product	0.81×10^6 g/mol	As for sample 1 but V catalyser
5	Lab product	0.75×10^6 g/mol	As for sample 1

Lateral weight average sizes of orthorhombic crystallites H_{110}, H_{200}, and H_{020} were obtained from the half-widths of the resolved peak profiles applying the Scherrer equation. The absolute degrees of crystallinity X_c and the crystalline disorder parameters k were determined after Ruland[3] and Vonk[2] from the whole corrected scattering curves. k is the parameter the scattering-angle-dependent damping D of crystalline WAXS reflections depends on:

$$D = \exp(-2ks^2) \tag{1}$$

with $s = (2 \sin \Theta)/\lambda$ and

$$k = k_T + k_1 + k_2. \tag{2}$$

The term k_T denotes thermal lattice vibrations and k_1 and k_2 represent first- and second-order lattice distortions, respectively.

Calorimetry

The melting behavior of the PE materials was investigated with a Perkin–Elmer DSC 1b differential scanning calorimeter calibrated with an indium standard. The heating and recooling rates were 8°K/min in all cases. The DSC curves were measured for two melting/recrystallization cycles and relative DSC crystallinities were determined from the thermograms using data given in ref. 4. The data are listed in Table III.

RESULTS AND DISCUSSION

The quantitative results of X-ray and DSC investigations are shown in Tables II and III, respectively. The main qualitative result is that all nascent samples contain a remarkable amount of the less stable triclinic crystalline modification in addition to the predominant orthorhombic one, while the molten and recrystallized samples only show orthorhombic crystallites.

All nascend materials do not differ significantly from each other in their absolute degrees of crystallinity. (Note: All tendencies discussed for the X_c parameters are also valid for the relative X_{DSC} values.) There are greater differences between the k parameters of samples 1–5. In this connection, it

Table II Quantitative Results of the Lateral Structure Investigations

Sample	Degree of Crystallinity $X_c/\%$	Disorder Parameter k	Average Lateral Crystallite Sizes		
			L_{110}/nm	L_{200}/nm	L_{020}/nm
1	72.3–76.3	3.8–4.4	7.5	6.8	7.3
1a	46.9–48.4	0.1–0.3	11.2	10.4	10.3
2	70.2–71.4	1.6–1.8	8.9	8.0	8.5
2a	51.6–53.0	0.1	10.7	10.1	9.9
3	68.3–70.4	1.5–1.8	8.6	8.6	8.3
3a	55.4–56.8	0.2	10.9	10.4	10.3
4	71.9–73.2	2.4–2.5	8.5	7.6	8.1
4a	47.3–48.9	0.3–0.4	11.1	10.1	10.1
5	74.3–76.4	1.8–2.1	9.5	8.9	9.3
5a	59.7–61.3	0.2–0.4	11.5	10.3	10.5

Table III   Results of DSC Investigations

Sample	Melting Temp. $T_{m1}/°$	DSC Crystallinity $X_{DSC}/\%$	Melting Temp. $T_{m2}/°$
1	416	0.60	408
1a	410	0.45	410
2	413	0.62	405.5
2a	406	0.50	406.5
3	413	0.64	409.5
3a	409	0.52	409
4	417	0.60	407
4a	407	0.47	408
5	410	0.65	408
5a	408	0.53	408.5

m1, first melting/recrystallization cycle; m2, second melting/recrystallization cycle.

should be mentioned that k may have relatively great systematic errors due to the fit procedure used in Vonk's method. Nevertheless, a reasonable tendency is seen: The smaller the lateral dimensions of the crystallites the higher the k parameters. The content of triclinic material is greatest for the material with the highest M_w (sample 1) and smallest for sample 5, which has the lowest M_w. This tendency is valid for the samples with a relatively high temperature in the zone of macromolecular growth T_{mg} (samples 1, 3, 4, and 5; cf. Table I) only. The Hostalen gur sample 2 ($M_w = 1.5 \times 10^6$), however, which is assumed to have been produced with a lower T_{mg} at the catalyser grains, has about the same triclinic content as the lower-macromolecular-weight samples, 3 and 4. A low M_w PE material ($M_w = 2 \times 10^5$) measured for comparison did not show any triclinic modification and the melting/recooling procedure resulted in a slight increase of crystallinity for this sample.

On the one hand, the melting procedure effects typical results, namely increases of the lateral dimensions of the orthorhombic crystallites and of the crystalline perfection (k decreases considerably). On the other hand, the crystallinities are substantially lower for the melt-treated UHMW PE samples 1a–5a than for the nascend materials. No triclinic material portion can be detected after the melting procedure.

The occurrence of the triclinic PE phase is assumed to be associated with strains acting on the molecules during crystallization. In the course of this process, twist disclinations of chain segments have to be formed since only a twist of the planar zigzag chain is needed to transform the orthorhombic unit cell into the triclinic one.[5,6] Obviously, even the con-

ditions of relatively low pressure during polymerization of high-molecular-weight linear PE used here are sufficient to create such twist disclinations of the very long PE chains, while the polymerization conditions used for the preparation of the low-molecular-weight PE sample do not. Besides the molecular weight M_w, the actual temperature T_{mg} of synthesis at the catalyser grains seems to be the most important processing parameter in this connection. The higher this temperature, the higher the mobility of chains near the catalyser and, therefore, the higher the probability of twist disclination and chain entanglement formation.

The nascent structure of polyethylene after polymerization is assumed to be often composed of extended chain crystals that will be transformed into lamellar crystalline material after melting.[1,7–9] Such a structure can be detected by the DSC melting temperature T_{m1} of above 410°K for nearly all nascent samples, while all melt-treated samples contain lamellar crystalline material (cf. Table III). Only sample 5 with the lowest molecular weight M_w may consist of lamellar crystalline material even in the nascent state. [Note: For a given M_w, the use of a V catalyser (cf. sample 4) causes more perfect (longer) extended chain crystallites than the use of a Ti catalyser (cf. samples 3 and 5).]

As stated above, melting/subsequent cooling creates samples without triclinic crystallites and with a lower crystallinity than the nascent samples, i.e., in this case the twist disclinations show a considerably broader distribution in the sample volume than in the nascent state. Therefore, more material in the neighborhood of twist disclinations is excluded from crystallization in the molten/recrystallized state than in the nascent state, where the twist dis-

clinations are segregated in relatively small sample regions. The crystallinity after the melting treatment is, of course, also effected by a considerably higher concentration of chain entanglements.

It is interesting to compare the results obtained for several starting materials for the preparation of high-strength/modulus PE samples with the respective behavior of the latter ones. High-modulus PE fibers produced in a surface growth apparatus usually contain a triclinic phase, the portion of which is greater the higher the take-up forces. The triclinic crystallites are smaller than the orthorhombic ones.[5,10,11] The twist disclinations are segregated in the noncrystalline regions in the neighborhood of triclinic crystallites. If, on the one hand, those samples are annealed unconstrained for a certain time with a temperature above the α-relaxation temperature ($T_\alpha = 343°K$), but below the melting temperature, the triclinic crystallites are transformed into noncrystalline material, i.e., the twist disclinations are statistically distributed in the noncrystalline regions between orthorhombic extended chain crystallites after the disappearance of the triclinic material portion. Therefore, after melting/recooling recrystallization processes are impossible in these noncrystalline regions. If, on the other hand, the surface-grown fibers are subjected to a hot zone drawing process with T being higher than 410°K, all triclinic material and an additional small amount of noncrystalline material is converted in orthorhombic extended chain one after recooling.[10,11] Under those drawing conditions, the mobility of chains obviously becomes high enough that the twist dis-

clinations can be removed from the inside of microfibrils.

High-modulus/strength PE gel spun/hot drawn fibers investigated by us never showed a content of triclinic material, obviously due to the special ultradrawing conditions.[12]

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