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Wide-angle X-ray scattering studies on polyethylene at low temperatures

K. Schauer, W. Wilke

Abteilung Experimentelle Physik, Universität Ulm, D-89069 Ulm, Germany

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Summary

Linear polyethylene (Lupolen 6041 D) and a polyethylene fraction (PE 2000) were investigated by WAXS at temperatures 8 K < T < 293 K. From the position and integral widths of the reflections the lattice constants (and expansion coefficients) and lattice distortions are determined. Lattice distortions are of the strain type, induced by inherent stresses. They increase with decreasing temperature up to ~50 K and then to lower temperatures a decrease is observed. This is explained by the decrease of the thermal expansion coefficients. For PE 2000 for some reflections a minimum in the integral widths at T ~ 38 K occurs. The explanation of this effect is given by the occurence of a stress induced martensitic transformation (orthorhombic to monoclinic) of part of the material. The corresponding weak reflections are observed.

Introduction

Previous investigations (1,2) on a polyethylene fraction (PE 2000) and on linear polyethylene (Lupolen 6041 D, BASF) showed a strong increase of the integral width of the WAXS-reflections at decreasing temperature. This could be explained by increasing inherent stresses (and therefore also increasing strains) during cooling. At temperatures below 100 K the increase levels out as a result, at least partly, of the decreasing thermal expansion coefficients of the a- and c-axes of the crystals below 100 K. But for some reflections an indication of a decrease of the integral width at about 50 K was observed. The number of measuring points in the low temperature region was insufficient to prove this effect. If it exists, a possible explanation could be the occurrence of a stress induced martensitic transformation (3). After the transformation of part of the crystals the inherent strains are lowered and the line width decreases.
In this work the low temperature range below 100 K is investigated carefully with the aim to clarify this question.

Experimental

Two different polyethylene samples were investigated:

1. A fraction of linear polyethylene PE 2000 (Polymer Lab.): molecular weight M = 2000, polydispersity index $M_w/M_n < 1,1$, density $\rho = 0,9805$ g cm^{-3} and melting temperature $T_m = 122,5\,°C$. The crystallization temperature was $T_c = 114,8\,°C$. The brittle sample has a high degree of crystallinity.
2. Linear polyethylene Lupolen 6041D (BASF): density $\rho = 0,9669$ g cm^{-3}, branching content $CH_3/1000$ C < 1, and crystallinity $w_c \sim 77\%$.

Isotropic thin films (thickness d < 200 μm) were used for the X-ray measurements to reduce the contribution to line broadening by sample thickness. For the wide angle X-ray experiments a Guinier camera was used with Cu Kα_1 radiation (λ = 0,154 nm). The films were exposed only in the linear range. The intensity curves were separated into scattering contributions from crystalline parts, amorphous parts and background scattering. Overlapping reflections were separated by a computer program. The integral widths were determined as mean values over five independent exposures at each temperature. The measured integral widths were corrected for sample thickness contribution and beam divergence. Measurements were carried out in the temperature range from 8 K to 293 K, using a cryostat cooled with N_2 resp. He, as described in (1).

Theory

Different contributions to the integral width $\delta\beta_n$ of a reflection h with Miller indices $(h_1,h_2,h_3)=h$ must be considered: contributions by crystallite size and by lattice distortions. It is assumed, that the different contributions are independent and can be added. Furthermore, because the line profile can be described approximately by a (Lorentz)^2-function, a simple algebraic addition is a good approximation (4).

Therefore we have for the integral width

$$\delta\beta_h = \delta\beta_h(S^2) + \delta\beta_h(Z) \tag{1}$$

The contribution by crystallite size is given by (5)

$$\delta\beta_h(S^2) = \frac{1}{D_h} \tag{2}$$

where D_h is the mean crystallite size in the directions of normals of the lattice planes $\{h\} = \{h_1, h_2, h_3\}$ (9).

The form of $\delta\beta_h(Z)$ depends on the type of lattice distortion. In the case of crystals with quasi long range order (QLRO) (6) $\delta\beta_h(Z)$ can be calculated with the model of the ideal paracrystal (7,8). For powder diagrams the result is

$$\delta\beta_h^p(Z) = \frac{\pi^2 g_s^2}{d_{\hat{h}}} \cdot p^2 \tag{3}$$

where g_s is a measure of the lattice distortion (relative distance fluctuation of the net planes: $\Delta d_h/d_h$), h are the Miller indices without common measure and p is the order of reflection. The samples investigated show a very small, temperature independent contribution of this type. The main contribution, which is discussed in the following, arises from elastic strains, caused by inherent stresses which are produced by the decreasing temperature. The line-width is influenced by the strain distribution. Assuming a Gaussian strain distribution one gets (9)

$$\delta\beta_h^s(Z) = \frac{\sqrt{2\,\pi}}{d_{\hat{h}}}\cdot\sqrt{\langle\epsilon_h^2\rangle}\cdot p \qquad (4)$$

$<\epsilon_h^2>$ is the mean strain fluctuation of the net planes d_h.

The measured set of $\delta\beta_h^s(Z)$ gives a set of $<\epsilon_h^2>$ and by transformation one can calculate the strain fluctuation tensor $<\epsilon_{ij}>$. From this, with the help of the elastic constants, the stress fluctuation tensor $<\sigma_{ij}>$ can be calculated.

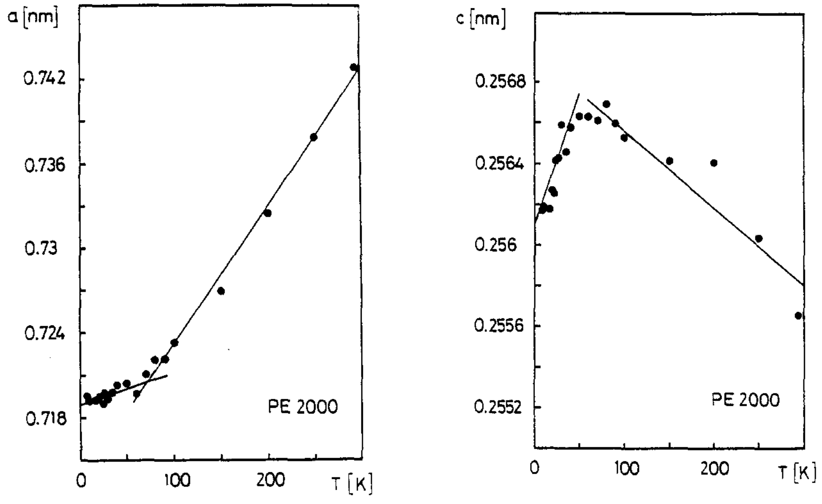
To discriminate between the two types of lattice distortions, one has to extrapolate the measured values of $\delta\beta_h$ to $p = 0$ for different temperatures. Because of the different dependence on p (compare eqs. (3) and (4)) only for the correct type of lattice distortion one point of intersection with the $\delta\beta$-axis is found (see figs. 4 and 5). This intersection point is determined by the crystallite size (see eq.2), which is temperature independent below room temperature. (The small change due to thermal expansion can be neglected.)

Results and discussion

1. Lattice parameters

The lattice parameters a,b,c (a_1, a_2, a_3) of the orthorhombic cell are measured for temperatures between 10 K and 293 K, but with priority for $T \leq 100$ K. Figs. 1 and 2 show, as an example, the results for PE 2000. The lattice parameters a_i for $T < 200$ K are given by

$$a_i = AT + B\,|T - T_1| + D \qquad (5)$$



Figs. 1 and 2: Lattice Constants a and c of PE 2000 and the thermal expansion coefficients

$$\alpha_i = \frac{1}{a_{oi}} \cdot \frac{da_i}{dT} \tag{6}$$

$$a_{oi} : a_i \; at \; T = 293K$$

change at temperature T_1.
The error of the lattice parameters a_i is about 0,1%.
For PE 2000 we found $T_1 = 65$ K and for L6041D the value $T_1 = 80$ K. In the following tables the thermal expansion coefficients are given:

Table 1:

PE 2000:			
Temp.range [K]	α_a [10^{-5} K^{-1}]	α_b [10^{-5} K^{-1}]	α_c [10^{-5} K^{-1}]
10 - 65	3,18	5,41	4,96
65-200	12,93	5,41	-1,45

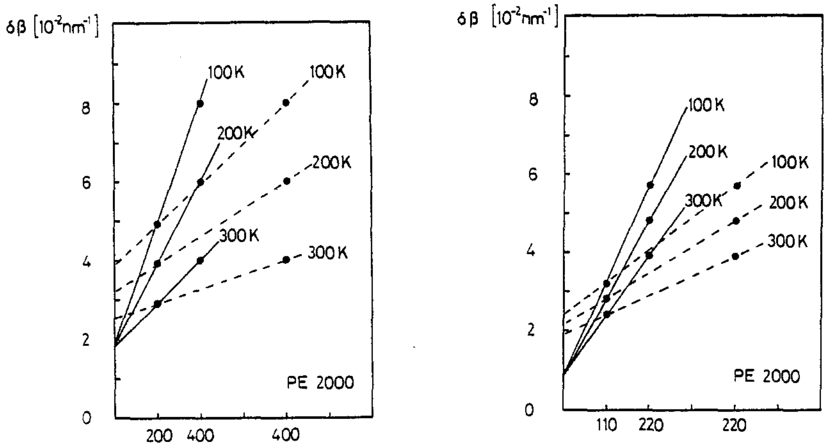
Table 2:

L 6041 D			
Temp.range [K]	α_a [10^{-5} K^{-1}]	α_b [10^{-5} K^{-1}]	α_a [10^{-5} K^{-1}]
10 - 80	4,19	5,56	2,31
80 - 200	11,22	5,56	-1,87

For PE 2000 the values for the low temperature range $T < 65K$ should be more accurate (because of the larger number of measuring points) than those given in (1), the differences are in the order of 20% to 30%.
The positive value for α_c at temperatures $T < T_1$ can be explained by the fact that torsional vibrations are not activated (for further discussion see (1), (10)).

2. Integral widths in the range 100 K < T < 290 K

There is a strong increase of the measured integral width $\delta\beta_h$ with decreasing temperature. Figures 3 and 4 show $\delta\beta_h$ for the reflections 200 - 400 resp. 110 - 220 for three temperatures, plotted against p resp. p^2 (p: order of reflection). Only for a linear dependence $\delta\beta_h$-p one point of intersection at p = 0 occurs. Therefore the temperature



Figs. 3 and 4: Integral widths vs. p resp. p^2 for different temperatures

dependent part of lattice distortions is described by $\delta\beta_h{}^s(Z)$ and caused by inherent stresses which are increasing with decreasing temperature. The strain fluctuations (and therefore the stress fluctuations) are lower for the Lupolen sample then for the highly crystalline PE 2000 sample (11). This is explained by the fact, that the amorphous part acts like a soft matrix for the crystals, if one assumes, that the fluctuations are proportional to the absolute values.

3. Integral widths in the range T < 100 K

For $T < 50$ K the increase of $\delta\beta_h$ with decreasing temperature is strongly reduced for some reflections in the case of the linear polyethylene L 6041 D. This is explained by the decrease of the thermal expansion coefficient α_a. The increase of inherent stresses, caused by different thermal expansion coefficients of adjacent crystallites with different orientations, is smaller.

For the fraction PE 2000 a relative minimum at $T \sim 38$ K for some reflections (110, 220, 210, 201, 211) is observed (see figs. 5-7), the increase of $\delta\beta_h{}^s$ is strongly influenced by $<\epsilon_{12}{}^2>$.

With the assumption mentioned above: $<\epsilon_{12}{}^2> \sim \epsilon_{12}{}^2$, this means, the shear stresses in the a-b-plane have also a minimal value at $T \sim 38$ K. These observations are interpreted by a stress induced martensitic transformation from the orthorhombic to the monoclinic structure. For this transformation a shear in the a-b-plane is necessary. If a small fraction of the crystallites is transformed, the change of the shape (due to the transformation) reduces the stresses and strains at the adjoined crystallites and therefore the inherent stresses and the integral widths of the reflections. Because of the required activation energy at very low temperatures no martensitic transformation can occur and $<\epsilon_h{}^s>$ and $\delta\beta_h$ again increase. This explains the relative minimum in $\delta\beta_h$. The martensitic transformation is observed only for PE 2000 because of the higher inherent stresses, compared with L6041D.

to prove this interpretation, we looked for reflections of the monoclinic phases.

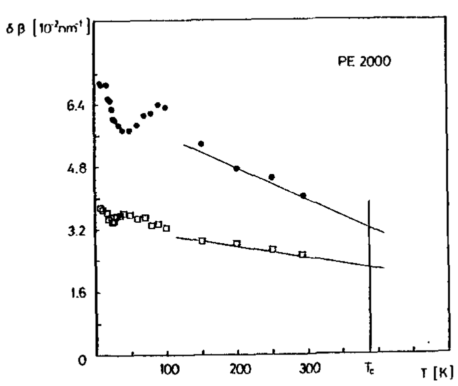
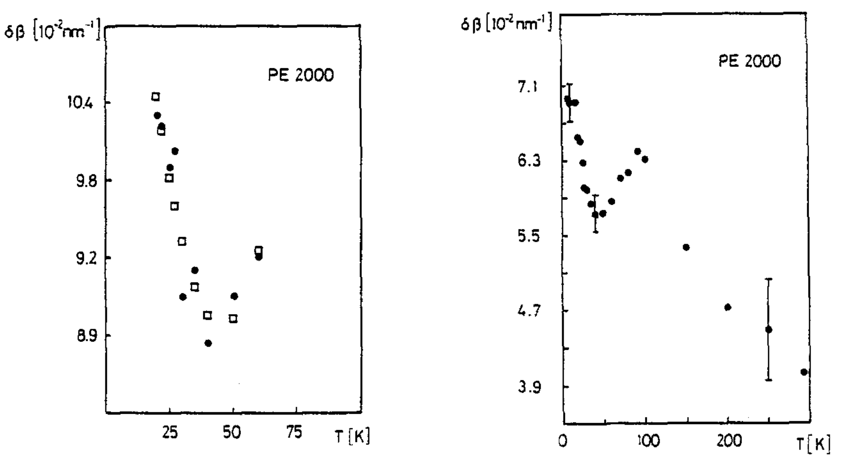


Fig.5: Integral width of the reflection 110 (□) and 220 (•) as a function of temperature



Figs. 6 and 7: Integrals width of reflection 211 resp. 220 as a function of temperature

4. Additional reflections in the range T < 100 K

For the sample L 6041 D no additional reflections were found.
For the sample PE 200 two weak additional reflections for temperatures T < 60 K at Bragg angles $\Theta = 9{,}19°$ and $\Theta = 9{,}79°$ are observed. They can be indexed as 010-reflections of the phases monoclinic 1 and monoclinic 3 (12). At T = 293 K no additional reflections are observed and cyclic measurements T = 20 K → 293 K → 20 K proved the reversibility of the effect.

Therefore we conclude, that the observations can be interpreted by the assumption, that a small part of the crystallites in PE 2000 undergoes a stress induced martensitic transformation from the orthorhombic to the monoclinic phase at low temperatures.

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