DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

DESY SR-79/18
September 1979

STUDY OF THE CRYSTALLIZATION PROCESS OF ORIENTED POLYETHYLENE THEREPHTHALATE BY MEANS OF SYNCHROTRON RADIATION

by

G. Elsner and H. G. Zachmann

Abteilung Angewandte Chemie der Universität Hamburg

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A. Introduction

Oriented amorphous polyethyleneterephthalate crystallizes very quickly when heated above 95°C. In order to study the change of the small angle x-ray scattering during crystallization a very strong x-ray source and a very sensitive detector is necessary. As a strong source the synchrotron radiation of the storage ring DORIS in the EMBL laboratory at DESY, Hamburg, was used (Fig. 1). The x-ray scattering was registered by an silicon intensified vidicon developed by Reynolds, Milch and Gruner (1). This detector is capable of recording x-rays over an area of 40 mm in diameter without the count-rate limitation inherent in x-ray counters. The data from the camera are stored directly in digital form on a disk connected to a PDP-11 computer. The total small angle x-ray scattering of a sample could be registered within 10 seconds with storage ring currents of 10 to 20 mA at 4.8 GeV.

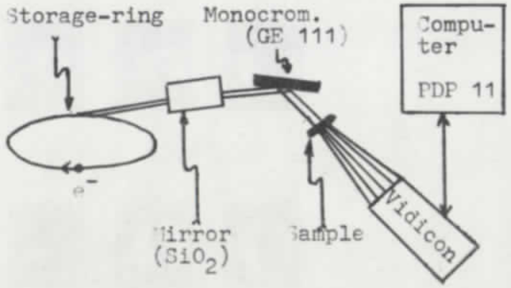

Fig. 1: Schematic representation of the experimental device.

Amorphous films of polyethyleneterephthalate (250 μ thick) were oriented by stretching at $T_V = 92^\circ C$. The oriented samples with birefringences Δn_0 lying between $9 \cdot 10^{-3}$ and $40 \cdot 10^{-3}$ were crystallized at temperatures T_K ranging from 90°C up to 110°C. During the crystallization the small angle x-ray scattering was registered.

B. Results

Fig. 2, upper row, shows the scattering patterns of a sample with initial birefringence $\Delta n_0 = 9 \cdot 10^{-3}$ obtained at three different crystallization times during crystallization at the temperature $T_K = 105^\circ C$. In the lower row the results are shown for a sample with $\Delta n_0 = 19 \cdot 10^{-3}$ at the crystallization temperature $T_K = 97{,}5^\circ C$. The data from the patterns obtained in this way were stored in the computer. From the data the spacings between the peak intensities and the azimuthal half widths of the reflections were determined. From the spacing between the peak intensities the long period was calculated in the usual way. The azimuthal half widths were taken as a measure of the orientation. The smaller the half width, the higher the orientation of the crystal surfaces.

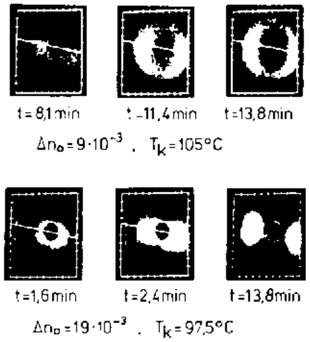

Fig. 2: Examples for the change of the small angle x-ray pattern of oriented samples during isothermal crystallization. T_K = crystallization temperature, t = crystallization time, Δn_0 = initial birefringence.

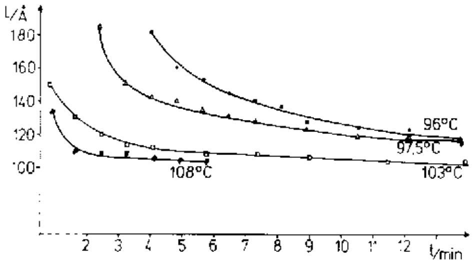

Fig. 3: Long period L as a function of crystallization time t for samples with initial birefringence $\Delta n_0 = 19 \cdot 10^{-3}$. The crystallization temperature is written at each curve.

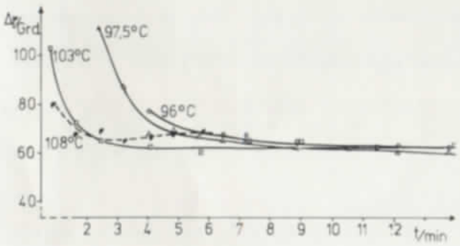

Fig. 4: Azimuthal half width $\Delta\varphi$ of the reflexion as a function of crystallization time t for samples with initial birefringence $\Delta n_o = 19 \cdot 10^3$. The crystallization temperature is written at each curve.

Fig. 3 shows the long period as a function of the crystallization time for a sample with an initial birefringence $\Delta n_o = 19 \cdot 10^{-3}$. The parameter written at each curve is the crystallization temperature. One sees that the long period decreases with increasing crystallization time. The value reached at the end of the crystallization seems to decrease with increasing crystallization temperature.

Fig. 4 shows the corresponding values of azimuthual half width of the reflexion. Generally the azimuthal half width decreases with increasing crystallization time. At some temperatures in addition a small intermediate maximum can be observed.

The Figs. 5, 6, and 7 show the corresponding results for the samples with the initial birefringence $\Delta n_o = 41 \cdot 10^{-3}$ and $9 \cdot 10^{-3}$ respectively. For $\Delta n_o = 9 \cdot 13^{-3}$, due to the low orientation, it was not possible to make reproducible measurements of the azimuthal half width.

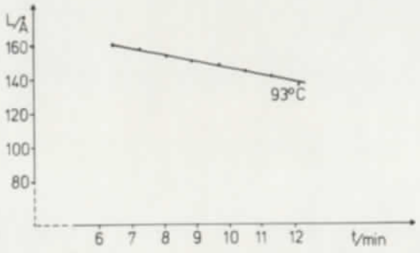

Fig. 5: Long period L as a function of crystallization time t for samples with initial birefringence $\Delta n_o = 41 \cdot 10^3$. The crystallization temperature is written at each curve.

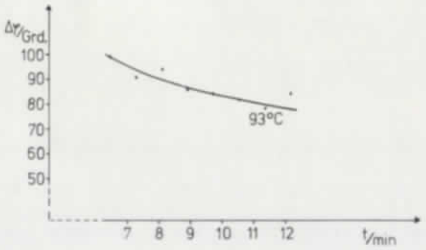

Fig. 6: Azimuthal half width $\Delta\psi$ of the reflexion as a function of crystallization time t for samples with initial birefringence $\Delta n_o = 41 \cdot 10^{-3}$. The crystallization temperature is written at each curve.

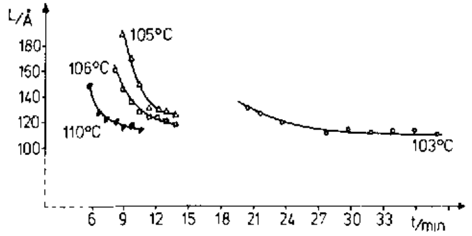

Fig. 7: Long period L as a function of crystallisation time t for samples with initial birefringence $\Delta n_o = 9 \cdot 13^{-3}$. The crystallization temperature is written at each curve.

C. Discussion

A decrease of the long period of polyethyleneterephthalate during crystallization has already been observed with unoriented samples which have been quenched to room temperature (2). The present results show that the decrease occurs also with oriented samples and that it is not an artificial effect caused by quenching but that it can be measured also at the crystallization temperature without interruption of the crystallization process.

Fischer and Fakirov (3) have measured the long period of oriented polyethyleneterephthalate during crystallization by quenching the samples to room temperature; they did not obtain a decrease of the long period with time. The difference to our results is probably due to the fact that these authors used considerable higher

crystallization temperatures than applied in this work; the crystallization occurred so rapidly that it was almost completed before the first measurement was performed.

It is also interesting to note that the end value of the long period decreases with increasing crystallization temperature. Such a behaviour has been observed also by other authors (4, 5). The half widths of the wide angle reflections seem to remain constant (6). This means that the orientation of the chains remains constant and only the orientation of the crystal lamella surfaces improves.

A model explaining this behaviour is shown in Fig. 8. One has to assume bended lamella which flatten during annealing while the chain orientation does not change. The observed decrease of the long period may be attributed to the fact that one has a broad distribution of crystal thicknesses which becomes smaller with time.

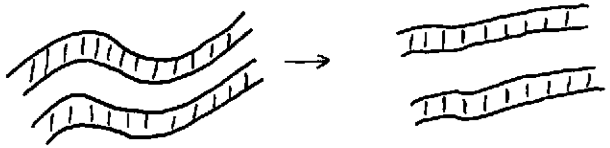

Fig. 8: Change of morphology during crystallization.

In some cases the increase in orientation does not occur monotonically. In agreement with this result also the birefringence (7) and the shrinkage stress (6) do not change monotonically. Obviously the molecular process during crystallization of oriented polymers are quite complex.

We want to thank Dr. J.R. Milch for having the possibility to use the vidicon system and for many valuable discussions. We are also indebted very much to DESY and EMBL, specially to Prof. Dr. Stuhrmann, for getting the permission to perform the measurements.

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