PHYSICAL CHEMISTRY

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1964

SovietRxiv

Abstract

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TEMPERATURE CHANGES OF THE LONG PERIOD IN ORIENTED POLYMERS

The long period is usually taken to mean the quantity $d = \lambda/2\theta$, where λ is the wavelength and 2θ is the diffraction angle corresponding to the maximum in the intensity distribution of small-angle X-ray scattering. The study of long periods, in particular at different temperatures (1), is of great interest, since it makes it possible to judge differences in the degree of order in the structure of polymers. We investigated the change in the long period in oriented fibers of low-pressure polyethylene in the temperature range from room temperature to 116°. X-ray photographs at large angles showed that the degree of orientation of the crystallites in the fibers was very high and practically did not change after the temperature exposures, since the fibers in the specimen were in a stretched state. The maximum deviation of the chain axes from the fiber axis (texture scattering) did not exceed 10–15°. The oriented specimen of fibers was placed in a furnace mounted on the small-angle camera. The temperature was controlled to an accuracy of ±2°. At a given temperature the entire small-angle scattering curve was recorded. The remaining experimental conditions were the same as in (2,3). The scattering curves were recorded over several successive heating and cooling cycles of one and the same specimen. The measurements were repeated many times, and the results were well reproduced. The intensity distribution curves of the meridional small-angle reflection obtained in the first cycle on raising the temperature to 113° are shown in Fig. 1, and on lowering the temperature to 20°, in Fig. 2. During the second and subsequent cycles the character of the change in the intensity curves remained approximately the same as during cooling in the first cycle (Fig. 2). The long-period values calculated from the intensity curves are given in Table 1. As is seen from Fig. 1, the intensity at the maximum increases with increasing temperature in the first cycle. When the temperature is lowered from 113° to room temperature, the change in intensity passes through a maximum at $t \sim 100°$. Since in subsequent cycles the position of the diffraction maximum changes almost not at all, in order to study the change in its intensity, instead of recording the entire curve point by point the counter was fixed at the point of maxi-

Fig. 1. Change in the position and intensity of the meridional small-angle reflection for polyethylene fiber on heating in the first cycle from 20 to 113°. *a*—initial specimen, at 20°; *b*—at 100°, *v*—at 113°, *g*—at 80°, *d*—at 105°

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Table 1

Change in the magnitude of the long period (in angstroms) as a function of the recording temperature during the first and second cycles (I—heating to 113°, cooling to 20°; II—heating to 113°, cooling to 20°)

T, °C	I cycle	II cycle	T, °C	I cycle	II cycle
20	178	266	100	286	286
80	178	–	90	286	286
90	–	286	80	286	–
100	196	286	40	269	270
105	219	–	20	266	270
113	286	295			

and the intensity was continuously recorded on an EPP-09 chart tape as the temperature was varied from 20 to 116° and back. The curves shown in Fig. 3 directly characterize the change in intensity at the maximum of the small-angle scattering distribution.

As can be seen from Fig. 3, the same intensity maximum is observed both on heating and on cooling. The experimental data presented in the table and in the graphs show that, during cyclic temperature variation, both reversible and irreversible changes occur. The irreversible changes occurring during the first cycle lead to an increase in the magnitude of the long period (from 178 to 286 Å) and to an approximately 2.5–3-fold increase in the intensity of the small-angle reflection when the specimen is cooled to 20° after the first heating (in comparison with the initial specimen). During subsequent cycles, only reversible changes in intensity occur, while the magnitude of the long period remains practically unchanged.

Fig. 2. Change in the position and intensity of the meridional small-angle reflection for a polyethylene fiber upon cooling in the first cycle from 113 to 20°. *a*—at 113°, *b*—at 90°, *v*—at 100°, *g*—at 20°. 1—the parasitic-background line.

In explaining the results described above, it is necessary to proceed from the fact that the magnitude of the long period is approximately equal to the sum of the lengths of the ordered and defective regions, while the intensity depends on the difference in densities in these regions. Therefore, the irreversible increase in the period and in the intensity of the small-angle reflection after the first cycle is associated with an increase in the dimensions of the ordered regions, with an improvement of the order within them, and with an increase in their density. This conclusion is confirmed by the fact that, after the first cycle, the number of reflections on wide-angle X-ray patterns increases and their sharpness increases.

Fig. 3. Change in reflection intensity in the third cycle during heating from 20 to 116° and cooling from 116 to 20°

Figure 3: Fig. 3. Change in reflection intensity in the third cycle during heating from 20 to 116° and cooling from 116 to 20°

In addition, the irreversible increase in the intensity of the small-angle reflection after the first cycle may be associated with a decrease in the density of the de-

defective regions, since, as the size of the ordered regions increases during annealing, some of the chains may pass from defective into ordered regions. It should be noted that during the first annealing, along with irreversible changes in intensity, reversible changes also exist.

The change in the magnitude of the long period in the subsequent cycles (Table 1), by no more than $\sim 10\%$, may be caused by thermal expansion. Obviously, variations of d in this case must be completely reversible and not associated with structural changes.

Of greatest interest is the reversible change in intensity (Fig. 3). We believe that this phenomenon is associated with different types of molecular mobility in defective and ordered regions [4]. When the temperature is raised to 90–100°, motions are intensified mainly in the defective parts of the structure. This causes a decrease in the density of these regions and an increase in the intensity of the small-angle reflection. It is possible that the fact that the expansion coefficient of the defective regions may be greater than that of the ordered ones also has an effect. With a further increase

Fig. 3. Change in reflection intensity in the III cycle during heating from 20 to 116° and cooling from 116 to 20°.

of temperature above 100°, intense molecular motions also begin in the latter, as a result of which the difference between the densities of the ordered and defective regions decreases, and the intensity of the small-angle reflection decreases.

Thus, if the irreversible changes in the small-angle scattering curves are associated with processes of enlargement of the ordered regions and of the degree of order within them during annealing, then all reversible changes are caused by thermal motions.

The results presented show that small-angle X-ray scattering can be successfully used to study both crystallization processes and the dynamics of molecular motions in polymers.

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Received
14 III 1964

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Note: Figure translations are in progress. See original paper for figures.