

STRUCTURAL CHANGES DURING CRYSTALLIZATION OF DOUBLY-ORIENTED POLYCAPROLACTAM

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Structural changes of doubly-oriented polycaprolactam at various annealing temperatures have been investigated depending on time. The samples were annealed with free ends in a silicone oil bath. The structural changes during annealing occur in two stages. In the first stage, which is very short, the structural parameters change very quickly and within a broad range; the long period, size, perfectness and density of the crystallites increase. The sample dimensions change anisotropically. In the second stage there are only insignificant changes in these parameters, and thus also small changes in the structure. The changes occurring in polycaprolactam in this stage differ from the behaviour of polyethylene and polypropylene under the same conditions. The structural changes are explained in terms of Peterlin's model of plastic deformation.

Annealing strongly affects the structure of oriented crystalline polymers. A number of authors¹⁻¹¹ have attempted to determine the structural model of these changes. Dismore and Statton^{2,3} investigated these effects on polyamides; they assumed that in highly oriented fibre the chains are extended with the exception of small residues of folds and become folded during annealing. Dumbleton and Buchanan^{4,5} assumed that an essential part of the chains is folded already in the original fibre, and the number of folds increases only very little during annealing.

Our preceding paper¹¹ was dealing with the effect of the annealing temperature on the structure of doubly-oriented polycaprolactam. The structural changes were explained in terms of Peterlin's two-stage model of plastic deformation. This paper reports on the results of an investigation of the annealing time on the structure of doubly-oriented polycaprolactam.

EXPERIMENTAL

Polycaprolactam film, thickness 0.5 mm, density 1.1389 g cm^{-3} , highly oriented by drawing and rolling, was used in the experiments. The films were annealed in silicone oil under isothermal conditions at temperatures T_A (120, 140, 160, 180, 200°C) for 1, 10, 100, and 1000 min. The bath temperature was maintained with an accuracy of $\pm 0.2^\circ\text{C}$. The required bath temperature was attained during 1–3 min after the sample had been immersed in the bath depending on T_A . This effect somewhat influences the conditions for samples annealed at 120 and 140°C. After removal from the bath the samples were rapidly cooled to room temperature in a methyl ethyl ketone bath. The samples were annealed with free ends.

Small-angle X-ray scattering. To obtain an undistorted distribution of diffracted intensity at small angles Kiessig's camera was used. The $\text{CuK}\alpha$ radiation was filtered through a nickel filter. Kratky's camera was used in the measurements of the small-angle reflexions along the meridian, and also for the intensity measurements. The $\text{CuK}\alpha$ radiation was recorded by means of a scintillation counter; it was monochromatized with a Ni-filter, and an amplitude analyzer was also used.

Wide-angle X-ray scattering. The diffraction patterns were obtained with a flat-film camera, the sample-to-film distance being 41.3 mm. The $\text{CuK}\alpha$ radiation was filtered through a nickel filter. The integral breadths of diffractions were measured with a powder Hilger and Watts diffractometer with a bent quartz monochromator in the diffracted beam. The $\text{CuK}\alpha$ radiation was recorded with a scintillation counter provided with an amplitude analyzer.

Density. The density measurements were carried out by the flotation method described earlier¹¹.

Dimensional changes. Shrinkage and expansion were measured with an Abbe's comparator and a contact thickness indicator.

RESULTS

The changes in the small-angle diffraction patterns were measured in the most interesting, that is, transversal direction, where their shape was that of a four-point diagram. The angle δ between the meridian and the four-point diagram reflexions decreased during the first minute of the annealing and afterwards remained constant¹¹. The reflexions obtained for a sample annealed at 200°C approached each other to such a degree that one broad maximum was formed. These changes are illustrated in Fig. 1* for samples annealed for 1 min. The angle δ of the four-point diagram is connected with the deflection of the crystalline layers of the supermolecular structure from the direction perpendicular to the fibre axis. The intensity of small-angle diffractions also increased steeply within one minute, but remained practically constant throughout the annealing time¹¹. Fig. 2 shows the dependence of the long period L on the time and temperature of annealing. After the initial rapid change from the original 83 Å which took less than one minute the long period has a decreasing tendency, which, however, is very weak, is several Å.

Wide-angle X-ray scattering. Fig. 3 shows diffraction patterns of polycaprolactam annealed at 200°C for 1000 min for the orientations of the primary beam in three characteristic directions (machine M, transversal T and normal N). It follows from the patterns that here we have a monoclinic α modification of polycaprolactam¹². The changes in the reflexion intensities during transition between the individual orientations indicate that the film has a uniplanar-axial texture. The (001) planes in which the chains are bonded by hydrogen bonds are parallel to the film plane¹³.

From the broadening of the crystalline diffractions (200), and (002), (202) corrected for the experimental broadening¹¹, the dimensions of the crystallites in the respective directions were calculated by using Scherrer's expression¹⁴ (Fig. 4). In this case too the greatest change occurs within the first minute; by annealing to 200°C, the crystallite size is doubled within 1 min. The changes taking place during the following course of annealing are already very small. The crystallites somewhat increase, or their structure becomes improved. It also follows from Fig. 4 that the size of the crystallites is not isotropic.

Changes in dimensions in directions M, N, T. The measurements show that these changes have a strongly anisotropic character (Table I). A strong shrinkage occurs in the machine direction M, the rate of which rapidly decreases with increasing annealing time. In the normal direction N

* See insert facing page 1508.

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Structural Changes During Crystallization of Doubly-Oriented Polycaprolactam

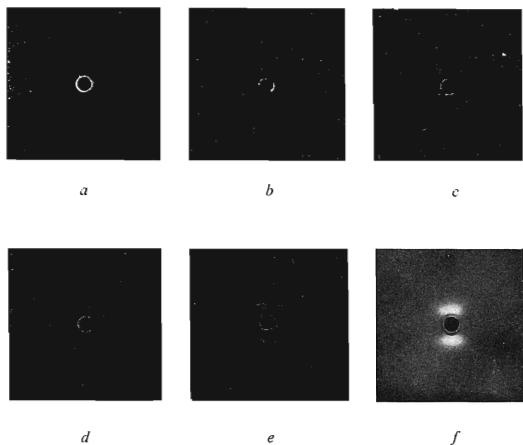


FIG. 1

Small-Angle Diffraction Patterns of Polycaprolactam

Original (*a*) and annealed 1 min at 120°C (*b*), 140°C (*c*), 160°C (*d*), 180°C (*e*), 200°C (*f*), (the primary beam is parallel to the direction T).

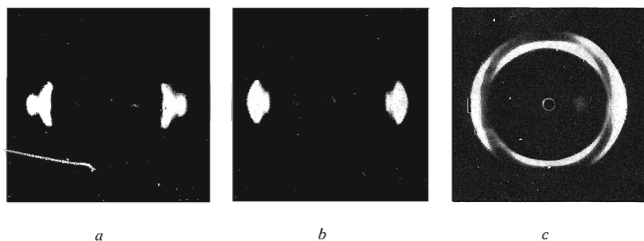


FIG. 3

Wide-Angle Diffraction Patterns of Polycaprolactam Annealed for 1 000 min at 200°C at the Primary Beam Orientations in the Directions N (*a*), T (*b*), and M (*c*)

there is a strong expansion in the first minute of annealing; this is followed by shrinkage which proceeds similarly to the direction M, that is, practically linear with the logarithm of time. The shrinkage in the direction N cannot, within 1000 min, compensate for the initial expansion. The changes measured in the direction T lie within the limit of errors; however, it follows from the measurements that the shrinkage taking place in this direction is proportional to the temperature of annealing, and its value for $T_A = 200^\circ\text{C}$ is 0.5% of the original length.

Density. The measurements indicated a practically linear increase in density depending on the logarithm of the time of annealing, t_A (Table I). Here we have again an initial rapid increase in the measured value except for the densities at $T_A = 120^\circ\text{C}$. This temperature is obviously too low for the initial rapid change in density.

DISCUSSION

The time course of the changes in the long period, in the δ angle of the four-point diagram, in the crystallite size, density, and dimensions of polycaprolactam during annealing can be divided into two stages. The first stage is characterized by a very rapid change in the values and takes a very short time. This time is shorter than the shortest possible time 1 min at which a defined annealing can be carried out. (A shor-

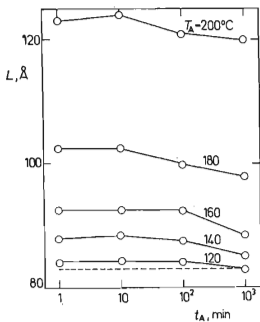


FIG. 2
Changes in the Long Period of Polycaprolactam Depending on Time (t_A) and Temperature (T_A) of Annealing (----- original sample)

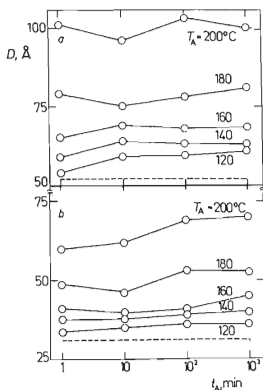


FIG. 4
Size of Polycaprolactam Crystallites Depending on Time (t_A) and Temperature (T_A) of Annealing Calculated from the Broadening of the X-Ray Diffractions
a) (200), b) (202), (002); ----- original sample.

ter time would bring about distorted results with respect to the time of establishment of the thermal equilibrium, *cf.* Experimental). It can be said, therefore, that the essential structural changes during annealing taking place in this initial stage occur within such a short time that their course is virtually imperceptible. The first stage of annealing appears to a considerable degree at temperatures above $T_A = 120^\circ\text{C}$.

The second stage of annealing is characterized by a very smooth change in the measured structural parameters with time t_A . Both stages have also been observed for other polymers^{6,8,12}.

Both the δ angle of the four-point diagram and the intensity of small-angle diffraction changed steeply in the first stage; afterwards, however, they remained within the limits of experimental error at the same level up to $t_A = 10^3$ min. The long period insignificantly decreased. This seems to point out that in the second stage of annealing there is no pronounced change in the supermolecular structure of polycaprolactam. The crystallite size increases up to double its original value;

TABLE I
Size and Density Changes of Polycaprolactam During Annealing

T_A $^\circ\text{C}$	t min	Shrinkage Δ/l_0 in direction		Density gcm^{-3}
		M, %	N, %	
120	1	2.59	— 2.85	1.1390
	10	3.76	— 3.60	1.1418
	10^2	4.53	— 3.50	1.1429
	10^3	5.02	— 2.28	1.1436
140	1	5.31	— 4.46	1.1425
	10	6.10	— 4.60	1.1461
	10^2	6.63	— 3.50	1.1475
	10^3	7.82	— 2.40	1.1517
160	1	7.28	— 5.27	1.1451
	10	7.06	— 4.97	1.1461
	10^2	9.49	— 5.15	1.1495
	10^3	10.78	— 2.67	1.1540
180	1	10.65	— 9.91	1.1480
	10	10.53	— 8.06	1.1501
	10^2	13.99	— 6.74	1.1545
	10^3	14.37	— 5.49	1.1585
200	1	17.49	—12.17	1.1519
	10	17.67	—10.45	1.1550
	10^2	25.13	—11.20	1.1588
	10^3	22.84	— 6.99	1.1655

in the second stage the increase in size is very small. In other words, while in the first stage the transversal dimensions of fibrils increased steeply and their structure was improved, further annealing brought about only a very slow improvement of these structural properties.

Similarly to polyethylene⁶ and polypropylene⁸, the first stage of annealing of polycaprolactam is very fast. In the second stage the behaviour of polycaprolactam differs from that of the former two polymers. While for the former two compounds the long period and the intensity of small-angle diffractions increase with time t_A , in the case of polycaprolactam the intensity has attained saturation in the first stage and does not change any more, and the long period has a somewhat decreasing tendency. This is related to the differences in the structure of the polyethylene and polypropylene chains, on the one hand, and of the polycaprolactam chains, on the other. The chains of the former two polymers exhibit a much higher mobility, since they are not bonded by hydrogen bonds as in the case of polycaprolactam.

The dimensional changes in the characteristic directions exhibit a strongly anisotropic behaviour related to the double-orientation of the polycaprolactam film. This behaviour can be explained in terms of two mechanisms. The pressure which was acting upon the film in the direction N during orientation led to a very close packing of fibrils in this direction. This in turn caused stacking of the crystallites into layers deflected from the plane perpendicular to the fibre axis (four-point diagram) and led to a considerable internal stress in the direction N. This stress relaxed very quickly during the first stage of annealing, the structure was trying to get into the state prior to the deformation, and the sample expanded proportionally to the annealing temperature. This phenomenon was accompanied by shrinkage in the direction M. The shrinkage is due to the fact that the fibrils which are strongly extended by plastic deformation and have a higher mobility owing to the elevated temperature slide against each other and refolding of the interfibrillar tie-molecules occurs, and the stress within the fibrils relaxes as a result. The crystallite layers gradually orientate into a direction perpendicular to the fibre axis, are arranged side by side, and form broader layers. This process is accompanied by a considerable increase in the long period, density, crystallite size, and also by an improvement in their structure.

During the very quick relaxation of the stress in the film in the first stage of annealing, not all the chains drawn out from the lamellae had enough time to be refolded. They formed a transient disordered layer between the fibrils. The molecules passing through this layer are refolded while the process of annealing is going on, thus leading to shrinkages in the direction N and in the direction M. This behaviour is accompanied by a small increase in the transversal crystallite dimensions and by the disappearance of defects in the crystalline phase. The amorphous regions stressed by plastic deformation return to the state of thermodynamical equilibrium. These changes cause the slow increase in density observed in our experiments.

REFERENCES

1. Fischer E. W., Schmidt G. F.: *Angew. Chem.* **74**, 551 (1962).
2. Dismore P. F., Statton O. W.: *J. Polym. Sci.* **B2**, 1116 (1964).
3. Dismore P. F., Statton O. W.: *J. Polym. Sci.* **C13**, 133 (1966).
4. Dumbleton J. H., Buchanan D. R.: *J. Polym. Sci. A-2*, **6**, 1527 (1968).
5. Buchanan D. R., Dumbleton J. H.: *J. Polym. Sci. A-2*, **113** (1969).
6. Loboda-Čačkovič J., Hosemann R., Wilke W.: *Kolloid-Z. u. Z. Polym.* **235**, 1162 (1969).
7. Peterlin A.: *J. Polym. Sci.* **C9**, 61 (1965), **C15**, 427 (1967), **C18**, 123 (1967).
8. Baltá-Calleja F. J., Peterlin A.: *Makromol. Chem.* **141**, 91 (1971).
9. Meinel G., Peterlin A.: *J. Polym. Sci* **B3**, 783 (1965); *J. Appl. Phys.* **36**, 3028 (1965).
10. Hansen D., Kracke W. F., Falender J. R.: *Polymer Preprints* **10**, 1044 (1969).
11. Baldrian J., Pelzbauer Z.: *J. Polym. Sci.* **C38**, 289 (1972).
12. Holmes D. R., Bunn C. W., Smith D. J.: *J. Polym. Sci.* **17**, 159 (1955).
13. Baldrian J.: *This Journal* **30**, 3648 (1965).
14. Alexander L. E.: *X-Ray Diffraction Methods in Polymer Science*. Wiley-Interscience, New York 1969.

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