ROLLING OF POLYCAPROLACTAM

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The changes in structure during rolling and annealing of rolled polycaprolactam were investigated. The original unoriented polycaprolactam foil, the crystalline phase of which was of the α modification, was rolled at room temperature to various $1/1_0$ ratios. Annealing proceeded at 145°C two hours in water vapours. The pole figures of the crystalline planes (200) and (002) were constructed by means of X-ray diffraction. The structural changes taking place during the rolling of polycaprolactam may be divided into two stages. The first stage gives rise to an unstable structure with crystallites situated at a defined angle with the plane and the direction of rolling. For this structure, a decrease in the degree of orientations is observed during annealing. In the second stage the structure becomes fibrillar. The crystallites are oriented by their (002) planes parallel to the film plane and the chains are oriented in the direction of rolling. The texture of these samples does not change with annealing.

The structural changes due to plastic deformation have been investigated on a number of polymers, such as polyethylene[1-14], polyoxymethylene[15,16], poly(ethylene terephthalate)[17], polypropylene[18-20] and polyamides[15,21-26]. The main feature of such changes consists in the transition of the spherolitic unoriented structure into the fibrillar structure having a high degree of fibre or two-dimensional orientation. At lower deformations the sample structure passes through a state when molecular chains are tilted at certain angles with respect to the direction of the acting force[1,11,12,15]. Changes in tilt proceed during deformation suddenly for some polymers (POM), or gradually for others, *e.g.* nylon 11 (ref.[15]). During the annealing of nylon 11 the degree of tilt does not change[15].

It is known that during the rolling or drawing of polycaprolactam foil the (002) planes of its stable α modification in which the zig-zag chains are bonded with hydrogen bonds become oriented parallel with the film surface[22-26]. The chains become oriented in the direction of rolling or drawing. This final effect is usually obtained at considerable deformations of the sample. It is not known, however, through which stages the structure of polycaprolactam passes during the transition from the original unoriented state to the final effect described above. This paper describes the changes in the texture of the polycaprolactam foil during rolling and the effects of annealing on the structure thus obtained.

EXPERIMENTAL

An unoriented polycaprolactam foil, 1·15 mm thick, was used as the starting material. The foil contained 1% of products extractable with boiling water, its intrinsic viscosity was 1·375 dl/g and the average degree of polymerization was 166. The foil was rolled at room temperature to thicknesses 0·8, 0·6, 0·4 and 0·3 mm; consequently, the degrees of rolling ($\lambda = l/l_0$) are **0·70**, 0·52, 0·35 and 0·26 respectively and the relative elongation is respectively 1·43, 1·92, 2·85 and 3·85. These thicknesses were attained after rolling had been repeated several times. The sample was somewhat heated during the deformation. However, the increase in temperature was comparatively small, so that it did not affect the forming structure too much. The samples were then annealed in saturated water vapours at 145°C for two hours, in order to attain the highest possible degree of crystallinity.

The measurements of pole figures were carried out with a powder Hilger and Watts diffractometer. The diffractometer was provided with a special holder which allowed the use of the Schulz transmission method for measuring pole figures. To obtain the whole pole figure, the samples were cut into strips 1·5 mm thick in machine direction (M) and transversal direction (T). Such arrangement enabled the transmission method to be used for obtaining diffractograms of the samples at different basic orientations (normal, machine, transversal)[25]. The diffraction data obtained for the individual orientations were recalculated to a common scale by means of overlapping areas, corrected and plotted on the stereographic net. The CuK$_\alpha$ radiation filtered through a Ni filter and recorded with a scintillation counter was used for the measurements. A pulse analyzer was also employed.

RESULTS

The original foil was completely unoriented, the diffraction pattern in the M, N, T directions gave the same Debye-Scherer rings. It also followed from these patterns that the polycaprolactam foil crystallized during the production process into the monoclinic α modification.

To detect the changes in texture during rolling, the pole figures of the (200), and (002), (202) planes which gave the strongest reflexions were measured. Since the reflexion from the (002) planes is much more intensive than from the (202) planes, the pole figures describe the behaviour of the (002) planes. For more oriented (0·35, 0·26) and crystallized samples the contribution of the (202) planes was separated. Further reflexions did not possess sufficient intensity to be measured. In all cases the contribution of the amorphous halo was subtracted. In the case of reflexions of uncrystallized samples rolled to a low degree, λ equal to 0·70 or 0·52, when the sickles of the crystalline reflexions are situated round the whole diffraction ring, the subtraction was less precise. Under the given conditions the amorphous halo has virtually a constant intensity along the whole diffraction ring. An inaccurate reading of its intensity in the positions of the recorded diffractions is reflected only in an increase by a constant value of values indicating the density of normals on the pole figure. The character of the texture remains unchanged.

Fig. 1 shows the pole figures of the (200) and (002) planes for unannealed samples; Fig. 2 gives the same figures for annealed samples for the individual degrees of de-

formation. After sample deformation the maximum pole density in the pole figures is concentrated in the surroundings of the equator. Reflexions 200 and 002 are equatorial and the corresponding planes are parallel to the polymer chains. Consequently, the polymer chains become gradually oriented during rolling in the direction of rolling, M.

For the rolling ratio λ 0·70 the pole figure of the (200) plane of an unannealed sample has the maximum pole density near its margin and two local maxima near its centre; the maxima are symmetrically deflected from the equator. The angle between the maxima is 42°C. On the annealing of samples the character of the texture remains unchanged, but local maxima change their angle to 40° (Fig. 2). The (002) planes symmetrically deflected from the equator give only two maxima on the meridian in the pole figure. The angle between these maxima is smaller than in the case of the (200) planes, *viz.*, 38°. Annealing affects the orientation of these planes much more than that of the (200) planes; the angle between the maxima in the pole figure drops to 16°.

On annealing of the foil to the ratio λ 0·52 the concentration of the poles in the surroundings of the equator became more pronounced for the pole figure of the (200) and (002) planes. For the (200) plane, two side maxima at an angle of 38° were again observed on the meridian of the pole figure. The comparatively small effect of annealing of these maxima appeared here too; the angle decreased only by 4°, that is, to 34°. In the case of the (002) planes the meridional maxima in the pole figure coincide into one broad maximum in the centre of the pole figure. By resolving this maximum into two symmetrically deviated from the equator, one obtains 19° for the angle between the (002) planes. Annealing makes this broad maximum still narrower, yielding a single maximum in the centre of the pole figure (Fig. 2).

If plastic deformation proceeds further ($\lambda = 0.35$ and 0·26), the maxima of the pole density are concentrated on the equator only. The (002) planes have their maximum in the centre of the pole figure. The (200) planes give two maxima at angles corresponding to the orientation of these planes with respect to the (002) plane so that the latter is given by the unit cell of the crystalline α modification of polycaprolactam, *i.e.* around 67°. Transition from λ 0·35 to 0·26 makes the maxima in the pole figures sharper: the orientation has become more perfect. The effect of annealing on the pole figures for these rolling conditions is much smaller. The texture does not virtually change. A small increase in the density of normals with respect to the state before annealing may be assigned at the expense of the increase in crystallinity leading to the increase in the number of normals due to the newly formed crystalline planes. In these cases one can speak about a uniplanar-axial texture[27].*

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*   Uniplanar-axial texture: crystalline *b*-axis (of polycaprolactam) is parallel to the reference direction M and the (002) plane is parallel to the reference plane MT.
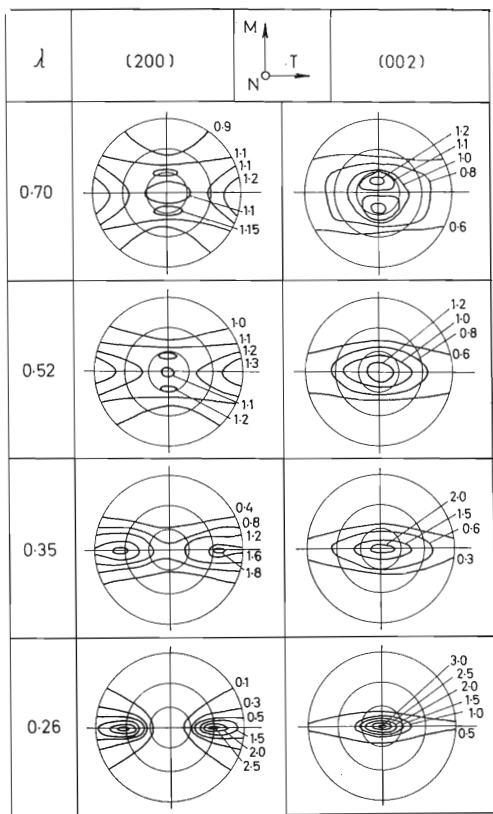
Fig. 1

Pole Figures of the Crystalline Planes (200) and (002) of Polycaprolactam Rolled to Various Degrees λ
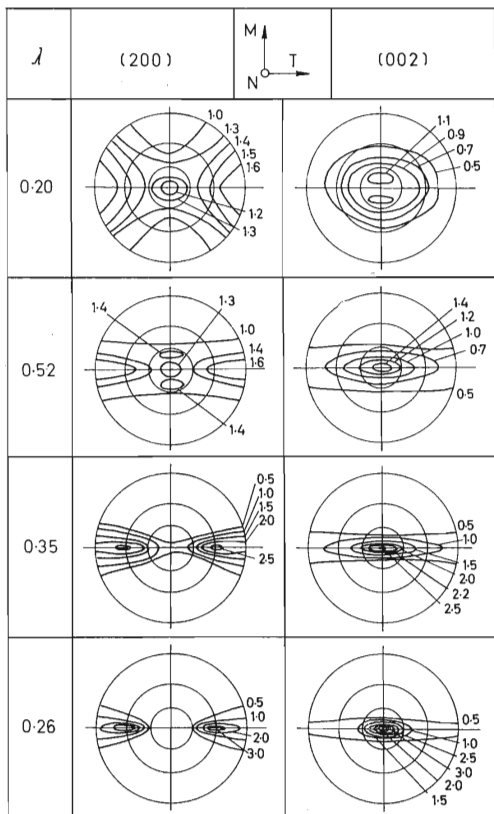
FIG. 2
Pole Figures of the Crystalline Planes (200) and (002) of Polycaprolactam Rolled to Various
Degrees λ and then Annealed

DISCUSSION

The original spherolitic structure of the polycaprolactam foil is transformed by the effect of plastic deformation. With the increasing degree of deformation the foil assumes still more and more pronounced uniplanar-axial texture. It follows from the pole figures that during rolling the (002) planes in which the chains are bonded with hydrogen bonds and which are virtually parallel to the plane of the zig-zag chains exhibit a tendency to become oriented parallel with the foil plane[23]. This tendency is reflected in the pole figures by the concentration of the maximum pole density of the (002) planes in the centre of the pole figure. The orientation of this type was unambiguously recorded at higher degrees of rolling (λ 0·35 and 0·26).

The situation becomes somewhat different at lower degrees of deformation. For λ 0·70 the pole figure corresponds to two systems of the (002) crystal planes deviated from the film plane by 19° and from the direction of rolling by 71°; considerable number of planes are oriented in these two directions. On rolling to λ 0·52 the angle of the (002) planes decreases by approximately one half (10°) with respect to the film plane. In the structure of the α modification of polycaprolactam the (200) planes are deviated from the (002) plane by 67°; this is reflected in the pole figures by the concentration of the maximum pole density near the margin of the pole figure. However, here too some planes exist which are deviated at a certain angle from the film plane and the direction of rolling (side maxima near the centre of the pole figure). Owing to the ratio of the pole number in the side maxima to the total pole number of the pole figure, the latter planes are not numerous. The angle of deviation of the (200) planes from the film plane is much less sensitive to the degree of rolling than that of the (002) planes. While for the (002) this angle decreased to one half (19° and 10°), for the (200) planes the decrease is several per cent only (21° and 19°) when passing from λ 0·70 to 0·52.

The structure arising by rolling of the polycaprolactam film to a low degree is not very stable. If the rolled film is annealed, its texture changes consideralby, and the angle at which the (002) planes deviate from the foil plane changes markedly. During the relaxation of chains due to the presence of water and to the elevated temperature (145°C), the structure has a tendency to relax all internal stresses caused by rolling and to return into the original unoriented state. This phenomenon was reflected in the pole figures by a decrease in the degree of orientation (the density of normals is distributed more uniformly). The deviation of the (002) and (200) planes from the film plane caused by rolling diminishes or disappears. Here too we have a considerable difference between the behaviour of the (200) and (002) planes. While for the (002) planes the angle strongly decreases or the deviation of the planes vanishes, for the (200) planes there is only a small change in the angle.

The pole figures of samples rolled to 0·35 and 0·26 do not virtually change by annealing. The character of the uniplanar-axial texture and also the degree of orienta-

tion of planes remain practically the same. It can be seen from the diffraction patterns that the crystallinity of all samples considerably increases during annealing.

The structure of the original polycaprolactam film is unoriented and spherolitic (Fig. 3a). The spherolites are deformed and gradually destroyed during rolling (Fig. 3b). The lamellar crystallites tend to become oriented in a suitable way with respect to the acting forces. These forces are represented during rolling by a force acting perpendicularly to the film plane (direction N) and by a tangential force caused by the rotation of the cylinders (direction M). These forces cause the lamellas to turn gradually so that the direction of their chains approaches the direction M. The zig-zag chain planes are turned to the direction parallel to the foil plane. Before this final texture is obtained, the structure passes through a number of intermediate stages at which the crystallites are deviated from the film plane so that their (002) planes form defined angles with the foil plane (Fig. 3c). Such orientation of the crystallites is likely to occur only in the (002) planes, since for the (200) planes no corresponding splitting could be observed in the pole figure. The side maxima in the pole figure of the (200) planes correspond to a small number of planes, and consequently only to a small number of crystallites oriented in this way. They are crystallites whose position during rolling was such that the acting force could not turn so as to make their (002) planes approximately parallel to the film plane. The crystallites involved
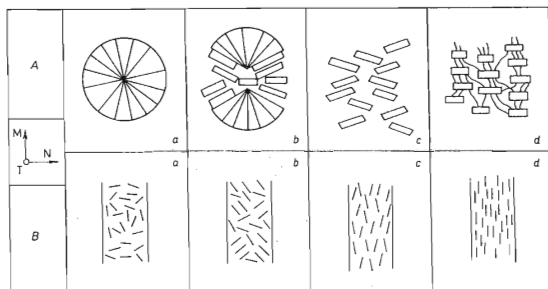

FIG. 3

Model of Supermolecular (*A*) and Molecular (*B*) Changes in the Polycaprolactam Structure During Rolling

a Original film, *b—d* rolled foil; in the series M short intercepts designate the projections of the (002) planes and long vertical intercepts designate the projection of the film plane on the MN plane.

here are those the (200) planes of which were practically parallel to the direction T during rolling. This fact is also corroborated by the finding that the angle of deviation of the (200) planes of these crystallites from the film plane does not vary too much with the degree of rolling or with annealing. Thus, it can be said that the crystallites are very strongly "held" in this orientation. Only at a higher degree of rolling these crystallites can be oriented so that the (002) planes are situated parallel to the foil plane.

Fig. 3 summarizes the structural model of changes in the supermolecular (orientation of crystallites) and molecular (orientation of the (002) crystalline planes) regions occurring during rolling. The changes occur in two stages. The original spherolitic structure has randomly oriented (002) planes, and thus also crystallites. In the first stage of deformation, in accordance with a model suggested by Hay and Keller[1], the spherolites are predominantly deformed nonhomogeneously by fracturing transversely and drawing apart from the fracture. The (002) planes in the deformed parts of the crystallite start being oriented in a direction parallel to the film plane (Fig. 3b). With proceeding deformation the spherolites continue to break and the crystallites form a structure in which they are deviated from the plane of rolling and from direction of rolling at a defined angle (Fig. 3c). This structure arising at low degrees of deformation is unstable. The degree of orientation of crystallites is reduced during annealing. From measurements at various degrees of deformation (0·70 and 0·52) and annealing behaviour it may be deduced that the defined deviation of crystallites varies continuously. Because of the instability of structure this deformation occurs without breaking of crystalline lamellae. The structure is subjected to a considerable stress due to rolling which during crystallization relaxes and partly returns the structure back to the original state. In the second state the crystallites split at the higher deformation and the samples pass into the fibrillar structure in which the (002) planes are oriented parallel to the film plane (Fig. 3). The orientation of chains which is random in the original samples owing to the random orientation of crystallites becomes parallel to the direction of rolling, M, during rolling in the final stage of the fibrillar structure. Similarly to lamellar crystallites the deformation of the chains passes in the initial stages through a number of intermediate degrees at which the chains are oriented at defined angles with respect to the direction of rolling.

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