

Effect of Water on the Mechanism of Deformation of Nylon 6

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Synopsis

Lattice spacings perpendicular to the molecular chain axes and crystallite orientation of dried and moist (boiled in water) bulk nylon 6 were determined by x-ray diffraction under tension of 30–300 kg./cm.². The deformation of the specimen was also measured. The lattice spacings are changed reversibly by the presence of water in nylon 6, but the elastic moduli of the lattice are not affected. The lattice elastic modulus in the direction of the hydrogen bonds is approximately double its value in the direction normal to the hydrogen bonds. The elastic modulus of the dried nylon 6 approaches the value of the lattice elastic modulus in the direction normal to the molecular axes, while the modulus of the moist nylon 6 is several times lower. From these facts, and especially from the relations between the lattice deformation, crystallite orientation, and specimen deformation, the principal differences in the deformation mechanism of dried and moist nylon 6 were deduced. The results obtained have also made possible some general conclusions about the crystalline structure of nylon 6 and the deformation mechanism of linear polymers.

Introduction

The study of the mechanism of deformation of crystalline polymers has hitherto been aimed predominantly at polyethylene.^{1–3} Of the polyamides, nylon 66 has been receiving the most attention in this respect,^{8–10} while for nylon 6, only data on the orientation of its molecules under different degrees of plastic deformation have been published up to present.^{9–11}

In studying the mechanism of deformation of nylon 6, the important question of the influence of water must not be left out. Water, which is absorbed by nylon 6 even from atmospheric moisture, markedly alters the deformation behavior of the polymer. Dry nylon 6 is well known not only to possess an appreciably higher elasticity modulus, but also to be very brittle, in particular as compared to moist nylon 6. A substantial difference may thus be assumed to exist in the deformation mechanisms of dry and moist nylon 6.

The present paper suggests an interpretation of the effect of water on the deformation mechanism of nylon 6 and at the same time contributes also to the understanding of the deformation mechanism of crystalline polymers in general. The changes produced in the structure of nylon 6 by stress have been estimated by means of x-ray diffraction under constant load and, at the same time, the deformation of the specimen has also been measured.

The x-ray diffraction measured directly under stress enables us to study the response of ordered crystalline regions to the load, so that in combination with the measurements of the total changes in the specimen it becomes possible to determine the behavior of the two principal structural constituents: the crystalline and the amorphous components. These possibilities offered by x-ray diffraction have, however, not as yet been fully exploited. Although the elastic moduli of the crystal lattices of a number of polymers have recently been measured by this method,¹²⁻¹⁶ this has been done mostly in the direction of the principal valencies of highly oriented specimens, which do not vary a great deal under the effect of stress. Our measurements were made on non-oriented specimens, and the changes of lattice constants have been investigated in the directions of the intermolecular bonds.

Experimental

The test specimen was made by machining from a block of nylon 6 prepared by polymerizing caprolactam with addition of sodium caprolactam (0.3 mole-%) and acetyl caprolactam (0.3 mole-%) at temperatures below the melting point of nylon 6. The cylindrical block (210 mm. diameter, 60 mm. high) contained spherulites with diameters of about 30 μ . Its density was 1.160 g./cm.³, corresponding to a degree of crystallinity of 49%. The mean degree of polymerization was 280. The low-molecular fractions extractable with water (about 3%) were removed from the test specimen by boiling it in water.

The test specimen had a cross-section of 10 \times 1.5 mm., thickened at both ends to 10 \times 2.0 mm. A specimen dried at 100°C. for 24 hr. is referred to as dry in the present paper; the same specimen after boiling in water for 5 hr. is referred to as moist. The water content of the specimen was not determined. The x-ray diffraction was effected on a conventional x-ray apparatus recording the diffracted radiation on a film. Ni-filtered CuK α radiation was used, the intensity of which required an exposure time of 3 hr. to obtain pictures suitable for evaluating the radial distribution of blackening by means of a recording microphotometer.

During the measurement of the x-ray diffraction, the test piece was exposed to a constant tensile load with the aid of a simple lever device. The arrangement of the measurements is schematically shown in Figure 1. The true load acting upon the test piece was determined by comparing the deformation on our loading device of a test piece made of Macrolon polycarbonate with the deformation of the same test piece on another loading device, which permitted an accurate determination of load. The measurements of x-ray diffraction under stress was started at a load of 30 kp./cm.², due to the lever's own weight. A certain stress was necessary in order to secure the correct position of the test piece.

The lattice constants were calculated by using the Bragg equation, from the values of 2θ determined from the radii of the diffraction rings; the radii were measured in the stress direction and in the direction perpendicular to

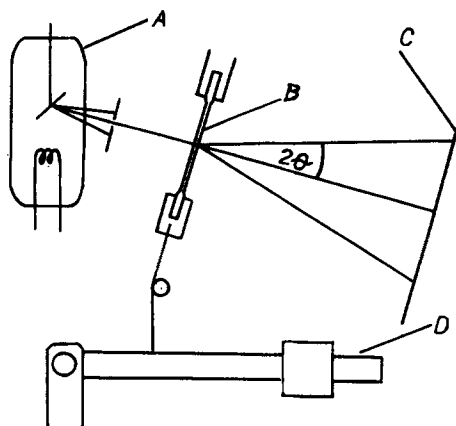


Fig. 1. Schematic representation of the arrangement of the x-ray diffraction measurements under tension: (A) x-ray tube, (B) specimen, (C) x-ray film, (D) lever with weight.

it. The stress dependence of the lattice constants was determined three times with good reproducibility. By repeated evaluations of the x-ray diffraction patterns with the recording microphotometer, an accuracy within ± 0.005 Å. was attained in the individual lattice constant measurements. The orientation was estimated as the ratio of the intensity of the diffraction ring in the stress direction to its intensity in the perpendicular direction.¹⁷ The differences due to the instrument were eliminated by using a uniform correction.

The macroscopic deformation of the test piece was measured at a constant load. The measurements were made with a micrometer, a slide caliper being used to determine the distance of the grips holding the test piece. Each value of deformation was measured ten times in this way. The (macroscopic) elastic moduli were determined from the deformation at 50 kg./cm.², which was read off from the stress-strain curves.

Results and Discussion

The dependence of the lattice constants $d_{(200)}$ and $d_{(002)(202)}$ on tensile stress for dry and moist nylon 6 are shown in Figures 2 and 3. Their character is linear, similarly to the character of analogical stress dependences of the lattice constant $d_{(110)}$ found for polyethylene by Kobayashi and Nagasawa.¹⁸ The slopes of these straight lines and thus the corresponding elasticity moduli of the crystal lattice are not appreciably changed by the presence of water in nylon 6. The presence of water in nylon 6, however, does change the two lattice constants (increasing $d_{(200)}$ and diminishing $d_{(002)(202)}$); this appears in Figures 2 and 3 as a parallel shift of the two d versus stress dependences. This change is reversible, as the specimen of nylon 6 after drying yielded values of d that agreed, within experimental error, with the values of d before boiling in water.

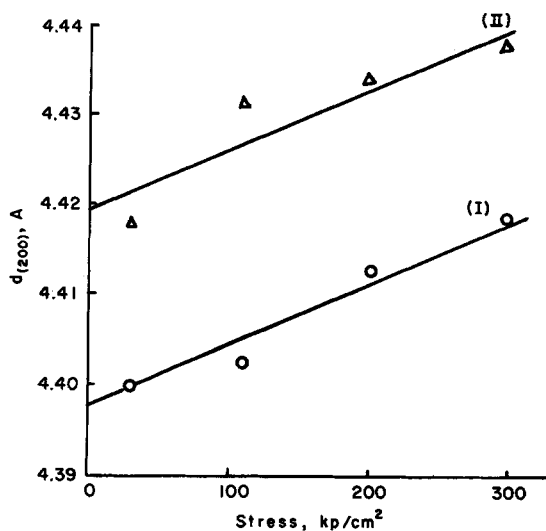


Fig. 2. Relationship between lattice spacing $d_{(200)}$ and stress of nylon 6: (I) dry; (II) moist.

The effect of water on the lattice constants of polycaproamide (nylon 6) will be the subject of a future publication.

The values of elastic moduli found for different directions are fairly different, in accordance with the anisotropic character of the crystal lattice of nylon 6. The modulus of elasticity corresponding to the lattice constant $d_{(200)}$ defined by the hydrogen bonds had approximately twice the value of the elasticity modulus for $d_{(002)(202)}$ (Table I).

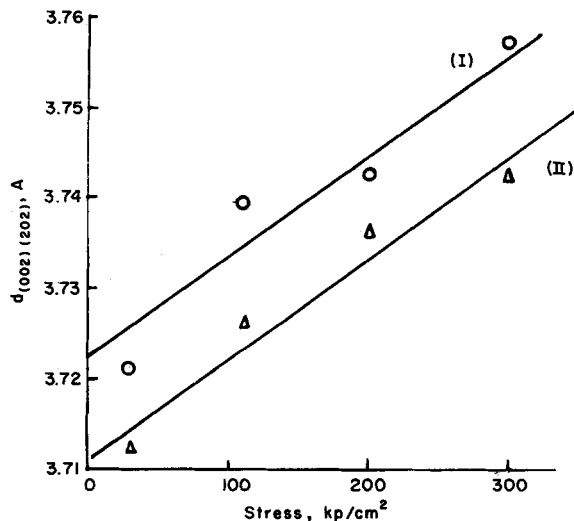


Fig. 3. Relationship between lattice spacing $d_{(002)(202)}$ and stress of nylon 6: (I) dry; (II) moist.

TABLE I
Moduli of Elasticity of Dry and Moist Nylon 6 and Its
Crystalline Lattice

Nylon 6	kg./cm. ² × 10 ⁻³	Lattice moduli, kg./cm. ² × 10 ⁻³	
		In the direction d(002)(202)	In the direction d(200)
Dry	35.7	33	67
Moist	8.5	32	66

As distinct from the elastic moduli of the crystal lattice, the macroscopic elasticity modulus of nylon 6 markedly decreases under the action of water; this appears as a greater deformation of a moist specimen at a given stress, as compared with a dry specimen (Fig. 4). The greater deformation of the moist specimen is accompanied by an orientation of the crystallites, which is not observed in a dry specimen even at the heaviest loads (Fig. 5). The orientation in the moist specimen increases with the deformation at a linear rate (Fig. 6). The 002 lattice planes, in which the hydrogen bonds and the folded molecular chains lie, are oriented parallel to the tensile stress direction. This character of the orientation in the initial stage of deformation is already known and has been accounted for by the orientation of the lamellae in the tensile stress direction.¹⁹ As the molecular chains lie in the direction of the thickness of the lamellae, the orientation of the lamellae in the tensile stress direction results in an orientation of the molecular chains perpendicular to the stress direction.

For an understanding of the mechanism of deformation it is also important to know the relation between the deformation of the specimen and the

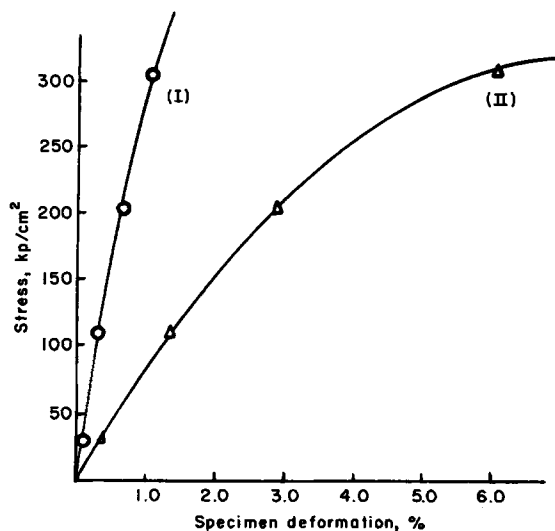


Fig. 4. Stress-strain curves of nylon 6: (I) dry; (II) moist.

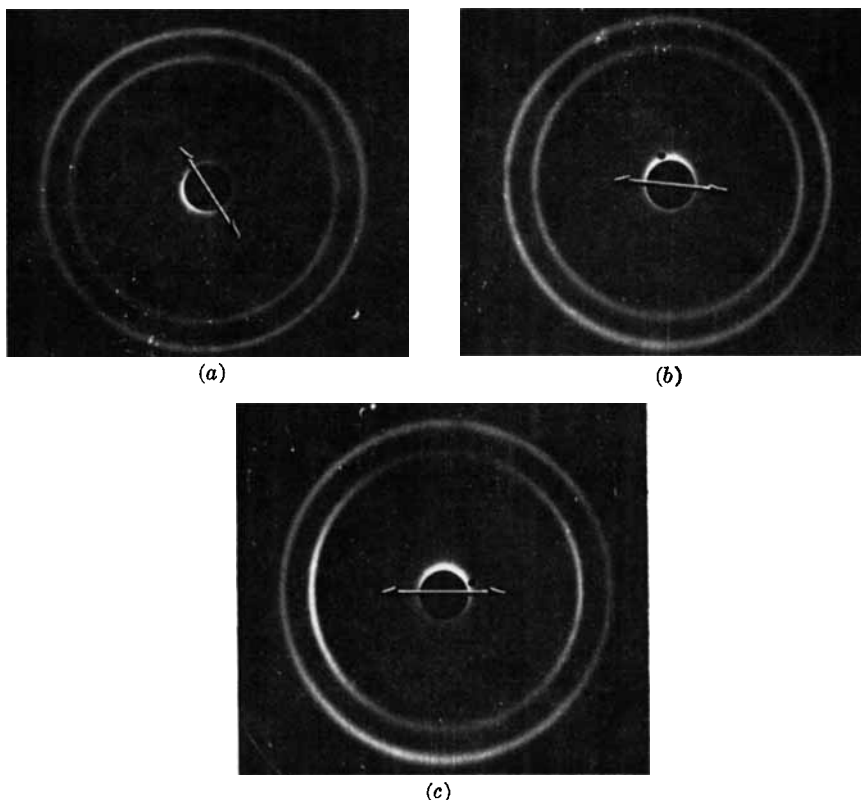


Fig. 5. X-ray diffraction patterns of nylon 6 under tensile stress: (a) nylon 6 dry, 30 kg./cm.²; (b) nylon 6 dry, 300 kg./cm.²; (c) nylon 6 moist, 300 kg./cm.². The arrows indicate the stress direction. Non-uniform sharpness of the diffraction rings is caused by an ellipse-shaped cross-section of the x-ray beam (it was narrower in the stress direction).

deformation of the chemical bonds within the specimen. In our case, the deformation of the lattice constant $d_{(200)}$ furnishes information on the deformation of the hydrogen bonds, and the deformation of $d_{(002)}$ tells about the deformation of intermolecular bonds in the direction approximately perpendicular to $d_{(200)}$. Their relation to the deformation of the specimen is evident from Figures 7 and 8; from these diagrams it follows that in dry nylon 6 the deformation of the specimen increases linearly with the increase of the two lattice constants, the relative change of the length of $d_{(002)}$ agreeing with the relative change of the length of the whole specimen quantitatively also, while the relative change of the length of the hydrogen bonds is roughly one half of this. On the other hand, the specimen deformation versus lattice deformation curves for moist nylon 6 show that the deformation is controlled from the beginning by some additional mechanism besides the lattice deformation. This mechanism plays an increasingly important part as the deformation increases, so that at the greatest deformations its role becomes decisive. It is also known to be reversible, as moist nylon 6

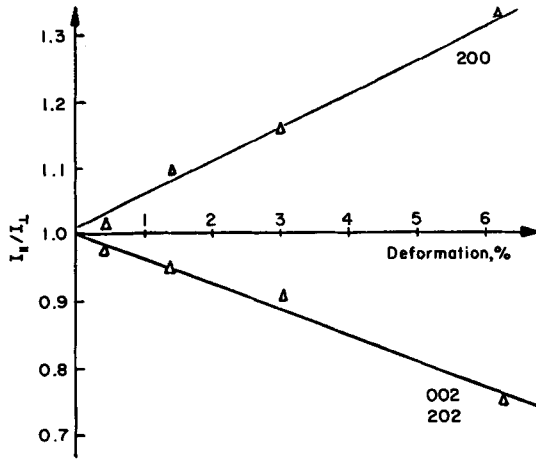


Fig. 6. Relationship between the intensity ratio $I_{||}/I_{\perp}$ of the x-ray diffraction rings and the deformation of moist nylon 6, where $I_{||}$ = intensity of the rings measured in the stress direction; I_{\perp} = intensity of the rings measured in a direction normal to the stress.

returned almost to the original length after unloading. In addition, Figure 6 suggests a close association of this mechanism with the orientation of the crystalline formations, which was also reversible.

All these data suggest that, in addition to instantaneous elasticity (deformation of bonds), the mechanism of delayed elasticity (change of conformation) also comes into play in a decisive degree in the deformation of moist nylon 6. This mechanism, however, can take place only in the amorphous regions above the temperature T_g ; simultaneously, with the conformation

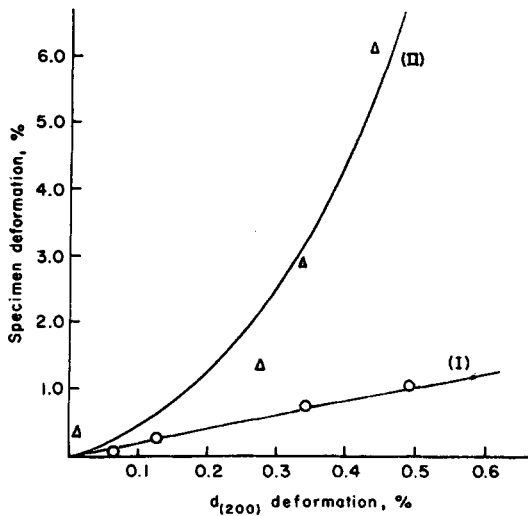


Fig. 7. Relationship between the deformation of the specimen and of lattice spacing $d_{(200)}$ of nylon 6: (I) dry; (II) moist.

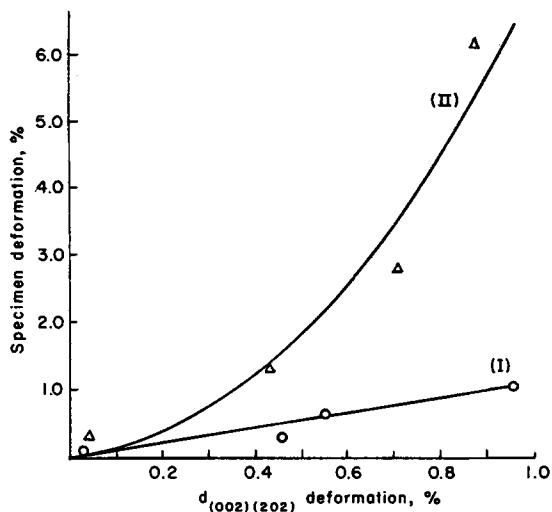


Fig. 8. Relationship between the deformation of the specimen and of the lattice spacing $d_{(002)(202)}$ of nylon 6: (I) dry; (II) moist.

changes of portions of molecular chains in the amorphous regions, the crystalline formations (lamellae) become oriented in the stress direction.

The differing deformation mechanisms of dry and moist nylon 6 are a result of the plasticizing action of water, which lowers the glass transition temperature of this polymer. At room temperature (about 20°C.), at which our measurements have been made, dry nylon 6 is in the glassy state.^{20,21} Water converts it isothermally into the rubbery state, in which the rotary motion about the single bonds is released, thus permitting conformation changes of molecular segments in the amorphous regions. The portions of molecular chains forming the amorphous interlamellar layer thereby acquire the possibility of rubberlike elastic deformation, necessary for the mutual shift of the lamellae, as shown in Figure 9.

The orientation of the lamellae is not possible in the course of the deformation of dry nylon 6. The formations of the crystalline structure in the bulk material do not change their position, all that goes on is a deformation of the individual bonds. It is known, that in these circumstances the deformation of nylon 6 is terminated by a brittle fracture at low values of deformation. On the other hand, in moist nylon 6 the first stage of deformation, in which the lamellae become oriented in the tensile stress direction, is followed by plastic deformation. Nylon 6 behaves in such conditions as a tough and ductile material. The question arises, whether a certain orientation of the lamellae enabling the interlamellar regions to fall into a direction near the maximum shear stress, is not a necessary condition for the plastic deformation of moist nylon 6. This assumption is corroborated by the fact that the ductility of nylon 6 disappears as a result both of the glassy state of the amorphous regions and of a decrease in the proportion of the amorphous fraction. With a reduced amount of the amorphous fraction there will not

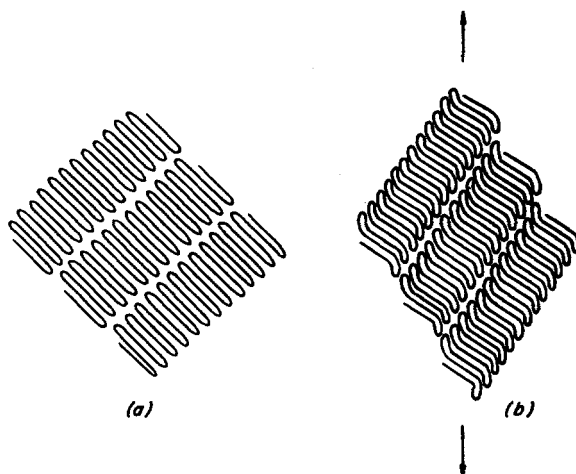


Fig. 9. Schematic representation of the mutual positions of three crystalline lamellae in a specimen of nylon 6: (a) nondeformed, (b) moist, deformed. The arrows indicate the direction of the stress.

be enough room for the reorientation of the lamellae required to start their plastic mutual shift, followed by a disintegration of the lamellae. It is well known from the studies of metallic materials that the crystalline lattice as a rule has certain preferred directions of plastic slip deformation, while in other directions there is considerably greater resistance to external forces.²²

The deformation mechanism observed in dry nylon 6 is likely to be common, in its principal features, to all thermoplastics, both crystalline and amorphous, in the glassy state. The mechanism observed in moist nylon 6 again is common, in its main features, to all crystalline thermoplastics at temperatures above T_g , unless their content of the amorphous fraction is low. Amorphous polymers above T_g are characterized by a deformation mechanism based on principles of rubberlike elasticity. Accordingly, three principal types of deformation mechanisms may be distinguished in linear polymers.

Furthermore, our results enable us also to draw certain conclusions concerning the distribution of crystalline and amorphous regions in nylon 6 and presumably also in other polymers with a corresponding degree of crystallinity. As water does not change the elastic modulus of the crystalline lattice, the severe decrease of the macromodulus of nylon 6 can be ascribed solely to the amorphous regions. If in the relatively highly crystalline nylon 6 (49%), on which our measurements were made, the amorphous fraction formed only defective spots enclosed in the crystalline fraction,¹⁰ it would be difficult to explain why the modulus decreases so sharply when solely these isolated amorphous islets were plasticized with water. Similar difficulties would be encountered also when trying to account for the orientation of the crystalline formations in moist nylon 6 under the action of tensile stress.

We conclude that both these facts suggest the existence of crystalline formations of a limited size, which are enclosed by a larger or smaller layer of amorphously arranged portions of the molecular chains (probably these are the portions protruding from the lamellae, i.e., primarily the folds of the chains). This amorphous wrapping of the crystalline formations must be arranged continuously enough to have a decisive influence upon the behavior of the bulk material under external stresses.

The measurements of the diameters of diffraction rings in the direction perpendicular to the tensile stress have shown that these diameters either do not change at all under the action of stress or they vary so slightly that the changes do not exceed the errors of measurement. Owing to the fact that in the tensile stress direction the lattice constant increases and, consequently, the diameter of the diffraction ring decreases, the x-ray patterns of the specimens subjected to a tensile stress exhibit the interesting effect of flattening of the diffraction rings in the stress direction (Table II). An

TABLE II
Differences in the Diameters of the X-Ray Diffraction
Rings Measured in Two Mutually Perpendicular Directions^a

Stress, kg./cm. ²	$R_{\perp} - R_{\parallel}$ of nylon 6, mm.			
	Dry		Moist	
	200	002,202	200	002,202
30	0.04	0.09	0.06	0.13
108	0.12	0.14	0.18	0.27
200	0.26	0.34	0.38	0.50
300	0.44	0.82	0.59	0.76

^a R_{\perp} = diameter perpendicular to the stress direction; R_{\parallel} = diameter in the stress direction.

analogous effect was observed by other authors in the x-ray patterns of a muscular tissue that was restrained from contracting.²³ The rings of these x-ray patterns were also flattened in the direction parallel to the muscle fibers, i.e., in the direction of stretching and contraction of the muscles. Our findings here demonstrate that in a stretched muscle there is a considerable internal tensile stress.

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Résumé

Les périodes de réseaux perpendiculaires à l'axe des chaînes moléculaires et à l'orientation des cristallites de nylon-6 humides et séchés (bouillis dans l'eau) ont été déterminées par diffraction aux rayons-X sous tension de 30 à 300 Kg/cm². La déformation des échantillons a également été mesurée. Les espacements du réseau sont modifiés de façon réversible par la présence d'eau dans le nylon-6, mais les modules élastiques du réseau ne sont pas affectés. Le module élastique du réseau dans la direction des liaisons hydrogènes est approximativement le double de sa valeur dans la direction normale aux liaisons hydrogènes. Le module élastique du nylon-6 séché se rapproche de la valeur du module élastique du réseau dans la direction normale à l'axe moléculaire, alors que le module du nylon-6 humide est beaucoup plus faible. De ces faits, et particulièrement au départ des relations entre la déformation du réseau et l'orientation des cristallites et la déformation de l'échantillon, les principales différences du mécanisme de déformation du nylon-6 sec et humide sont déduites. Les résultats obtenus rendent également possible certaines conclusions générales concernant la structure cristalline du nylon-6 et le mécanisme de déformation de polymères linéaires.

Zusammenfassung

Gitterabstände senkrecht zu den Molekülkettenachsen und die Kristallitorientierung von getrocknetem und feuchtem (in Wasser gekocht) Nylon 6 in Masse wurden durch Röntgenbeugung unter einer Spannung von 30 bis 300 kg/cm² bestimmt. Die Deformation der Probe wurde ebenfalls gemessen. Die Gitterabstände werden durch die Anwesenheit von Wasser in Nylon-6 reversibel geändert, der Elastizitätsmodul des Gitters wird dagegen nicht beeinflusst. Der Gitter-Elastizitätsmodul besitzt in Richtung der Wasserstoffbindungen etwa den doppelten Wert als in Richtung normal zu den Wasserstoffbindungen. Der Elastizitätsmodul von getrocknetem Nylon-6 nähert sich dem Wert des Gitter-Elastizitätsmoduls in Richtung normal zu den Molekülachsen, während der Modul des feuchten Nylon-6 mehrmals kleiner ist. Aus diesen Befunden und besonders aus den Beziehungen zwischen Gitterdeformation, Kristallitorientierung und Deformation

der Probe wurden die Hauptunterschiede im Deformationsmechanismus zwischen getrocknetem und feuchten Nylon-6 abgeleitet. Schliesslich ermöglichten die Ergebnisse auch einige allgemeine Schlüsse auf die Kristallstruktur von Nylon-6 und auf den Deformationsmechanismus linearer Polymere.

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