

Anisotropy of some polymer systems. II. Polyamide fibers (PAD-6f)

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Infrared absorption spectroscopy was used to study the influence of different conditions of deformation on the orientation of ordered (crystalline) and disordered "amorphous" regions of polyamide fibers. Absorption band at 963 cm^{-1} corresponding to the vibration of $-\text{CONH}-$ groups in α -monoclinic structure modification was chosen for evaluation of the factor of orientation of ordered regions. Absorption band at 1130 cm^{-1} corresponding to symmetric vibrations $-\text{C}-\text{C}-$ was used to study the orientation of disordered regions.

The process of uniaxial deformation is one of the basic operations in the preparation of PAD-6f. Since the arrangement of macromolecular chains and morphological formations changes in this process, desired properties can be obtained or changed in this way. Uniaxial deformation of fibers gives rise to an anisotropic polymer system. Measure of anisotropy of polymer systems is the degree of orientation, which reflects the arrangement of macromolecular chains in the direction of acting force. Since the mechanical properties are functions of the orientation of ordered and disordered regions it is very important to determine the orientation of these regions.

The aim of this paper is to show the changes of orientation of both ordered and disordered regions of PAD-6f in the process of uniaxial deformation at normal (22°C) and increased (160°C) temperature of medium. For this purpose the factors of orientation of ordered and disordered regions were determined from infrared absorption spectra.

Experimental

PA-6 belongs to the group of polymers having in the infrared spectra absorption bands corresponding to both ordered and disordered regions. Absorption band at 963 cm^{-1} assigned to the vibrations of $-\text{CONH}-$ groups in α -monoclinic structure modifications corresponds to the ordered regions [2]. It exhibits σ -dichroism. This band is relatively little pronounced in the infrared spectrum. Since the band is typical for monoclinic structural modification its values of dichroism can be combined with the factors of orientation obtained from X-ray measurements [3].

Absorption bands of disordered regions are more pronounced because of chaotic intermolecular interaction [4]. Absorption band at 1130 cm^{-1} corresponding to the sym-

metric $-C-C-$ vibrations [5] was chosen for studying the orientation of disordered regions. This band exhibits π -dichroism [2]. The factor of orientation of disordered regions was calculated from the combined infrared and sound velocity data.

Preparation of fiber samples

Undrawn fibers with titer 4410 dtex prepared by technological process of polyamide cords in Chemlon, Humenné were used for anisotropy studies. Relative viscosity of the initial PA-6 granulate was $\eta_{rel} = 3.03$. Uniaxial deformation of undrawn fibers with heating body was done at deformation speed 100 m/min. By this process we obtained fibers having various deformation degrees at normal (22°C) and increased (160°C) temperature of medium.

Evaluation of fiber samples

Samples were prepared, measured, and evaluated by the method described in our previous paper [1]. Base-lines for the studied absorption bands were chosen as follows

Absorption band at $963\text{ cm}^{-1} < 890\text{ cm}^{-1}$
 1020 cm^{-1}

Absorption band at $1130\text{ cm}^{-1} < 1100\text{ cm}^{-1}$
 1145 cm^{-1}

Results are presented in Figs. 1 and 2 where the dependence of the ratio $(R - 1)/(R + 2)$ on the deformation degree is plotted for two temperatures of medium (22 and 160°C).

These plots show the influence of temperature and deformation force on the orientation of ordered and disordered regions of PAD-6f.

If the uniaxial deformation of fibers at normal temperature is performed, one can observe the difference between the orientation of ordered and disordered regions. In the first phases of deformation (to $\lambda = 2.0$) predominantly the orientation of disordered

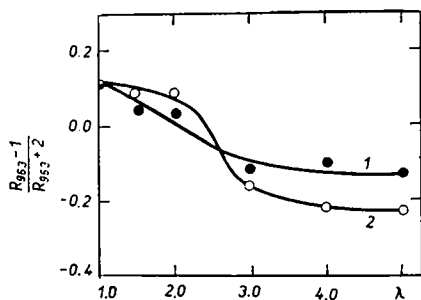


Fig. 1. Dependence of the ratio $(R - 1)/(R + 2)$ of absorption band at 963 cm^{-1} on deformation degree.

1. At normal temperature of medium (22°C); 2. at increased temperature of medium (160°C).

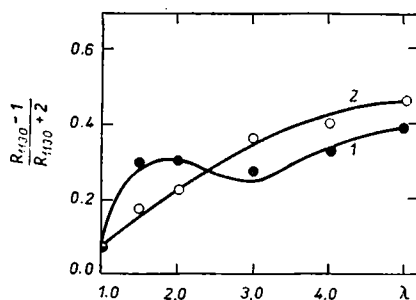


Fig. 2. Dependence of the ratio $(R - 1)/(R + 2)$ of absorption band at 1130 cm^{-1} on deformation degree.

1. At normal temperature of medium (22°C); 2. at increased temperature of medium (160°C).

regions occurs. In the following phases of deformation ($\lambda = 2.0-3.0$) partial decrease of orientation is observed. This fact can be explained by the change of smectic-hexagonal regions and highly ordered "amorphous" regions to the monoclinic structural arrangement. During the last phases of the deformation process, the orientation of disordered regions increases a little. The orientation of ordered regions increases in the whole region of deformation degrees. The sharpest change occurs at $\lambda = 2-3$, which corresponds to a decrease of the factor of orientation of disordered regions.

When the temperature at deformation is increased, the orientation of ordered regions in the first phases of deformation is lower than the orientation at normal temperature. Orientation of disordered regions changes uniformly in the whole region of deformation degrees.

Ratios $(R - 1)/(R + 2)$ cannot be compared if the studied bands differ in the type of dichroism (π , σ). This problem is eliminated in a suggested method by comparing the factors of orientation rather than the ratios $(R - 1)/(R + 2)$. The evaluation of the factors of orientation requires knowledge of the angles of the transition moments of absorption bands. Values of these angles were determined in a similar way in our previous paper [1].

In Table 1 are presented the data obtained from X-ray and sound velocity measurements, values of dichroism required for determination of the angles of transition moments, and calculated values of angles.

If the determined values of the angles of transition moments are substituted into eqn (3) of paper [1], the factors of orientation of ordered and disordered regions of PAD-6f are determined by the following equations

$$f_{R\ 963} = \frac{R_{963} - 1}{R_{963} + 2} \cdot \frac{2}{3 \cos^2(63^\circ 45') - 1}, \quad (1)$$

$$f_{R\ 1130} = \frac{R_{1130} - 1}{R_{1130} + 2} \cdot \frac{2}{3 \cos^2(31^\circ 10') - 1}. \quad (2)$$

Table 1

Physical properties of PAD-6f prepared by one-step deformation at normal (22°C) and increased (160°C) temperature of medium

t [°C]	λ	$\frac{R_{963} - 1}{R_{963} + 2}$	f_x	$\frac{R_{1130} - 1}{R_{1130} + 2}$	$f_{x\ am}$	$f_{R\ 963}$	$f_{R\ 1130}$	f_α
	N	0.109	—	0.077	—	-0.476	0.128	0.191
	1.5	0.039	—	0.288	—	-0.039	0.481	0.214
	2.0	-0.032	—	0.296	—	0.140	0.494	0.385
22	3.0	-0.121	—	0.270	—	0.529	0.451	0.613
	4.0	-0.109	0.928	0.332	0.674	0.476	0.555	0.705
	5.0	-0.121	0.926	0.390	0.689	0.529	0.651	0.722
	1.5	0.082	—	0.171	—	-0.361	0.285	0.305
	2.0	0.068	0.470	0.222	0.465	-0.297	0.371	0.366
160	3.0	-0.159	0.908	0.351	0.536	0.695	0.586	0.774
	4.0	-0.213	0.938	0.403	0.646	0.930	0.673	0.699
	5.0	-0.228	0.959	0.455	0.669	0.995	0.760	0.705

The dependence of the factors of orientation of ordered and disordered regions of PAD-6f calculated from eqns (1, 2) is plotted in Figs. 3 and 4.

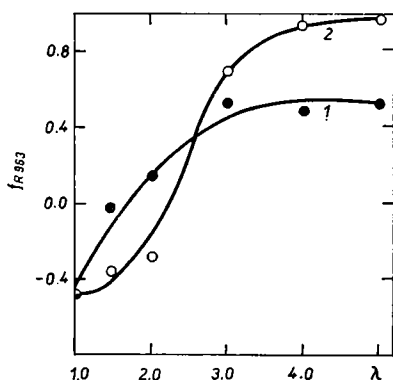


Fig. 3. Dependence of the factor of orientation of ordered regions on deformation degree.

1. At normal temperature of medium (22°C); 2. at increased temperature of medium (160°C).

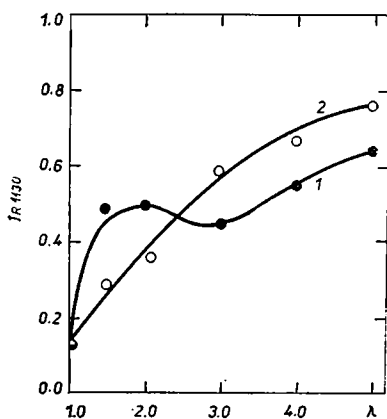


Fig. 4. Dependence of the factor of orientation of disordered regions on deformation degree.

1. At normal temperature of medium (22°C); 2. at increased temperature of medium (160°C).

The plots of the factors of orientation coincide with the corresponding plots of ratios $(R - 1)/(R + 2)$. Fig. 3 shows that in the first phases of deformation ($\lambda < 2.0$), the factors of orientation of ordered regions are negative. With respect to the definition of the factor of orientation it can be assumed that the ordered regions are placed perpendicularly to the axis of fiber [6]. In the process of uniaxial deformation they are placed in the direction of the axis of fiber and positive factors of orientation result.

Discussion

The process of uniaxial deformation of PAD-6f leads to significant changes in molecular and morphological structure of the polymer system. These changes depend on the magnitude of deformation force and on the temperature at deformation and influence the final properties of fibers. The changes consist predominantly in the transition of disordered and mesomorphous smectic-hexagonal arrangement to the structural arrangement corresponding to α - and β -monoclinic structure.

In our previous papers [7, 8] we noted that the deformation of PAD-6f at normal temperature of medium leads to the transition of smectic-hexagonal structural arrangement to the monoclinic one at higher deformation degrees ($\lambda = 3.0$). When the deformation is carried out at increased temperature of medium, this transition is observable already at lower deformation degrees.

Deformation at normal temperature of medium causes the slow transition of smectic-hexagonal structural arrangement to the predominantly β form of monoclinic structure. Partial transition of β to α form occurs in the region of higher de-

formation degrees. Deformation at increased temperature of medium gives rise to α -structural modification already at lower deformation degrees.

Similar conclusions were drawn from the evaluation of the orientation of ordered and disordered regions of PAD-6f prepared by uniaxial deformation, when infrared absorption spectroscopy was used. The advantage of this method is that information on the orientation of both ordered and disordered regions is obtained from one section of the prepared fiber. This can be explained by the fact that the bands characteristic of both ordered and disordered regions appear in the infrared absorption spectra of this fiber. From the dichroic values of the band at 1130 cm^{-1} , the ratios $(R - 1)/(R + 2)$ are obtained, which show the orientation of disordered regions. Precision of these values is limited only by errors of measurement. The method used until now for evaluating the orientation of disordered regions is based on the assumption of the two-phase structure of fibers [6]. Determination of the factor of orientation of ordered regions by X-ray diffraction and the determination of average orientation by optical birefringence or sound velocity measurements leads to the following relationship

$$f_{\alpha \text{ am}} = \frac{f_x - \beta f_x}{1 - \beta}, \quad (3)$$

where β is the crystalline fraction calculated from density [6].

Equation (2) which we propose for calculation of the factor of orientation of disordered regions is based on the measured values of dichroism of the "amorphous" absorption band. It should be noted that PAD-6f differs from polypropylene fibers [1] in that the calculated angles of transition moments are independent of deformation temperature. The maximum difference found among the angles determined at five different temperatures was 4° , which is not considered to be a significant change [4]. Therefore the average values of angles were calculated and substituted in eqns (1, 2). Thus the factors of orientation of ordered and disordered regions can be calculated according to eqns (1, 2) from the dichroic ratios of the corresponding absorption bands. Those expressions in eqns (1, 2) which depend solely on the values of angles of transition moments are constants for a given fiber and deformation. Eqns (1, 2) were used for calculation of the factor of orientation of ordered and disordered regions of PAD-6f. From Table 1 and the plots presented in Fig. 3 it follows that the obtained results are confirmed by other physical methods (X-ray diffraction, sound velocity measurement). At lower deformation degrees ($\lambda \leq 2.0$) the orientation of ordered regions is higher at normal temperature of medium. At higher deformation degrees ($\lambda > 3.0$) the orientation of ordered regions increases considerably with increasing temperature. The fact that in the initial phases of deformation values $f_{R\ 963}$ are lower at 160°C than those at 22°C can be explained in the following way. The increased temperature of medium in the process of deformation significantly reduces the internal resistance of fibers which is one of the dominant factors influencing the orientation. It can be seen from the shape of dependence of the factor $f_{R\ 963}$ at two temperatures of medium that in the last phases of deformation the stable values were reached.

The dependence of the factor $f_{R\ 1130}$ on deformation degrees at two different temperatures is shown in Fig. 4. From this dependence it follows that the initial effect of orientation is considerably higher at normal temperature than at the temperature of 160°C . However, it follows also from the measured dependences that the high

values of the factors of orientation of disordered regions were not obtained and that they could be increased by an appropriate change in technology of the preparation of PAD-6f. Therefore considerable attention should be paid in future to the increase of orientation of disordered regions during the preparation of PAD-6f with high tenacity.

Symbols

- $f_{\alpha \text{ am}}$ factor of orientation of disordered "amorphous" regions calculated from X-ray diffraction and sound velocity measurements
- $f_{R 9}$ factor of orientation of ordered (crystalline) regions calculated from the values of dichroism of the absorption band at 963 cm^{-1}
- $f_{R 1130}$ factor of orientation of disordered "amorphous" regions calculated from the values of dichroism of the absorption band at 1130 cm^{-1}
- PA-6 polyamide-6 (polymer)
- PAD-6f polyamide-6 fibers

Other symbols were explained in our previous paper [1].

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