Anisotropy of some polymer systems. III. Polyethyleneterephthalate fibers

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Infrared absorption spectroscopy was used to study molecular orientation of ordered and disordered regions of polyethyleneterephthalate fibers. Experimental data were employed to calculate the factors of orientation of ordered and disordered regions. The orientation factors calculated in this way were compared with those obtained from X-ray structure analysis and sound velocity measurements. The orientation of ordered regions was evaluated from dichroism of the absorption band at 437 cm⁻¹ and the orientation of disordered regions from dichroism of the absorption band at 502 cm⁻¹.

The structure of polyethyleneterephthalate fibers (PETf) is characterized by coexistence of the two forms of rotational isomers. These two forms differ in steric arrangement of the ethyleneglycol unit $-O-CH_2-CH_2-O-$. The *trans* form is an elongated form of polyethyleneterephthalate molecule, while gauche form is a relaxed form.

It was found [1] that the ordered regions of PETf contain *trans* isomers and the disordered regions both gauche and *trans* isomers. Therefore the content of *trans* isomers cannot be identified with that of ordered regions (degree of crystallinity). Structural changes of PETf in the process of deformation and heat treatment manifest themselves clearly in the infrared absorption spectrum.

In infrared spectra can be found the bands for evaluation of the content of gauche and *trans* isomers, the bands for evaluation of the content of ordered and disordered regions, as well as the bands for evaluating the molecular orientation of ordered and disordered regions (Table 1).

The aim of this paper is to find relations for calculation of the orientation factors of ordered and disordered regions from infrared experimental data. The orientation factors calculated in this way can be compared with the values obtained by other physical methods.

Experimental

The absorption bands at 437 and 502 cm⁻¹ were chosen for evaluation of the molecular orientation of PETf in a similar way as in our previous papers. The band at 502 cm⁻¹ corresponds to deformation vibrations $C-C=O$ with oxygen atom vibrating in the direction of molecular axis. Both bands exhibit π-dichroism. Results of the infrared spectra measurements were compared with the results of X-ray structure analysis and sound velocity measurements. Application of the last two methods to synthetic fibers was described elsewhere [5].

Table 1

Characteristic absorption bands for evaluation of the structure of PETf

Wavenumber [cm^{-1}]	Type of vibration	Type of structure
437	Deformation vibrations of $-C-C-O-$ groups [2, 3]	Ordered (crystalline) regions
502	Deformation vibrations of $C-C=O$ groups [2, 3]	Disordered "amorphous" regions
896	Rocking vibrations of $-CH_2-CH_2-$ groups [4]	gauche Isomer
973	Stretching vibrations of $-C-C-O-$ groups [4]	*trans Isomer*

Preparation of fiber samples

Undrawn PETf of the type of technical silk with total titer 4990 dtex was used for the studies of molecular orientation. Limiting viscosity number of the original polymer $[\eta] = 86.6 \text{ ml g}^{-1}$ was determined at $t = 30°C$ in tetrachloroethane—phenol $(1 : 3)$ solvent. Uniaxial deformation was carried out on a model laboratory equipment of the Research Institute of Chemical Fibers at deformation speed 100 m/min and four different temperatures: 75, 90, 105, and 130°C. Since the temperature of second-order transition of PETf is about 70°C, it was not possible to deform these fibers at normal temperature as in the case of POPf or PAD-6f.

Evaluation of fiber samples

The preparation of fiber samples for determining the dichroism (R) from infrared spectra was already described [6]. Absorption bands were evaluated by the base-line method as follows

Absorption band at 502 cm^{-1} $\Big\langle$ 460 cm^{-1}
560 cm^{-1}

Absorption band at 437 cm^{-1} $\Big\langle$ 410 cm^{-1}
460 cm^{-1}

In Tables 2 and 3 we present the measured physical values and the calculated orientation factors of PETf prepared by uniaxial deformation at various temperatures.

The angle of transition moment of the absorption band at 437 cm^{-1}, $\alpha_{437} = 18°25'$ was calculated from the values of the orientation factors obtained from X-ray structure analysis and values $(R - 1)/(R + 2)$. It was found that for PETf (like PAD-6f) [9] the value α_{437} does not depend on the deformation temperature. If the angle of transition moment calculated in this way is used, the orientation factor of ordered regions of PETf can be determined from the following equation

$$f_{R\,437} = \frac{R - 1}{R + 2} \frac{2}{3 \cos^2 18°25' - 1} . \tag{1}$$

This equation is valid for the studied PETf in the region of deformation temperatures from 75 to 130°C.

On the basis of the type of vibrations corresponding to the absorption band at 502 cm^{-1}

it can be assumed that the angle of transition moment of this band is equal to zero [2]. Then the equation for calculating the factor of orientation of disordered regions of PETf can be written in a following form

$$f_{R\ 502} = \frac{R - 1}{R + 2}. \tag{2}$$

Equations $(1-2)$ were employed to calculate the orientation factors of ordered and disordered regions of PETf for various deformation degrees and four temperatures of deformation. The plots of calculated factors are presented in Figs. 1 and 2.

It can be seen from both figures that the orientation of both ordered and disordered regions increases with increasing deformation degree. From comparison of the values $f_{R\ 437}$ and $f_{R\ 502}$ at the same deformation degree it follows that the orientation of ordered regions is much higher than that of disordered regions. Fig. 1 also shows the influence of deformation temperature on the orientation of ordered regions of PETf. At all deformation temperatures the sharpest change of orientation occurs at $\lambda = 3.0$. The mobility of macromolecules in this region at the lowest deformation temperature (75°C) is relatively low and consequently high strain arises at deformation. When deformation temperature is increased, supplied thermal energy causes the decrease of internal resistance of fibers against deformation with simultaneous increase of the speed of relaxation processes, which is reflected in lower values of $f_{R\ 437}$. This region is also characterized by a transition of gauche isomers to *trans* isomers [7].

In the region of higher deformation degrees ($\lambda > 3.0$) the influence of deformation temperature on the values $f_{R\ 437}$ is opposite to its influence at lower deformation degrees. It is assumed that in this region the increase of content of *trans* isomers is minimal.

Table 2

Physical properties of PETf prepared by uniaxial deformation at various temperatures

t [°C]	λ	$\dfrac{R_{437} - 1}{R_{437} + 2}$	$\dfrac{R_{502} - 1}{R_{502} + 2}$	c [km s^{-1}]	HAB		C_p [%]
					(010)	(100)	
	1.0	0.190	0.123	1.48	—	—	17.0
	2.0	0.474	0.174	1.81	—	—	18.3
75	3.0	0.686	0.359	2.98	—	—	29.3
	4.0	0.751	0.456	3.41	13.7	11.9	38.7
	5.0	0.706	0.540	3.87	11.8	8.8	42.9
	2.0	0.416	0.143	1.84	—	—	13.5
	3.0	0.710	0.314	2.67	—	—	20.5
90	4.0	0.775	0.465	3.35	23.8	12.2	39.6
	5.0	0.704	0.429	3.87	9.8	7.6	40.4
	2.0	0.330	0.176	1.96	—	—	12.6
	3.0	0.727	0.344	2.43	19.0	10.4	20.1
105	4.0	0.770	0.400	3.30	9.4	8.0	39.1
	5.0	0.791	0.529	3.94	6.8	5.2	48.8
	2.0	0.311	0.148	1.52	—	—	12.1
	3.0	0.661	0.333	1.89	24.4	17.0	20.1
130	4.0	0.810	0.452	3.22	9.3	8.7	41.2
	5.0	0.845	0.510	3.94	6.9	6.4	51.3

Predominant process is their orientation, this being higher at higher temperature of medium. The highest values of the orientation factors $f_{R\ 437}$ were obtained at $t = 130°C$, when the dependence acquires saturated character.

In Fig. 2 are shown the orientation factors of disordered regions calculated according to eqn (2) at deformation temperatures $t = 75$ and $130°C$. The remaining values $f_{R\ 502}$ are presented in Table 3. From the dependence of $f_{R\ 502}$ on deformation degrees it follows that the orientation of disordered regions increases with increasing deformation degree. This dependence in the whole region of deformation degrees does not reach the state of saturation as in the case of orientation of ordered regions. While in the region $\lambda = 3.0$ the values $f_{R\ 437}$ varied relatively little, the larger change was observed for $f_{R\ 502}$.

From the evaluation of the measured values we have come to the similar conclusions as *Baranova et al.* [8], that there is still some reserve in the orientation of disordered regions. The total increase of anisotropy of the system requires exactly the increase of the orientation of disordered regions.

Discussion

Unlike X-ray structure analysis which can be used only for the evaluation of the orientation of ordered domains of PETf, infrared absorption spectroscopy can be used for evaluation of the orientation of both ordered and disordered regions from the values of dichroism of absorption bands at 437 and 502 cm^{-1}. The application of this method is very advantageous, since a long segment of fiber (≈ 50 m) is used for the analysis and the structure of original fiber remains in the process of sample preparation unchanged.

Table 3

Orientation factors of PETf prepared by uniaxial deformation at various temperatures

| t [°C]	λ	$f_{R\ 437}$	$f_{R\ 502}$	f_x	f_α	$f_{\alpha\ am}$
	1.0	0.223	0.123	—	0.105	—
	2.0	0.551	0.174	—	0.402	—
75	3.0	0.807	0.359	—	0.779	—
	4.0	0.883	0.456	0.858	0.831	0.815
	5.0	0.830	0.540	0.905	0.869	0.842
	2.0	0.489	0.143	—	0.421	—
	3.0	0.835	0.314	0.799	0.725	0.732
90	4.0	0.912	0.465	0.894	0.825	0.781
	5.0	0.870	0.429	0.933	0.869	0.826
	2.0	0.388	0.176	—	0.489	—
	3.0	0.855	0.344	0.835	0.668	0.626
105	4.0	0.905	0.400	0.929	0.820	0.750
	5.0	0.936	0.529	0.939	0.874	0.811
	2.0	0.365	0.148	—	0.152	—
	3.0	0.771	0.333	0.910	0.451	0.579
130	4.0	0.952	0.452	0.929	0.811	0.749
	5.0	0.993	0.510	0.961	0.874	0.811
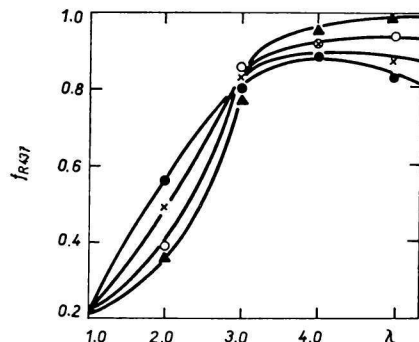
Fig. 1. Dependence of orientation factors of crystalline regions on deformation degree at various temperatures.

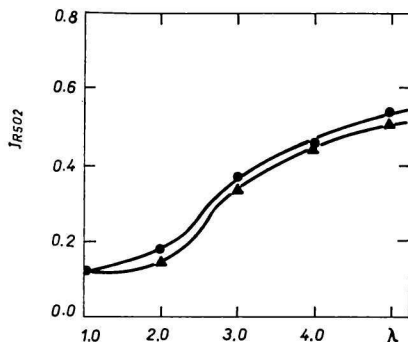● 75°C;   ○ 105°C;   × 90°C;   ▲ 130°C.

Fig. 2. Dependence of orientation factors of "amorphous" regions on deformation degree at two deformation temperatures.

● 75°C;   ▲ 130°C.

A significant contribution to the evaluation of the fiber structure are the values $f_{R\,502}$, *i.e.* the orientation factors of disordered regions. These values cannot be obtained directly by any of the methods employed so far. They can be calculated according to eqn (*3*) of our previous paper [7] where the two-phase structure of fibers is assumed, *i.e.* that fiber is composed of ordered and disordered regions. However, it is known that the fibers contain besides ordered and disordered regions also regions which differ in a degree of planar and steric arrangement [9]. Neglect of these regions can introduce some inaccuracies into the results of evaluation.

It is interesting to compare the calculated ($f_{\alpha\,am}$) and measured ($f_{R\,502}$) values of orientation factors of disordered regions. In all cases the values $f_{R\,502}$ are lower than $f_{\alpha\,am}$. This discrepancy can be caused by the following factors. It is possible that the angle of transition moment of the absorption band at 502 cm^{-1} has a certain nonzero value. But this cannot be confirmed with respect to the lack of suitable methods for determination of the angles of transition moments of the absorption bands. The second reason for mentioned discrepancy can be uncertainty of crystalline part, which is determined by flotation method also under the assumption of two-phase structure of fibers [5].

It will be the subject of our further studies to look for such suitable methods of fiber structure evaluation which are mutually independent and are not based on the assumption of two-phase structure.

Conclusion

In this and our previous papers [6, 7] we have investigated changes of orientation of ordered and disordered domains of the polymer systems POPf, PAD-6f, and PETf using infrared absorption spectroscopy. The obtained results were compared with those of other physical methods (X-ray structure analysis, birefringence, sound velocity) and their combination with infrared absorption spectroscopy was used to derive relationships for calculation of the orientation factors of ordered and disordered

regions. It can be stated on this basis that the infrared absorption spectroscopy brings new possibilities of structural change investigation and extends the scope of orientation studies to the whole region of deformation degrees. Another valuable contribution of the presented method is the possibility of direct studies of the orientation of disordered regions. The results obtained from infrared spectra are sensitive to the changes in orientation depending on deformation force and temperature. This was confirmed by our studies of polymer systems POPf, PAD-6f, and PETf.

It has already been stated in Part I of this series (POPf) that the values of orientation factors of ordered regions increase with increasing deformation force and temperature of medium. The evaluation of disordered regions of POPf is not possible as there are no absorption bands characteristic of "amorphous" arrangement in the spectral region studied (700—1800 cm^{-1}). Therefore only average orientation was evaluated for POPf from the changes of dichroism of the absorption band at 1256 cm^{-1}.

In Part II (PAD-6f) the changes of orientation of ordered and disordered regions were evaluated as dependent on deformation force and temperature of medium. From the results presented in this part it follows that in the final phases of uniaxial deformation the increase of temperature favourably influences the orientation of both ordered and disordered regions.

In the last (III) part of this series (PETf) we obtained results that lead to conclusion that the influence of temperature on orientation of ordered regions is favourable, while the orientation of disordered regions is not substantially affected by temperature. For PETf, unlike PAD-6f, the obtained values of orientation factors of disordered regions are relatively low.

Symbols

$f_{R\ 437}$ orientation factor of ordered regions
$f_{R\ 502}$ orientation factor of disordered regions
c sound velocity
HAB   half angle of blackening
C_p crystalline part
PETf   polyethyleneterephthalate fiber (polymer)

References

1. Schmidt, P. G., *J. Polym. Sci. A*, *1*, 1271 (1963).
2. Novak, I. I., Suchkov, V. A., and Zosin, L. P., *Vysokomol. Soedin. A*, *11*, 1325 (1969).
3. Baranova, S. A., Geller, V. E., Ajzenshtein, E. M., Pakshver, A. B., and Shablygin, M. V., *Khim. Volokna 5*, 17 (1971).
4. Koenig, J. L. and Cornell, S. W., *J. Polym. Sci. C*, *22*, 1019 (1969).
5. Jambrich, M., Diačik, I., and Mitterpach, I., *Faserforsch. Textiltech. 1*, 28 (1972).
6. Diačik, I., Mitterpach, I., and Ďurčová, O., *Chem. Zvesti 29*, 68 (1975).
7. Ďurčová, O., Diačik, I., and Mitterpach, I., *Chem. Zvesti 29*, 75 (1975).
8. Baranova, S. A., Geller, V. E., Papulova, L. V., and Shablygin, M. V., *Khim. Volokna 2*, 17 (1970).
9. Jambrich, M., *Fyzikálne metódy pre výskum vláken.* (Physical Methods in Fiber Research.) P. 103. Slovchémia, Bratislava, 1971.

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