

Anisotropy of some polymer systems. I. Polypropylene fibers

I. DIAČIK, I. MITTERPACH, and O. ĎURČOVÁ

*Research Institute of Chemical Fibers,
059 21 Svit*

Received 29 March 1974

Accepted for publication 26 July 1974

Infrared absorption spectroscopy was used to study the molecular orientation of ordered regions and average orientation of polypropylene fibers. Experimental data were used to calculate the functions of orientation which in turn made it possible to calculate orientation factors. The orientation factors obtained in this way were compared with the results of X-ray structure analysis and optical birefringence. It was found that average orientation of polypropylene fibers can be judged in a convenient manner from the absorption band at 1256 cm^{-1} , while the absorption band at 997 cm^{-1} can be used to deduce the dependence of orientation of ordered regions in the overall range of deformation degrees.

The progress in the preparation of synthetic fibers is closely connected with the research in the field of preparation of new or modified types of polymers as well as with the research in the field of technology of fiber procession. It has been found that the desired physical and mechanical properties are not only a function of chemical structure and molecular weight but they are significantly influenced also by molecular and morphological structure.

A complicated structural state, we are dealing with when studying high-molecular compounds makes it impossible to derive quantitative mathematical relationships for determination of fibers having preplanned properties. Therefore it is necessary to use a series of physical properties which enable one to draw conclusions concerning the behaviour and the change of some structural factors of fiber-forming polymers in dependence on the conditions of the process of preparation which influences also the final properties. In the study of the fiber-forming polymer systems we are trying in the first place to characterize the structural modifications, state of order and to evaluate the degree of anisotropy using physical methods, such as wide and small angle X-ray scattering, determination of the density of packing of polymer system, infrared absorption spectroscopy and measurement of birefringence and sound velocity.

Experimental

The absorption spectrum of polypropylene consists of two important regions:

a) the region of stretching symmetric and asymmetric vibrations of $-\text{CH}_2-$ and CH_3- groups, *i.e.* the region $1376-4329\text{ cm}^{-1}$ [1];

b) the region of rocking and twisting vibrations of C—C, —CH₂—, and CH₃— groups, *i.e.* the region 810—1357 cm⁻¹ [1].

For the studies of structure parameters, an absorption band at 997 cm⁻¹ corresponding to ordered domains and the absorption band at 1256 cm⁻¹ corresponding to mixed regions can be used [2]. There are some other absorption bands typical for isotacticity and other bands which can be used as internal standards [1].

The absorption band at 997 cm⁻¹ corresponding to the rocking vibration of carbon backbone was used in this paper to determine anisotropy of ordered domains. This band exhibits strong π -dichroism [1]. For evaluation of the average orientation *Samuels* used the band at 1256 cm⁻¹ which corresponds to twisting vibrations of the —CH₂— groups in both ordered and disordered regions [2]. This band also exhibits π -dichroism. In order to compare the i.r. results, the orientation of ordered domains was studied also by means of X-ray structure analysis. The average orientation was calculated from the birefringence values according to the methods suggested by *Jambrich et al.* [3].

Preparation of fiber samples

Undrawn polypropylene fibers prepared from the melt of CHISSO 5078 polymer with $[\eta] = 170.7 \text{ ml g}^{-1}$ and index of flow 9.35 g/10 min, were used for the study of anisotropy under various deformation conditions. Deformation of undrawn fibers was carried out using laboratory equipment. Deformation velocity 100 m/min and four temperatures of medium were used.

Evaluation of fiber samples

Monofil fiber was manually spun on a metal frame [4]. In order to minimize the loss of energy caused by scattering of light on fibers, the surface of fibers was wetted by nujol. After the consistent film of nujol had been formed the frame was fixed in a holder of

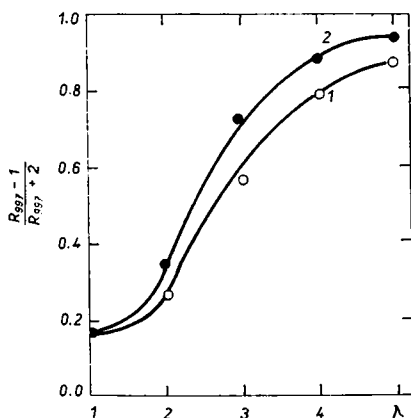


Fig. 1. Dependence of the ratio $(R - 1)/(R + 2)$ of the absorption band at 997 cm⁻¹ on deformation degree.

1. At normal temperature of medium;
2. at increased temperature of medium.

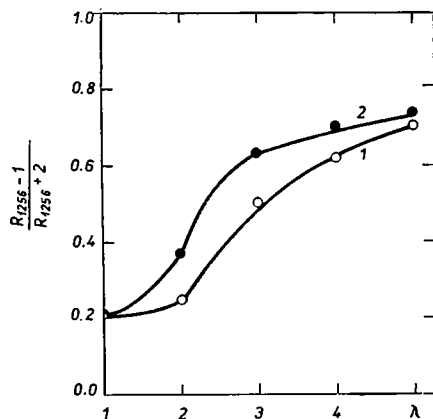


Fig. 2. Dependence of the ratio $(R - 1)/(R + 2)$ of the absorption band at 1256 cm⁻¹ on deformation degree.

1. At normal temperature of medium;
2. at increased temperature of medium.

selenium polarizer. Infrared absorption spectra were measured with a UR-10 (Zeiss, Jena) spectrophotometer using NaCl prism in the region 700–1300 cm^{-1} .

Absorption bands were evaluated by the base-line method. For the evaluation of molecular orientation the values of dichroic ratios were used, *i.e.* the values of absorbances in directions parallel and perpendicular to the direction of electric vector of monochromatic light. With respect to π -dichroism of the absorption band R is equal to 1 for isotropic system and $R = \infty$ for ideally oriented system. The ratio $(R - 1)/(R + 2)$ is also a quantitative measure of molecular orientation. Unlike dichroic ratios, the values of $(R - 1)/(R + 2)$ are in the interval $\langle 0,1 \rangle$.

Figs. 1 and 2 illustrate the dependence of the ratio $(R - 1)/(R + 2)$ on deformation degrees for both 997 and 1256 cm^{-1} bands at deformation temperatures 22 and 110°C, respectively.

Comparing the values $(R - 1)/(R + 2)$ presented in Figs. 1 and 2 it is possible to estimate the change of molecular orientation in the process of uniaxial deformation.

Values $(R - 1)/(R + 2)$ increase with the increasing temperature of medium which is in agreement with the results obtained from X-ray structure analysis and optical birefringence. It has been found that when the temperature of medium is increased, more oriented system results.

In order to compare the results obtained by different methods, it is necessary to convert the studied quantities to a common value; in this case it is a factor of orientation. For calculation of the factors of orientation from dichroic ratios, one must first calculate the angles of transition moments of absorption bands. For the absorption bands at 997 and 1256 cm^{-1} , the angles of transition moments were calculated from the plot of dependence $(R - 1)/(R + 2) = f(f_x)$ and f_0 respectively [2].

Table 1

Physical properties of polypropylene fibers prepared by one-step deformation at various temperatures of medium

t [°C]	λ	$\frac{R_{997} - 1}{R_{997} + 2}$	f_x	$\frac{R_{1256} - 1}{R_{1256} + 2}$	f_0	α_{997}	
22	1.0	0.171	—	0.203	0.127		
	2.0	0.272	0.784	0.250	0.204		
	3.0	0.570	0.883	0.497	0.687		
	4.0	0.793	0.947	0.610	0.770	17°20'	20°54'
	5.0	0.865	0.971	0.703	0.809		
60	2.0	0.309	0.721	0.313	0.302		
	3.0	0.566	0.938	0.508	0.415		
	4.0	0.819	0.963	0.615	0.724	15°55'	16°09'
	5.0	0.890	0.969	0.697	0.795		
80	2.0	0.268	0.698	0.356	0.314		
	3.0	0.661	0.929	0.557	0.612		
	4.0	0.845	0.968	0.689	0.747	13°46'	13°53'
	5.0	0.902	0.964	0.749	0.802		
110	2.0	0.344	0.846	0.357	0.309		
	3.0	0.721	0.931	0.624	0.633		
	4.0	0.889	0.969	0.682	0.713	11°31'	10°05'
	5.0	0.933	0.984	0.705	0.789		

In Table 1 we present the values required for calculation of the angles of transition moments of the absorption bands. The angle for 997 cm^{-1} band was determined from the plot $(R - 1)/(R + 2) = f(f_x)$ and for the band at 1256 cm^{-1} from $(R - 1)/(R + 2) = f(f_0)$. Results presented in Table 1 suggest the linear dependence of the angles of transition moments on the deformation temperature for both bands. Calculation of the functions of orientation was based on eqn (1) derived by Fraser [5]

$$\frac{R - 1}{R + 2} = \frac{3 \cos^2 \Theta - 1}{2} = \frac{3 \cos^2 \alpha - 1}{2} \quad (1)$$

Using Hermans's definition of the factor of orientation

$$f = \frac{3 \cos^2 \Theta - 1}{2} \quad (2)$$

this factor can be expressed from the infrared data as a function of the dichroic ratio R and the angle of transition moment of the corresponding absorption band

$$f_R = \frac{R - 1}{R + 2} \cdot \frac{2}{3 \cos^2 \alpha - 1} \quad (3)$$

Thus eqn (3) can be used for calculation of the factor of orientation, assuming that the angle of transition moment is known.

In this paper the angles of transition moments of the absorption bands at 997 and 1256 cm^{-1} were calculated for the temperature interval $22\text{--}110^\circ\text{C}$. If a linear change $\alpha = f(t)$ is included into eqn (3), we obtain the final relationship for evaluation of the factor of orientation from the measured values of dichroism. Molecular orientation of ordered regions can be evaluated according to eqn (4)

$$f_{R\ 997} = \frac{R - 1}{R + 2} \cdot \frac{2}{3 \cos^2(19.46 - 0.07 t) - 1} \quad (4)$$

The average orientation of polypropylene fiber can be calculated from the following equation

$$f_{R\ 1256} = \frac{R - 1}{R + 2} \cdot \frac{2}{3 \cos^2(24.16 - 0.127 t) - 1} \quad (5)$$

Figs. 3 and 4 present the plots of dependence of the functions of orientation on deformation degrees for both absorption bands.

It can be seen from Fig. 3 that the increased temperature of medium leads to a more ordered arrangement of regions with monoclinic structure. The sharpest change of molecular orientation occurs at $\lambda = 2\text{--}3$.

From Fig. 4 it follows that the average orientation decreases with increasing temperature of deformation in the region of high deformation degrees. This effect can be explained by partial orientation of disordered regions in the process of deformation of polypropylene fibers at normal temperature of medium, where high strain arises in fibers. The increased temperature of medium relaxes these strains and consequently the partial orientation of disordered regions is decreased.

Calculated factors $f_{R\ 997}$ can be compared with the factors of orientation obtained from X-ray scattering measurements and the values $f_{R\ 1256}$ can be compared with those

of average molecular orientation determined from the values of optical birefringence. This comparison is presented in Table 2.

Values $f_{R\ 1256}$ and f_0 are almost identical, while there are differences between the $f_{R\ 997}$ and f_x values in the region of lower deformation degrees. Determination of f_x from X-ray

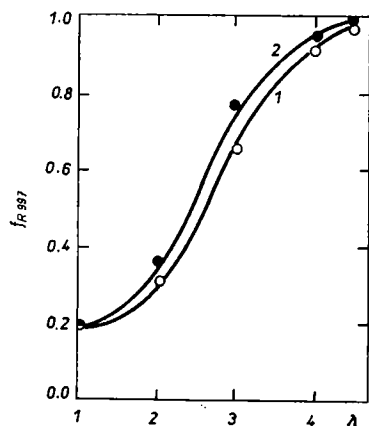


Fig. 3. Dependence of the factor of orientation of ordered regions on deformation degree.

1. At normal temperature of medium;
2. at increased temperature of medium.

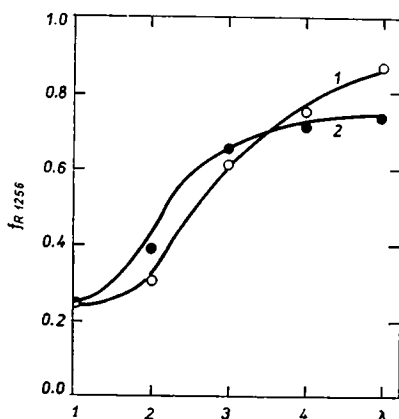


Fig. 4. Dependence of the factor of average orientation on deformation degree.

1. At normal temperature of medium;
2. at increased temperature of medium.

measurements is rather difficult because of the low intensity of paratropic reflection spots. From the infrared absorption spectra it is possible to determine orientation of ordered domains in the whole region of deformation degrees and also for undrawn fibers.

Table 2

Factors of orientation of polypropylene fibers prepared by one-step deformation at normal and increased temperature of medium

t [°C]	λ	$f_{R\ 997}$	$f_{R\ 1256}$	f_x	f_0
22	1.0	0.198	0.251	—	0.127
	2.0	0.315	0.309	0.784	0.204
	3.0	0.662	0.615	0.883	0.687
	4.0	0.977	0.797	0.947	0.770
	5.0	0.999	0.870	0.971	0.809
110	2.0	0.367	0.385	0.846	0.309
	3.0	0.769	0.654	0.931	0.633
	4.0	0.948	0.715	0.969	0.713
	5.0	0.995	0.739	0.984	0.789

Discussion

It can be seen from the plot $(R - 1)/(R + 2) = f(\lambda)$ for two different temperatures that infrared absorption spectroscopy is more sensitive for detection of the influence of temperature on the molecular orientation of polymer chains. The increased temperature of medium in the process of deformation gives rise to a more perfect arrangement which is reflected in the values of $(R - 1)/(R + 2)$.

From the factors of orientation calculated from the infrared absorption data it follows that if the temperature of medium is increased, more oriented polymer system results.

The average orientation which expresses simultaneous orientation in ordered and disordered regions for two different temperatures of medium is illustrated in Fig. 4. This plot shows unfavourable influence of the temperature of medium on the orientation of disordered regions. The increase of $f_{R\ 1256}$ at the deformation temperature 110°C and at higher deformation degrees requires increased strain at the deformation of fibers. Maximum obtained value $f_{R\ 1256} = 0.66$ suggests that there is a possibility of further increase by an appropriate change in a deformation process. It has been found that the calculated angles of transition moments depend linearly on the temperature of medium. This dependence is incorporated in eqns (4, 5). It is known from literature that the angle of transition moment of the absorption bands depends on the geometry of structure and is independent of the deformation degree [6]. The change of the angle of transition moment for the absorption bands at 997 and $1256\ \text{cm}^{-1}$ found in this work can be explained by the type of vibrations involved. These absorption bands correspond to deformation vibrations with the change of valence angles and this explains the changes of angles. The validity of eqns (4, 5) is limited to the temperature interval $22\text{--}110^\circ\text{C}$ for the process of one-step deformation of polypropylene fibers. The values $f_{R\ 997}$ and $f_{R\ 1256}$ obtained from the infrared data can be compared with the values of orientation factors obtained by other physical methods. The values f_0 and $f_{R\ 1256}$ are identical in the whole region of deformation degrees. The values f_x and $f_{R\ 997}$ differ in the region of lower deformation degrees while for higher deformation degrees, the difference is minimal.

We would like to emphasize that unlike X-ray scattering, infrared absorption spectroscopy can be used in the whole region of deformation degrees. From the obtained data it follows unambiguously that the orientation of ordered regions, caused by deformation force and temperature of medium, is in the direction of acting force. The values of functions of orientation increase with the increasing deformation force and temperature of medium until saturated state is reached. The evaluation of the average orientation shows that while the deformation force favourably influences the orientation of disordered regions, the influence of increased temperature of medium is unfavourable.

Symbols

λ	deformation degree
t	temperature
α	angle of transition moment
Θ	average angle of orientation
R	dichroic ratio
f_0	factor of average orientation calculated from optical birefringence measurements

f_x	factor of orientation of ordered regions calculated from X-ray scattering
f_R^{097}	factor of orientation of ordered regions calculated from infrared spectra
f_R^{1256}	factor of average orientation calculated from infrared spectra
$\bar{\nu}$	wavenumber
$[\eta]$	limiting viscosity number

References

1. Hummel, D. O., *Atlas der Kunststoff-Analyse*, Band I, p. 223. Verlag Chemie, München, 1968.
2. Samuels, R. J., *J. Polym. Sci., A*, **5**, 1741 (1965).
3. Jambrich, M., Diačik, I., and Mitterpach, I., *Faserforsch. Textiltech.* **1**, 28 (1972).
4. Ruscher, Ch. and Schmolke, R., *Faserforsch. Textiltech.* **8**, 383, 516 (1960).
5. Fraser, R. D. B., *Analytical Methods of Protein Chemistry*. (Alexander and Block, Editors.) Vol. 2, Chapt. 9. Pergamon Press, London, 1960.
6. Zbinden, R., *Infrakrasnaya spektroskopiya vysokopolymenov.* (Infrared Spectroscopy of High Polymers.) P. 355. Mir, Moscow, 1966.

Translated by K. Sarka