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Raman Study of Orientational Order in Polymers

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Summary: In this paper, we present some analytical results in the development of the classical Bower theory of Raman scattering in the partially oriented polymers. We consider more general case of arbitrary molecular orientation instead of Bower's assumption about sample having three mutually perpendicular two-fold axes of rotational symmetry. We also present here the experimental data on the study of structure of one-way-drawn polyethylene tapes and polysulfone hollow fiber membranes.

Introduction

Polymers play an important role in modern industry, with oriented polymers being of special interest because of their high mechanical properties. Investigations into these polymers are aimed particularly at the solution of two interrelated problems: study of the deformation mechanisms and optimization of the polymer production conditions, with the general purpose of obtaining high-strength oriented materials with mechanical characteristics approaching the theoretical limits.

The orientation distribution function (ODF) is one of the main characteristics of the structure and properties of oriented polymers. At present, several methods are used to determine this function based, in particular, on the measurements of birefringence[1], sound velocity[2], X-

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ray diffraction[3], and the IR[4] and Raman[5] spectra. Each of these methods has certain advantages and disadvantages and provides important, although limited information on the orientational order of macromolecules. For this reason, as a rule, several methods are used simultaneously, which allows one to give a more precise interpretation of the experimental data and obtain the more detailed information on the sample structure.

Owing to convenience, simplicity and high informativity, Raman spectroscopy has become one of the common methods used in the studies of the structure of solids. This technique has a very attractive and unique advantage over other methods. Namely, it allows, on the one hand, determination of orientation of macromolecules in different conformational states (like IR-spectroscopy) and, on the other hand, measurements of the coefficients in the ODF expansion up to the fourth order inclusively (like X-rays analysis). Application of Raman spectroscopy to the study of macromolecular orientation in polymers is based on the theory proposed by Bower[6,7] at the beginning of the 1970s. In particular, Bower showed that recording the Raman spectra for various polarization directions of the incident and scattered radiation provides necessary data on the second and fourth coefficients in the expansion of the ODF. In this work, we present some new analytical results in the development of the Bower theory, as well as experimental data on the study of polyethylene and polysulfone.

Theory

According to Roe[3], the ODF is presented as the expansion:

$$N(\xi,\psi,\varphi)=\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\sum_{n=-\ell}^{\ell}M_{\ell mn}Z_{\ell mn}(\xi)e^{-im\psi}e^{-in\varphi}, \qquad (1)$$

where $\xi=\cos\theta$; $Z_{\ell mn}(\xi)$ are the generalized associated Legendre functions; θ,ψ and φ are the Eulerian angles defining the orientation of the axes of a given scattering unit with respect to the coordinate system of the sample; and $M_{\ell mn}$ are the coefficients of expansion:

$$M_{\ell mn}=\frac{1}{4\pi^2}\int_0^{2\pi}\int_0^{2\pi}\int_{-1}^{1}N(\xi,\psi,\varphi)Z_{\ell mn}(\xi)e^{im\psi}e^{in\varphi}d\xi d\psi d\varphi. \qquad (2)$$

The Raman spectra of polymers contain the bands corresponding to the vibrations of various conformers and local groups[8]. Thus, depending on the choice of the Raman band, the ODF describes the orientation of some particular scattering units, such as crystallites, various conformers, terminal or side groups. The expansion coefficients obey the following relations:

$$M^*_{\ell mn} = (-1)^{m+n} M_{\ell\overline{m}\,\overline{n}}, \qquad M^*_{\ell m\overline{n}} = (-1)^{m+n} M_{\ell\overline{m}n}, \tag{3}$$

where $\overline{m} = -m$ and $\overline{n} = -n$.

The intensity of Raman scattering is described by the expression:

$$I_s = I_0 \sum \Big(\sum_{ij} l_i' l_j \alpha_{ij} \Big)^2, \tag{4}$$

where α_{ij} are the components of the tensor of polarizability derivative with respect to the normal coordinate of the scattering unit in the sample coordinate system XYZ ; l_i' and l_j are the direction cosines for the incident and scattered light in the same coordinates; and I_0 is a constant determined by the intensity of excitation light and the experimental system parameters. The summation is performed over all scattering units contributing to the Raman intensity. The derived polarizability tensor of a scattering unit α_{ij} in the coordinate system of the sample XYZ is calculated as:

$$\alpha = B\alpha^0 B^{-1}, \tag{5}$$

where α^0 is the derived polarizability tensor connected with the coordinate system of scattering unit, and the transition matrix B is the matrix of Eulerian angles θ, ψ, and φ. It was shown by Bower[6,7] that

$$\sum \alpha_{ij}\alpha_{pq} = 4\pi^2 N_0 \sum_{\ell mn} M_{\ell mn} B^{ijpq}_{\ell mn}. \tag{6}$$

Here N_0 is the total number of scattering units contributing to the measured intensity, $B^{ijpq}_{\ell mn}$ are the values depending only on the form of the derived polarizability tensor α^0:

$$B^{ijpq}_{\ell mn} = \frac{1}{4\pi^2} \int_0^{2\pi}\int_0^{2\pi}\int_{-1}^{1} \alpha_{ij}\alpha_{pq} Z_{\ell mn}(\xi) e^{-im\psi} e^{-in\varphi} d\xi\, d\psi\, d\varphi. \tag{7}$$

These values obey the following relations:

$$B^*_{\ell mn} = (-1)^{m+n} B_{\ell\overline{m}\,\overline{n}}, \qquad B^*_{\ell m\overline{n}} = (-1)^{m+n} B_{\ell\overline{m}n}. \tag{8}$$

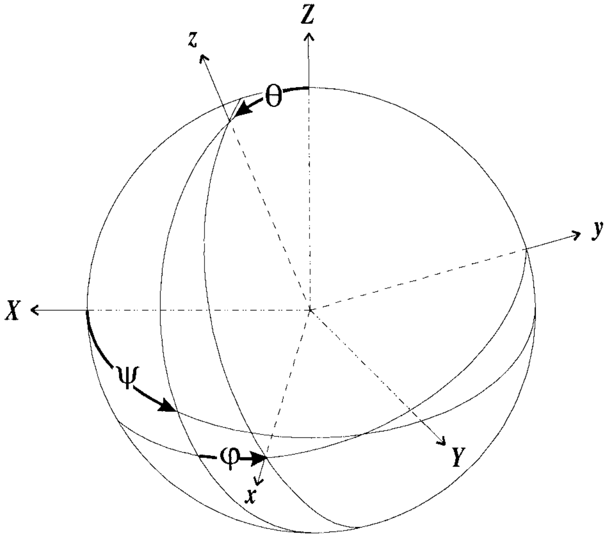

Figure 1. The definition of the Eulerian angles.

The Eulerian angles could be chosen by different ways. Use of different definitions of these angles leads to different values of $B_{\ell mn}^{ijpq}$. Let $Oxyz$ be the coordinate system connected with the scattering unit. In [6,7] the Eulerian angles are defined as follows: θ is the angle between the Oz and OZ axes, φ is the angle between the zOZ and xOz planes, and ψ is the angle between the zOZ and XOZ planes (Figure 1). For this definition of the Eulerian angles we calculate the relations between the values $B_{\ell mn}^{ijpq}$ with one negative and other positive indices. These data are summarized in Table 1. It is very important to note what the relations between the expansion coefficients $M_{\ell mn}$ with one negative and other positive indices analogous to the ones presented in Table 1 could not be obtained without imposing constraints on the ODF of macromolecules. In the case of a sample having three mutually perpendicular two-fold axes of rotational symmetry we have:

$$M_{\ell \overline{m} n} = (-1)^{\ell+n} M_{\ell mn} . \tag{9}$$

Symmetry properties of $M_{\ell mn}$ and $B_{\ell mn}^{ijpq}$ together with the relations (3) and (8) could be used to transform general equation (6) to the set of equations connecting Raman intensity and expansion coefficients $M_{\ell mn}$ for the certain cases.

Table 1. Relations between the values B_{lmn}^{ijpq} with one negative and other positive indices.

$B_{l\overline{m}n}^{ijpq} = B_{lmn}^{ijpq}$	$B_{l\overline{m}n}^{ijpq} = -B_{lmn}^{ijpq}$
$\sum\alpha_{XX}^2$, $\sum\alpha_{YY}^2$, $\sum\alpha_{XY}^2$, $\sum\alpha_{XZ}^2$, $\sum\alpha_{YZ}^2$, $\sum\alpha_{XX}\alpha_{YY}$, $\sum\alpha_{XX}\alpha_{ZZ}$, $\sum\alpha_{YY}\alpha_{ZZ}$, $\sum\alpha_{XX}\alpha_{YZ}$, $\sum\alpha_{XY}\alpha_{XZ}$, $\sum\alpha_{YY}\alpha_{YZ}$, $\sum\alpha_{YZ}\alpha_{ZZ}$	$\sum\alpha_{XX}\alpha_{XY}$, $\sum\alpha_{XX}\alpha_{XZ}$, $\sum\alpha_{XY}\alpha_{YY}$, $\sum\alpha_{XY}\alpha_{YZ}$, $\sum\alpha_{XY}\alpha_{ZZ}$, $\sum\alpha_{XZ}\alpha_{YY}$, $\sum\alpha_{XZ}\alpha_{YZ}$, $\sum\alpha_{XZ}\alpha_{ZZ}$

Under the assumption of symmetry of the derived polarizability tensor, the twenty-one values of $\sum\alpha_{ij}\alpha_{pq}$ are independent. The calculated values of $B_{\ell mn}^{ijpq}$ for this choice of the Eulerian angles were published partially by Bower in [7], and residuary values were published in our paper[9].

The case of uniaxial symmetry of the ODF is one of the most common and important for practical applications. If a polymer sample possesses uniaxial symmetry with respect to the certain direction, usually direction of drawing or extrusion, the intensity of Raman lines depends on the orientational order only through the quantities $\langle\cos^2\theta\rangle$ and $\langle\cos^4\theta\rangle$ averaged over all the orientation of macromolecules. These quantities, called as orientation parameters below, are related to the second and fourth coefficients in the expansion of the ODF:

$$
\begin{aligned}
C_0 &= \frac{1}{\sqrt{2}}, \\
C_2 &= \frac{\sqrt{5}}{2\sqrt{2}}\left[3\langle\cos^2\theta\rangle - 1\right], \qquad (10) \\
C_4 &= \frac{3}{8\sqrt{2}}\left[35\langle\cos^4\theta\rangle - 30\langle\cos^2\theta\rangle + 3\right].
\end{aligned}
$$

Here the expansion coefficients were renamed vis-à-vis the case of the arbitrary form of the

ODF (1) with the aim to prevent possible confusions. Thus, the ODF could be expanded in a series:

$$N(\theta) = N_0 \sum_{k=0}^{\infty} C_k \sqrt{\frac{2k+1}{2}} P_k(\cos\theta), \tag{11}$$

where $P_k(\cos\theta)$ are Legendre polynomials.

For the determination of two orientation parameters $\langle\cos^2\theta\rangle$ and $\langle\cos^4\theta\rangle$ it is convenient to measure two depolarization ratios of the Raman line. If the back-scattering geometry is applied, the wave vectors of incident and scattered radiation are parallel, and, thus, the following depolarization ratios could be measured:

$$R_1 = \frac{I_{XX}}{I_{XZ}}, \quad R_2 = \frac{I_{ZZ}}{I_{XZ}}. \tag{12}$$

Here, as before, $OXYZ$ is a coordinate system connected with the sample, and the Z-axis coincides with the direction of drawing; and I_{ij} is the intensity of the Raman line measured with the direction of polarization of excited and scattered light parallel to the i and j-axes, respectively.

In this work we consider two polymers as examples – polyethylene and polysulfone. These polymers are widely used in practice and are of interest in fundamental investigations. The Raman spectrum of polyethylene contains intense vibrations of $B_{2g} + B_{3g}$ mixed symmetry. Formulas relating the orientation parameters and the depolarization ratios of these vibrations (12) are expressed as follows:

$$\langle\cos^2\theta\rangle = \frac{-8R_1 + 7R_2 + 8}{8R_1 + R_2 + 8}, \qquad \langle\cos^4\theta\rangle = \frac{-8R_1 + 5R_2 + 8}{8R_1 + R_2 + 8}. \tag{13}$$

Note that the symmetry properties of these vibrations lead to the independence of depolarization ratios from the components of the derived polarizability tensor. It is convenient because in this case there is no need to measure the depolarization ratio in an isotropic sample for obtaining the relation between the different components of the derived polarizability tensor.

The Raman spectrum of polysulfone is rich in intense vibrations, part of which is more or less assigned[10]. However, data about the form of the derived polarizability tensors of most of the polysulfone vibrations are absent in the literature, and, therefore, at present they could not be used for the determination of orientational order. The only exception is the in-plane vibration

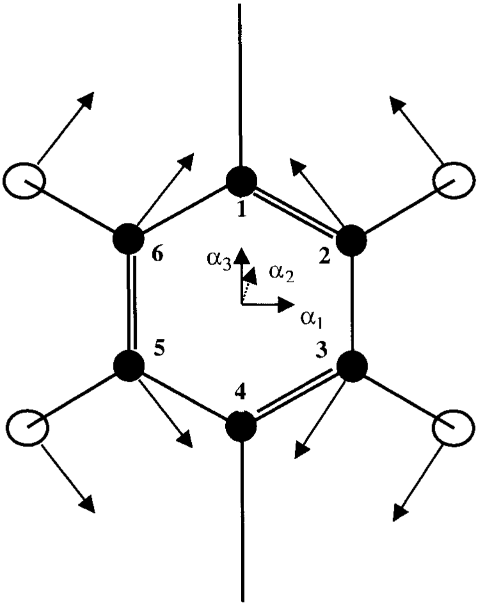

Figure 2. The form of in-plane vibration in the benzene ring.

of the benzene ring (Figure 2) at 1606 cm^{-1}. This line is also observed in the Raman spectrum of poly(ethylene terephthalate). For the latter case it was unambiguously demonstrated[11] that the derived polarizability tensor in the principal axes has cylindrical symmetry, that means $\alpha_{xx} = \alpha_{yy}$. One of the principal axes (Figure 2) of the tensor (corresponding to α_{zz}) is parallel to C1-C4 and another (corresponding to α_{xx} or α_{yy}) is perpendicular to the plane of the ring. If we use an approximation of cylindrical symmetry of the derived polarizability tensor of this vibration in the polysulfone Raman spectrum, formulae relating the depolarization ratios and orientation parameters take the forms:

$$R_1 = \frac{4\left(\left\langle\cos^2\theta\right\rangle - \left\langle\cos^4\theta\right\rangle\right)}{3\left\langle\cos^4\theta\right\rangle + 2a\left\langle\cos^2\theta\right\rangle + b}, \qquad (14)$$

$$R_2 = \frac{\left\langle\cos^2\theta\right\rangle - \left\langle\cos^4\theta\right\rangle}{2\left\langle\cos^4\theta\right\rangle - 4c\left\langle\cos^2\theta\right\rangle + 2c^2},$$

where $a = \frac{r^2 + 2r - 3}{(r-1)^2}$, $b = \frac{3r^2 + 2r + 3}{(r-1)^2}$, $c = \frac{r}{r-1}$ and $r = \frac{\alpha_1}{\alpha_3} = \frac{\alpha_2}{\alpha_3}$.

The value of r may be obtained by measuring the depolarization ratios for an isotropic sample, where $\left\langle\cos^2\theta\right\rangle = 1/3$ and $\left\langle\cos^4\theta\right\rangle = 1/5$. Thus, the equations (14) can be used for quantitative assessment of the orientation parameters in oriented samples.

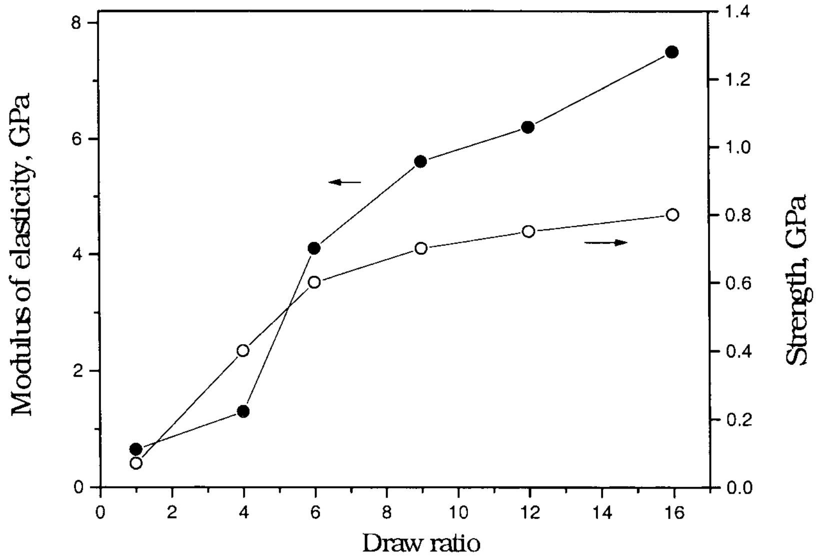

Figure 3. Modulus of elasticity (solid symbols) and strength (open symbols) as functions of draw ratio.

Experimental

Polyethylene

Polyethylene samples were obtained by the uniaxial drawing at 140°C of a film 0.2 mm thick prepared by the pressing of ultrahigh-molecular-weight polyethylene powder (M_w=2.2x10^6) at 200°C. The draw ratios of the samples studied were 1, 4, 6, 9, 12, and 16. The draw ratio equal to 16 is the limiting draw ratio for this material and the employed method of orientation. Further deformation leads to the rupture of a sample. Mechanical characteristics are presented in Figure 3.

To detect Raman spectra of polyethylene, we employed a Jobin Yvon U1000 double-pass monochromator and an Ar^+ laser generating radiation with a wavelength of 514,5 nm. The laser power on the sample did not exceed 70 mW. The signal was registered with a multichannel detector in the back-scattering geometry. All spectra were recorded with a spectral resolution of 5 cm^{-1}.

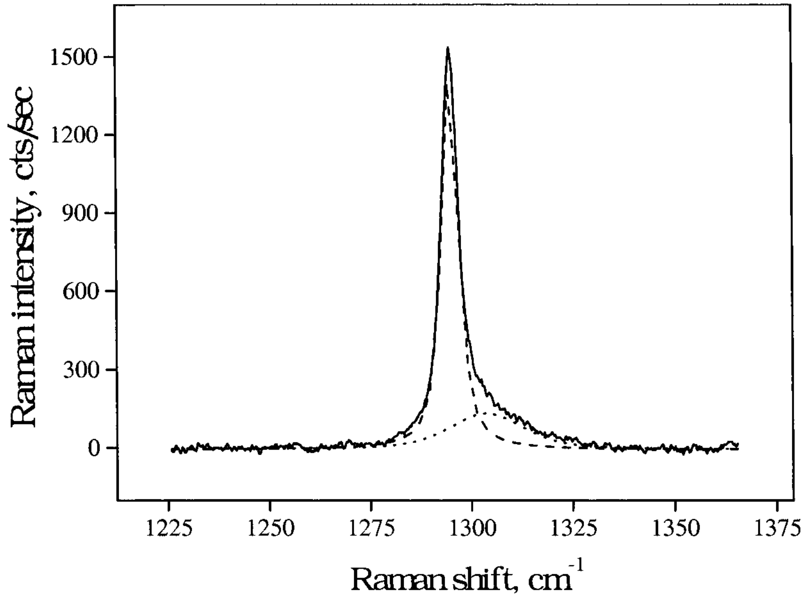

Figure 4. Raman spectrum in the range of twisting vibration of CH_2 group for an isotropic sample. The spectrum was recorded with parallel polarization direction of laser and scattered radiation. The solid line shows the measured spectrum. The dotted and dashed lines correspond to two groups of macromolecules (see text of the paper).

Raman spectra of polyethylene were measured within the range of the twisting vibration of the CH_2 group of B_{2g}+B_{3g} mixed symmetry (Figure 4). The intense and relatively narrow line with the peak around of 1295 cm^{-1} corresponds to vibrations of macromolecules in crystalline regions and long sequences of *trans*-segments in noncrystalline regions[8]. We call this group of macromolecules as **group** A. A relatively broad and weak band observed around 1305 cm^{-1} corresponds to the vibrations of macromolecules from **group B** in our notations. This denotes macromolecules with a considerable amount of *gauche*-conformers in noncrystalline regions. The decomposition of the spectrum within this range into two lines (Figure 4) makes it possible to determine averaged orientation parameters of macromolecules from groups A and B. Each of these lines was described by the sum of Lorentzian and Gaussian functions. The integral intensity was employed to find two depolarization ratios for each line. These depolarization ratios were then used to calculate orientation parameters (13).

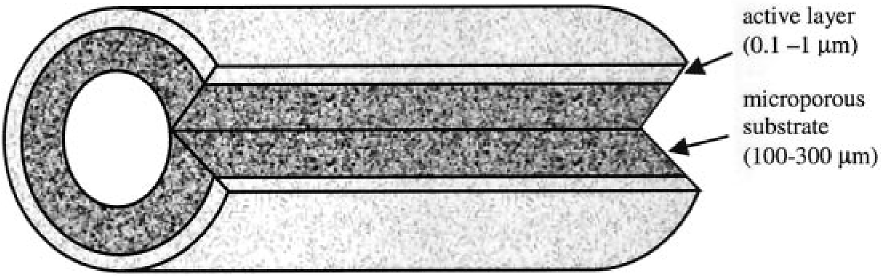

Figure 5. The structure of an asymmetric hollow fiber membrane.

Polysulfone

Asymmetric polysulfone hollow fiber membranes (Figure 5) for this study were fabricated from a commercially available polymer (Udel 1700) using a dry/wet spinning process. Fibers were spun at both low and high dope extrusion rates (DER) and hence at different levels of shear. All other conditions, including stretch ratio, were kept constant during spinning. The outer diameter of the fibers was approximately 0.6 mm, the internal diameter 0.3 mm. Thickness of a thin outer layer, which is responsible for the filtering properties and usually referred to as an active layer, was estimated as 0.1 mkm[12]. Selectivity tests have revealed that membrane performance of the fibers spun at the high DER was enhanced and even surpassed the recognized intrinsic selectivity of the membrane polymer[12]. An optically transparent isotropic sample of polysulfone was made by casting the spinning solution on a glass plate with subsequent drying in an oven at 100°C during 30 min.

The polysulfone Raman spectra were recorded using a Labram Raman spectrometer (Instruments SA, Ltd.) equipped with 1800 grooves/mm holographic grating, a holographic supernotch filter and a Peltier-cooled CCD detector. Micro-sampling was performed by means of an Olympus BX40 microscope and a helium-neon laser provided exciting radiation of wavelength equal to 632.8 nm. The microscope objective with a magnification of 50x was used both to focus the laser beam onto the sample and to collect the back-scattered radiation. Spectra were recorded at room temperature with a spectral resolution of 5 cm^{-1}.

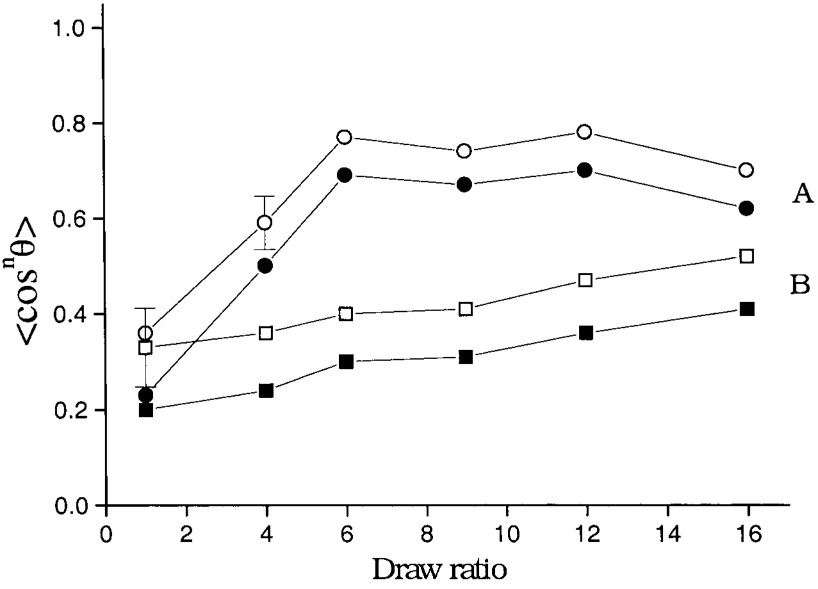

Figure 6. Orientation parameters for groups A and B of macromolecules as functions of draw ratio of the sample. Circles correspond to group A, squares – to group B. Open and solid symbols represent $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$, respectively.

Results

Polyethylene

Orientation parameters of macromolecules from groups A and B as functions of draw ratio are presented in Figure 6. Orientation parameters for group A rapidly grow at the initial stage of orientation, remaining almost constant for draw ratios close to limiting one. Orientation parameters of macromolecules from group B grow much slower than ones for group A, but its increase is observed up to the limiting draw ratio. Note that this dependence strongly correlates with the increase in the mechanical characteristics of the samples (Figure 3).

Polysulfone

Using Eqs. (14) and the value of a depolarization ratio measured for the isotropic sample, where R_1=R_2, the value of r = -0.14±0.01 was obtained. This is within the range of *r* obtained from data on isotropic poly(ethylene terephthalate)[11], and this fact may be considered as support for the assumption of a cylindrical symmetry for the derived polarizability tensor for the in-plane benzene ring vibration in polysulfone. Once the value of r had been determined, equations (14) were used again to calculate the orientation parameters for both low and high shear fibers. The results of these calculations are presented in Table 2.

Table 2. The orientation parameters of polysulfone membranes.

Sample	R_1	R_2	$\langle \cos^2\theta \rangle$	$\langle \cos^4\theta \rangle$
Isotropic (theory)			0.33	0.20
Low DER	0.66	0.81	0.33	0.17
High DER	0.76	0.61	0.38	0.22

It can be seen that the orientation parameters, measured on the basis of the benzene ring vibration, in the fiber spun at the high DER are slightly higher than those for the case of an ideal randomly oriented material are. This suggests that the sample may have some degree of molecular orientation. In contrast the orientation parameters for the sample spun at the low DER are the same as for the isotropic case. These results are in line with the data obtained previously by plane-polarized reflectance IR spectroscopy for the same samples[12], where a small, but distinct, degree of molecular orientation in the active layer was revealed in the high shear sample but no orientation was found in the low shear sample.

Despite the relatively high shear rate applied during spinning, the molecular orientation in active layer of membranes appears to be very low. Apart from reasons which may relate to any peculiarities of membrane structure arising in the dry/wet spinning process, the measured orientation characteristics could be reduced due to the influence of partial scrambling of the light polarization by the microporous substrate below the active layer. This could occur because the penetration depth of the incident radiation is higher than the depth of the active layer, in which the maximum degree of orientation is expected. Another case, which could explain such very low molecular orientation, is different orientation of each of four benzene rings of the polysulfone repeat unit. The theoretical estimations[13] reveal that the rings can be sufficiently disorientated relative to each other even in the oriented sample.

Conclusion

In this paper we present some theoretical and experimental results on the study of polymer orientation by means of Raman spectroscopy. It was shown that using this technique the information on the coefficients in the ODF expansion could be obtained even for the case of the arbitrary symmetry of this distribution function. Experimental results reported here confirm that polarized Raman spectroscopy is convenient tool for determining molecular orientation in polyethylene and polysulfone.

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