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Raman study of uniaxial deformation of single-crystal mats of ultrahigh molecular weight linear polyethylene

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Abstract. We present for the first time a Raman spectroscopic study of the deformation process of solution-crystallized single-crystal mats of ultrahigh molecular weight linear polyethylene (UHMW PE). We study the deformed regions of the films, drawn only until the formation of the neck, and the films of much higher draw ratios, just before rupture starts. For comparison, we have also carried out Raman investigations of films produced by compression of UHMW PE powder. We have found that the uniaxial molecular orientation in the neck region of the single-crystal mat films develops more slowly as compared to the films, prepared by compression of the UHMW PE powder.

1. Introduction
Polyethylene (PE) with molecular weight $M_w < 10^6$ g/mol is one of the most important industrial polymers due to its excellent characteristics and reasonable cost. With regard to the strength, the chemical, temperature and wear resistance, the friction coefficient, and physiological inertness, ultrahigh molecular weight polyethylene (UHMW PE, $M_w \geq 10^6$ g/mol) possesses even better properties as compared to ordinary PE grades. As a matter of fact, UHMW PE has been successfully applied in the production of prostheses, light-weight and high-strength fibers and some other products. However, UHMW PE applications are limited because of difficulty of its processing, which is due to a steep increase in viscosity of UHMW PE melt at $M_w \geq 10^6$ g/mol. Ultrahigh molecular weight causes the large number of molecular entanglements, which prevent unfolding of macromolecules during drawing. To improve the UHMW PE processability, a number of special approaches are applied [1], including gel molding [2 - 4], solution drawing [5], solution growth of single-crystal mats [6, 7], synthesis of reactor blends [8 - 10], etc. Detailed investigations of the UHMW PE deformation mechanism could be very useful for overcoming this limitation and expanding the field of application of UHMW PE.

A number of techniques are traditionally used to monitor polymer structure as well as structural changes, which occur in polymers during deformation. The most common methods are wide angle (WAXS) and small angle (SAXS) X-ray diffraction technique, differential scanning calorimetry
(DSC), transmission (TEM) and scanning (SEM) electron microscopy, NMR, IR and Raman spectroscopy, and measurements of birefringence. Raman spectroscopy is one of the most suitable methods to evaluate polymer structure both in non-deformed and deformed states. This technique is non-destructive and highly informative about both crystalline and amorphous states of molecules. In particular, Raman spectra contain information on the conformational and phase compositions and the orientation of PE macromolecules [11 - 14]. Conventional Raman investigations do not require any sample preparation, which could affect the sample structure, and a spatial resolution of a few microns (both over a surface and in depth) can be achieved on solid samples.

Raman spectrum of PE is well investigated, and almost all PE Raman-active lines are reliably assigned [15, 16, Table 1]. Raman spectrum of a PE single macromolecule in the all-trans conformation consists of the lines with symmetry $A_g$, $B_{1g}$, $B_{2g}$ and $B_{3g}$. Intermolecular interaction between two molecules in trans-conformation in the PE orthorhombic unit cell causes splitting of the Raman lines of a single PE molecule [17]. Therefore, Raman spectrum of the PE orthorhombic crystallites consists of doublets of the lines with symmetry $A_g$ and $B_{1g}$ or $B_{2g}$ and $B_{3g}$ [16, 17]. At room temperature this splitting can be observed only for the doublet of lines at 1415 cm$^{-1}$ (symmetry $A_g$) and 1440 cm$^{-1}$ (symmetry $B_{1g}$). This effect was successfully used to evaluate PE crystallinity in non-deformed [11, 12] and uniaxially drawn [14] samples. Besides, recording of polarized Raman spectra allows evaluation of the degree of uniaxial orientation of PE macromolecules in the trans- and gauche-conformations [13].

Table 1. Assignment of Raman-active lines of semicrystalline PE with orthorhombic crystalline phase.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency, cm$^{-1}$</th>
<th>Symmetry</th>
<th>Conformation</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>The asymmetric stretching vibration of C-C bonds</td>
<td>1062</td>
<td>$B_{2g}$+$B_{3g}$</td>
<td>trans</td>
<td>crystalline, amorphous</td>
</tr>
<tr>
<td>The stretching vibration of C-C bonds</td>
<td>1080</td>
<td>-</td>
<td>gauche</td>
<td>amorphous</td>
</tr>
<tr>
<td>The symmetric stretching vibration of C-C bonds</td>
<td>1130</td>
<td>$A_g$+$B_{1g}$</td>
<td>trans</td>
<td>crystalline, amorphous</td>
</tr>
<tr>
<td>The twisting vibration of CH$_2$ groups</td>
<td>1295</td>
<td>$B_{2g}$+$B_{3g}$</td>
<td>trans</td>
<td>crystalline, amorphous</td>
</tr>
<tr>
<td>The twisting vibration of CH$_2$ groups</td>
<td>1305</td>
<td>-</td>
<td>gauche</td>
<td>amorphous</td>
</tr>
<tr>
<td>The bending vibration of CH$_2$ groups</td>
<td>1415</td>
<td>$A_g$</td>
<td>trans</td>
<td>crystalline</td>
</tr>
<tr>
<td>The bending vibration of CH$_2$ groups</td>
<td>1440</td>
<td>$B_{1g}$</td>
<td>trans</td>
<td>crystalline</td>
</tr>
<tr>
<td>The symmetric stretching vibration of CH$_2$ groups</td>
<td>2848</td>
<td>$A_g$</td>
<td>trans</td>
<td>crystalline, amorphous</td>
</tr>
<tr>
<td>The asymmetric stretching vibration of CH$_2$ groups</td>
<td>2882</td>
<td>$B_{1g}$</td>
<td>trans</td>
<td>crystalline, amorphous</td>
</tr>
</tbody>
</table>

PE has complex semicrystalline structure [18], where macromolecules in the crystallites are in the trans-conformation, while the amorphous phase contains both trans- and gauche-conformers. It is well known, that uniaxial hot-drawing leads to preferred orientation of PE macromolecules along the direction of drawing. A number of structural models of the uniaxial deformation mechanism of PE were extensively discussed in literature [18 - 24]. During this process, the PE crystalline structure reorganizes from the lamellar to the fibrillar one [18], both having the orthorhombic unit cell. Simultaneously, the amount of trans-conformers in the amorphous phase grows, while the amount of gauche-conformers decreases. In particular, X-ray diffraction studies [19] have shown that the amorphous phase of uniaxially stretched PE contains significant amount of straightened tie molecules in trans-conformation, and most of these molecules are the direct continuations of the crystallite chains and connect adjacent crystallites along the axis of uniaxial orientation. With the growth of the degree of deformation, the number and lengths of such linear systems increase.
At uniaxial hot-drawing, transformation of the lamellar crystalline structure of original PE into the fibrillar one with preferred molecular orientation along the direction of drawing mainly takes place in the transition area of the neck region [18]. The neck region has spatially non-uniform supramolecular structure, altering from the non-deformed to the uniaxially oriented state. A length of the structure transformation region depends on both structure of non-deformed sample and the conditions of drawing (temperature and rate of deformation) and is usually of tens of micrometers. Further deformation leads to improving the chain orientation along the direction of drawing. All stages of the PE deformation process are of particular interest for fundamental and applied researches.

Most of published papers on UHMW PE study are related to investigation of the mechanisms of elastic and inelastic uniaxial deformation. Authors of paper [25] have studied structure of commercial and experimental UHMW PE powders, synthesized using different catalysts and under different conditions. Elastic uniaxial deformation of UHMW PE was studied by Raman spectroscopy [26], X-ray analysis [7, 27] and by EPR spectroscopy [28]. In particular, X-ray analysis was successfully applied to investigate features of uniaxial deformation of UHMW PE single-crystal mats [7]. Authors of the paper [7] have revealed that uniaxial deformation of the PE single-crystal mats leads to change in the dimensions of the PE unit cell and in the crystallite sizes. They also have observed anomalous relation between the micro- and macro-deformation characteristics of the samples, which was explained by non-uniform structure of the amorphous phase of the films, in particular, by wide distribution of lengths of the straightened tie molecules in the films, preliminarily hot-drawn up to low draw ratios. It was found that the deformation of UHMW PE crystalline lattice includes reversible and nonreversible components. The nonreversible deformation component was manifested in the reduction of the parameter \( a \) of the orthorhombic unit cell, and this effect was explained by conformational gauche-trans transitions under mechanical loading and nonreversible disappearance of these defects.

A number of investigations of inelastic deformation mechanism of UHMW PE have been reported [1, 29 - 41]. However, with the exception of two papers of our group [40, 41], there are no Raman spectroscopic studies of the PE neck region. We have found only two papers on micro-Raman study of neck region in polymers – for poly(vinylidene fluoride) [42, 43] and for polypropylene [42].

The mechanism of necking of thin UHMW PE films, prepared from dilute solution, was investigated by TEM [30]. DSC technique, IR spectroscopy, mechanical testing, measurements of density, birefringence and sonic velocity were applied to investigate uniaxial deformation of UHMW PE fiber, obtained by gelation/crystallization from solution [31]. Solid state drawing of solution-crystallized UHMW PE was studied by WAXS and SAXS techniques [32]. WAXS technique was also applied to analyze structure and alteration in crystallite orientation during melting of gel-drawn UHMW PE films [33, 34]. Polarized confocal Raman microscopy in combination with WAXS technique was used to characterize structure of UHMW PE fibers of various molecular weights, uniaxially drawn by solid-state extrusion [35]. WAXS technique, SEM, mechanical testing and numerical simulation were applied to study pre-swollen uniaxially drawn UHMW PE films [1]. WAXS and SAXS techniques, mechanical testing, and measurements of density were applied to uniaxially drawn UHMW PE films, produced by gelation/crystallization at various temperatures [36]. Series of papers [37-39] is connected with investigation of high-strength gel-spun UHMW PE fibers by WAXS technique, low frequency Raman and IR spectroscopy, and mechanical testing.

X-ray analysis investigation of PE single-crystal mat films has shown that samples, produced from PE with low molecular weight, are much more fragile than samples, produced from PE with medium and high molecular weights [29]. This effect was explained by very low amount of tie molecules, connecting lamellar crystallites in low molecular weight PE single-crystal mats.

Raman spectroscopy was applied to study alterations in the phase composition and molecular orientation in UHMW PE prosthesis components, subjected to various sterilization methods as well as after testing on movement-wear simulators [44 - 47]. Raman spectroscopy, WAXS, SAXS and DSC techniques were successfully applied to evaluate structural changes in UHMW PE of two different molecular weights [48] during \( \gamma \) irradiation in air, which is used as a sterilization method.
UHMW PE can be also applied to produce nanocomposites with multi-wall carbon nanotubes, having the improved mechanical properties [49]. Employment of Raman spectroscopy [15, 50] and X-ray analysis [15] to UHMW PE, subjected to elevated pressure and temperature, allowed to determine spectral features in the UHMW PE Raman spectrum, corresponding to the monoclinic, orthorhombic, and hexagonal crystalline modifications and melt.

In this work we present a Raman spectroscopic study of uniaxially hot-drawn films of solution-crystallized UHMW PE single-crystal mats. We study the deformed regions of the films, drawn only until the formation of the neck, and the films of much higher draw ratios just before rupture starts. The single-crystal mats are the stacks of folded-chain lamellae, which are sufficiently homogeneous in thickness and are interlinked by a small number of tie molecules [6, 19]. A very small amount of chain entanglements in the amorphous regions of UHMW PE single-crystal mats leads to the special mechanism of uniaxial deformation compared with PE films, produced by sintering of UHMW PE reactor powder. During uniaxial drawing, macromolecules in the single-crystal mats are able to relatively easy straighten and to be aligned along the direction of deformation. Uniaxially deformed UHMW PE single-crystal mat films contain large amount of straightened tie molecules and possess very high mechanical characteristics, in particular, draw ratio and the elastic modulus [6, 19].

For comparison, here we also discuss results of Raman study of UHMW PE films, produced by compression of UHMW PE powder [40, 41].

2. Experimental

We study two series of UHMW PE single-crystal mat films (molecular weight $M_w=10^6$ g/mol), which were subjected to uniaxial hot-drawing. The production method of these samples is described in detail in the paper [6]. Films, designated as series N 1 and N 2, were crystallized from solution of UHMW PE in xylene with UHMW PE concentration of 0.05 and 0.20 mass %, respectively, and were drawn at temperatures of 130 and 110°C, respectively. Length of the structure transition area in the neck for both series was about 600 μm.

As a result of the special production method and according to the X-ray diffraction data [6, 19], orientation of $c$-axes of orthorhombic crystallites in the non-deformed single-crystal mat films was predominantly perpendicular to the film surface. For the uniaxially drawn single-crystal mat films of both series N 1 and N 2, orientation of the $c$-axes was predominantly along the direction of drawing. In addition, for the drawn films from series N 2, the orientation of the $b$-axes of the orthorhombic crystallites was predominantly in the plane of the films. For the drawn films from series N 1, the orientation of the $a$ and $b$-axes of the orthorhombic crystallites was random in the plane, perpendicular to the direction of drawing.

Series of the films N 3 was produced by compression of UHMW PE powder with $M_w=2.2\times10^6$ g/mol at 200°C. These films were uniaxially drawn at 130°C, and length of the structure transition area in the neck was about 150 μm. According to the X-ray diffraction data, macromolecular orientation in the original film of series N 3 was isotropic. For the uniaxially drawn films from this series, molecular orientation of the $c$-axes was predominantly along the direction of drawing with random orientation of axes $a$ and $b$ in the plane, perpendicular to the direction of drawing.

The mechanical characteristics of the single-crystal mat films were much higher compared to that of the films, produced by compression of the UHMW PE powder. In particular, the ultimate draw ratio, that is the draw ratio $\lambda$, after which rupture of a sample occurs, was equal to 225 for the series N 1 and N 2 and only 16 for the series N 3.

Experimental setup for recording the Raman spectra included Ar$^+$-laser, double monochromator (U1000, Jobin Yvon), Olympus microscope, water-cooled photomultiplier, operating in the photon counting mode. Raman spectra were recorded in the back-scattering geometry with spectral resolution of 3 cm$^{-1}$. For excitation of the Raman spectra we used the laser line at 514.5 nm. Exciting and scattered radiation was collected using objective (100X, N.A. 0.95). Laser power at the sample surface was about 50 mW. Diameter of the laser spot on the sample surface was adjusted to be 10 μm in order to prevent local overheating of the sample and changing of its structure. To avoid influence of edge effects, Raman spectra were recorded in the central part in width of the samples. While considering
results of the neck region investigation, \( l \) denotes distance from the non-deformed part \( (l=0, \text{draw ratio } \lambda=1) \) towards the oriented part along the direction of drawing. We analyzed two most informative regions in the PE Raman spectrum – from 1000 to 1550 cm\(^{-1}\) and from 2700 to 3050 cm\(^{-1}\).

**Figure 1.** Experimental geometry for recording the Raman spectra of single-crystal mat films. For details, please, refer to the text.

Raman spectra were recorded in two scattering geometries - \( X(Z,Z)X \) and \( X(Z,Y+Z)X \). In these notations axis X is normal to the sample surface, axis Z is in the plane of the sample surface and coincides with the direction of drawing (figure 1). In all experiments the direction of the laser polarization was along axis Z, and wave vectors of the exciting and scattered radiation were along axis X. For the \( X(Z,Z)X \) geometry the direction of polarization of scattered light was parallel to axis Z. In order to select required polarization of scattered light, polarizer was placed before the monochromator entrance slit. In the \( X(Z,Y+Z)X \) geometry we collected all scattered radiation and used \( \lambda/4 \) plate instead of a polarizer. This allowed avoidance of incorrect measurements of relative Raman intensities, which can be caused by influence of selectivity of Raman setup optical elements relative to different polarization directions of the scattered light.

### 3. Results and Discussion

Typical Raman spectra for the film N 1 of single-crystal mats, recorded in the neck region in the \( X(Z,Z)X \) and \( X(Z,Y+Z)X \) geometries, are presented in figures 2 and 3, respectively. The top spectra in these figures are the spectra of the same film, uniaxially deformed to draw ratio \( \lambda=200 \). Figures 4 and 5 show the corresponding spectra for the film N 2. Two top spectra in these figures are the spectra of the same film, uniaxially deformed to draw ratios \( \lambda=23 \) and 90. For illustrative purposes, the peak intensities of all lines in figures 2 – 5 are normalized to the peak intensity of the line at 1130 cm\(^{-1}\). We chose this line as a reference line because its intensity changes relatively little with increase in \( l \) and in \( \lambda \) in both scattering geometries. Spectra of the film N 3 in the neck region can be found in [41].

For both scattering geometries, changes in the intensities of the PE Raman lines with increase in \( l \) are very similar for all three films under study. In accordance with selection rules for the \( X(Z,Z)X \) geometry, all PE Raman lines, that is of \( A_g, B_{1g}, B_{2g} \) and \( B_{3g} \) symmetry, can appear in the spectrum of PE film with isotropic molecular orientation. In case of complete uniaxial molecular orientation along the drawing direction (axis Z), only \( A_g \) symmetry lines can be observed in the \( X(Z,Z)X \) geometry. Therefore, intensity ratio of the lines with mixed symmetry \( B_{2g}+B_{3g} \) and \( A_g+B_{1g} \) in the \( X(Z,Z)X \) geometry can serve as a measure of the degree of uniaxial molecular orientation.
Figure 2. Raman spectra of the single-crystal mat film N 1 in the X(Z,Z)X geometry. The spectra were recorded in the neck region at \( l = 0, 500, 540 \) and 600 \( \mu \text{m} \). The top spectrum is the spectrum of the film N 1, deformed up to draw ratio \( \lambda = 200 \).

Figure 3. Raman spectra of the film N 1 in the X(Z,Y+Z)X geometry. For details, please, refer to the caption of figure 2.
Figure 4. Raman spectra of the single-crystal mat film N 2 in the X(Z,Z)X geometry. The spectra were recorded in the neck region at l=0, 500, 540 and 640 μm. Two top spectra are the spectra of the film N 2, deformed up to draw ratios λ = 23 and 90, respectively.

Figure 5. Raman spectra of the film N 2 in the X(Z,Y+Z)X geometry. For details, please, refer to the caption to figure 4.
As in the case of the X(Z,Z)X geometry, in the X(Z,Y+Z)X geometry Raman lines of A_g, B_{1g}, B_{2g} and B_{3g} symmetry can appear in the spectrum of a PE film with isotropic molecular orientation. In the case of complete uniaxial molecular orientation along the drawing direction in this geometry we should observe only A_g, B_{2g} and B_{3g} symmetry lines. Recording spectra in the X(Z,Y+Z)X geometry is informative, because we can prove that changes in the intensities of the lines in the X(Z,Z)X geometry are due to changes in the molecular orientation, rather than due to other changes in PE structure.

As can be seen from figures 2 and 4, in the X(Z,Z)X geometry increase in l leads to decrease in the intensities of the lines at 1062, 1295, 1440, 2848 and 2882 cm\(^{-1}\) compared with the intensities of the lines at 1130 and 1415 cm\(^{-1}\). Simultaneously, reduction of the intensities of the lines at 1440, 2848 and 2882 cm\(^{-1}\) is observed in the X(Z,Y+Z)X geometry (figures 3 and 5).

The line at 1130 cm\(^{-1}\) has A_g+B_{1g} mixed symmetry and corresponds to the symmetric stretching vibration of C-C bonds of trans-conformers, localized in both crystalline and amorphous phases (table 1). The line at 1415 cm\(^{-1}\) with A_g symmetry relates to the bending vibration of CH\(_2\) groups of macromolecules in the orthorhombic crystalline phase. Thus, these two lines should be observed in both used geometries irrespective of the degree of uniaxial molecular orientation.

The line at 1062 cm\(^{-1}\) corresponds to the asymmetric stretching vibration of C-C bonds, while the line at 1295 cm\(^{-1}\) - to the twisting vibration of CH\(_2\) groups (table 1). Both the lines relate to the vibrations of trans-conformers, localized in the crystalline and amorphous phases, and possess B_{2g}+B_{3g} mixed symmetry. In the case of isotropic molecular orientation, these lines should be apparent in the both scattering geometries. In case of perfect chain orientation along the drawing direction, the lines at 1062 and 1295 cm\(^{-1}\) should be observed in the X(Z,Y+Z)X geometry and should disappear in the X(Z,Z)X geometry.

![Figure 6](image1.png)  
**Figure 6.** The ratio I_{as}(C-C)/I_s(C-C) of intensities of the asymmetric and symmetric stretching vibrations of C-C bonds in the X(Z,Z)X geometry for three UHMW PE films vs. l.

![Figure 7](image2.png)  
**Figure 7.** The ratio I(CH\(_2\))/I_s(C-C) of intensities of the twisting vibration of CH\(_2\) groups and the symmetric stretching vibration of C-C bonds in the X(Z,Z)X geometry for three UHMW PE films vs. l.

As can be seen from the spectra, presented in figures 2 and 4, intensities of the lines at 1062 and 1295 cm\(^{-1}\) significantly decrease in the neck region in the X(Z,Z)X geometry, and this trend continues for the films, drawn up to high draw ratios. Figures 6 and 7 compare the peak intensity ratios of the lines at 1062 and 1130 cm\(^{-1}\) (I_{as}(C-C)/I_s(C-C)) and the lines at 1295 and 1130 cm\(^{-1}\) (I(CH\(_2\))/I_s(C-C)) in the X(Z,Z)X geometry at scanning the neck regions of three UHMW PE films under study. Scatter in the dependences of the intensity ratios can probably be explained by non-uniform spatial structure of the neck region.

The intensity ratios I_{as}(C-C)/I_s(C-C) and I(CH\(_2\))/I_s(C-C) for the film N 3 are decreasing more rapidly than that for the films N 1 and N 2 (figures 6 and 7). This experimental fact is explained not only by different length of the structure transformation region for these samples, but also by different
molecular orientation. The values of the intensity ratios $I_\text{as}(C-C)/I_\text{s}(C-C)$ and $I_\text{as}(\text{CH}_2)/I_\text{s}(C-C)$ at the end of the structure transformation region of the film N 3 is more than 2.5 times less than the same values for the films N 1 and N 2. On the contrary, in the X(Z,Y+Z)X geometry these intensity ratios are almost unchanged with increase in $l$ (figures 3 and 5).

![Figure 8](image1.png)  
**Figure 8.** The ratio $I_\text{as}(\text{CH}_2)/I_\text{s}(\text{CH}_2)$ of intensities of the asymmetric and symmetric stretching vibrations of CH$_2$ groups in the X(Z,Z)X geometry for three UHMW PE films vs. $l$.

![Figure 9](image2.png)  
**Figure 9.** The ratio $I_\text{as}(\text{C-C})/I_\text{s}(\text{C-C})$ of intensities of the asymmetric and symmetric stretching vibrations of C-C bonds in the X(Z,Z)X geometry for three series of UHMW PE films vs. $\lambda_n$.

![Figure 10](image3.png)  
**Figure 10.** The ratio $I_\text{as}(\text{CH}_2)/I_\text{s}(\text{C-C})$ of intensities of the twisting vibration of CH$_2$ groups and the symmetric stretching vibration of C-C bonds in the X(Z,Z)X geometry for three series of UHMW PE films vs. $\lambda_n$.

![Figure 11](image4.png)  
**Figure 11.** The ratio $I_\text{as}(\text{CH}_2)/I_\text{s}(\text{CH}_2)$ of intensities of the asymmetric and symmetric stretching vibrations of CH$_2$ groups in the X(Z,Z)X geometry for three series of UHMW PE films vs. $\lambda_n$.

There are no significant changes in the ratio of peak intensities of the lines at 1415 and 1130 cm$^{-1}$ with the growth of distance $l$ and draw ratio $\lambda$ in the both scattering geometries (figures 2 - 5). It means that the degree of crystallinity is not affected significantly by increase in $l$ and $\lambda$. The line at 1440 cm$^{-1}$ with B$_{1g}$ symmetry is the second component of the doublet of the bending vibration of CH$_2$ groups of macromolecules in the PE orthorhombic crystalline phase (table 1). This line disappears in both scattering geometries with growth of distance $l$ and draw ratio $\lambda$. As it is expected from the form of the derived polarizability tensor of B$_{1g}$ symmetry vibration, with growth of $l$ or $\lambda$ intensity of this line is decreasing faster in the X(Z,Z)X geometry compared with the X(Z,Y+Z)X geometry (figures 2 - 5). The same effect is also observed for the line at 2882 cm$^{-1}$, also having B$_{1g}$ symmetry.

The lines at 2848 and 2882 cm$^{-1}$ are related to the symmetric and asymmetric stretching vibrations of CH$_2$ groups and have A$_g$ and B$_{1g}$ symmetry, respectively [51, table 1]. Figure 8 shows the ratio
I_{as}(CH2)/I_{as}(CH3) of peak intensities of the lines at 2882 and 2848 cm\(^{-1}\) in the X(Z,Z)X geometry for three UHMW PE films as a function of \(l\). Interesting experimental observation is the reduction of intensity of the line at 2848 cm\(^{-1}\) with increase in \(l\) in the both X(Z,Z)X and X(Z,Y+Z)X geometries (figures 2 - 5). We suppose that this effect is due to a small value of the component \(\alpha_{cc}\) (here \(c\) is the chain axis) of the derived polarizability tensor compared with two other components for the vibration of \(A_g\) symmetry. This explanation is also confirmed by results, presented in [52, 53].

Figures 9, 10 and 11 present the ratios \(I_{as}(C-C)/I_{as}(C-C), I_{as}(CH2)/I_{as}(C-C)\) and \(I_{as}(CH2)/I_{as}(CH3)\), respectively, in the X(Z,Z)X geometry for three series of UHMW PE films as functions of normalized draw ratio \(\lambda_n\), that is the draw ratio \(\lambda\), divided by the ultimate draw ratio, after which rupture of a sample occurs. As it was mentioned early, the ultimate draw ratio was equal to 225 for the series N 1 and N 2 and only 16 for the series N 3. It is clear from figures 9 - 11, that when the relative degree of deformation is considered, the alterations in the molecular orientation for all three series are very similar. The most significant structural alterations take place in the neck region. Similar results were obtained for series of gelspun multifilament UHMW PE fibers with ultimate draw ratio, equal to 40 [40, 41].

Thus, in this work we used Raman spectroscopy for investigation of molecular orientation in the neck region of two single-crystal mat films, prepared from UHMW PE solution in xylene with UHMW PE concentration of 0.05 and 0.20 mass %, respectively. These data were compared with results of investigation of the film, produced by compression of the UHMW PE powder. We found out that uniaxial molecular orientation in the single-crystal mat films develops slower than that in the film, prepared by compression of the UHMW PE powder. Change in the molecular orientation along the transition area of the neck region for two single-crystal mat films was very similar. However, the degree of molecular orientation of trans-conformers in both the crystalline and amorphous phases was slightly higher at the end of the structure transformation area for the film, crystallized from more concentrated solution.

Different deformation mechanisms of the single-crystal mat films and the film, prepared by the UHMW PE powder compression, obviously could be explained by very different structure of the amorphous phase of these samples. In the films, produced by the powder compression, a large number of chain entanglements in the amorphous phase prevent the unfolding of chains during the uniaxial drawing and restrict the draw ratio. On the contrary, the amount of chain entanglements in the single-crystal mats is relatively small, and, hence, the chain unfolding of the lamellar crystallites can easy occur during deformation.

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**References**


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