Molecular orientation behavior of isotactic polypropylene under uniaxial stretching by rheo-Raman spectroscopy

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Abstract. The molecular orientation behavior of isotactic polypropylene (iPP) is investigated by using *in situ* Raman spectroscopy under tensile tests. A versatile method of the tilt-angle correction for the orientation parameters is newly developed, where the molecular orientation in highly oriented specimens is assumed to be entropically favorable. The real-time changes of orientation parameters and orientation distribution functions are determined for the molecular chain axis of iPP during uniaxial stretching. The molecular orientation remains random in the elastic region, and increases after the first yield point. In the yielding region, a broad distribution of orientation toward an intermediate angle of 30–70° from the stretching direction is observed. This is interpreted as reorientation of the crystalline chains being hindered by rigid, bulky lamellar cluster units. After the yielding region, orientation toward the stretching direction proceeds rapidly, approaching highly oriented states.

Keywords: mechanical properties, Raman spectroscopy, molecular orientation, isotactic-polypropylene

1. Introduction

Isotactic polypropylene (iPP) is a semi-crystalline polymer which exhibits high strength, workability and transparency and has low cost. iPP is commonly used in films, plastic moldings and structural materials. The molecular orientation of the crystalline and amorphous chains greatly influences the mechanical properties of such semi-crystalline polymers [1, 2]. For example, a high degree of orientation along the stretching axis is required for fabricating very strong fibers.

The molecular orientation of semi-crystalline polymers has been investigated by various experimental methods. Birefringence is a simple and fundamental technique which gives a qualitative measure of the overall orientation in bulk specimens, including the crystalline and amorphous regions [3, 4]. Wide-angle X-ray diffraction (WAXD) basically provides the distribution of molecular orientation of the crystalline chain, while that of the amorphous chains are

also determined by the synchrotron WAXD measurements [5, 6]. Infrared (IR) spectroscopy can separately evaluate the average molecular orientations of both crystalline and amorphous chains [7, 8], using its dichroic ratio. However, IR spectroscopy is unsuitable for thick samples such as plastic molds and structural materials, then, it has been applied for the sliced samples, because of high extinction coefficients in the IR region.

Recent improvements in laser light sources, optical devices and detectors have promoted the application of Raman spectroscopy across various research fields. Raman spectroscopy is a vibrational spectroscopy technique with several advantages over the above-mentioned techniques. First, its sufficiently short acquisition time enables measurements to be carried out *in situ* [9–11]. The stress relaxation upon unloading polymeric samples can result in appreciable structural changes, including molecular orientation. Rheo-Raman spectroscopy which is the simultane-

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ous measurement of Raman spectra and mechanical tests enables real-time monitoring of the microscopic deformation mechanism. Second, polarized Raman spectroscopy detects the molecular orientations of both crystalline and amorphous chains. Raman spectroscopy has been used to evaluate the molecular orientations of crystalline and amorphous chains in iPP films [12, 13], and *in situ* micro-Raman spectroscopy has also been applied to investigate the microscopic mechanism of iPP during uniaxial deformation [9]. Third, the distribution of molecular orientations is determined by calculating the orientation distribution function (ODF) from the orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ [14, 15]. In contrast, IR spectroscopy can only provide the orientation function as a measure of the average orientation. Finally, since typical optical setups for the scattering measurements are more flexible than those for the transmission measurements, Raman spectroscopy can provide non-contact and non-destructive technique to probe the molecular orientation of plastic molds without any pretreatments.

The crystalline chain of iPP has a 3_1 helical structure [16], so the principal axis of the Raman tensor is not parallel to the molecular chain axis [13, 17]. A correction for the tilt angle between these two axes is required to evaluate the orientation of the molecular chains. Tanaka and Young reported tilt-angle corrections using WAXD measurements [13, 18], and obtained ODF values using the 1000 cm^{-1} band of highly drawn iPP. The ODF values of poly(lactic acid), which also forms helical chains in the crystalline phase, have been determined from highly drawn samples [13, 18, 19].

In the current study, rheo-Raman spectroscopy is used to elucidate the molecular orientation behavior of iPP during elongation. A new method for correcting the tilt angle between the molecular axis and the principal axis of the Raman tensor is applied. ODF values and orientation parameters for the crystalline chains of iPP are obtained. The microscopic mechanism of deformation of iPP under uniaxial tensile testing is discussed, by comparing the current results with previous results for high-density polyethylene (HDPE) [10, 11].

2. Methods

2.1. Sample and apparatus

Ziegler-Natta-catalyzed homo iPP pellets ($M_w = 4.9 \cdot 10^5$, $M_w/M_n = 4.4$) supplied by Union Polymer Material Co., Ltd (Dalian, China, Grade: YD101-A) were used in this study. The pellets were compression molded in a hot press at 230°C and 20 MPa for 5 min, to prepare a sheet with thickness of about 1 mm. The sample sheet was removed from the hot press, quenched in boiled water at 100°C . The density of the sample was determined to be 908 kg m^{-3} by the Archimedes method. Its volumetric crystallinity was determined to be 66%, where the densities of the amorphous and crystalline regions were assumed to be $\rho_a = 854$ and $\rho_c = 936\text{ kg m}^{-3}$, respectively [20]. Test specimens for tensile tests were cut out of the sample sheet with a notch-shaped die (2 mm gauge length, 4 mm width in Figure 1).

The rheo-Raman spectroscopy apparatus is shown schematically in Figure 2. A custom-made tensile tester with a double-drawing mechanism was installed in the Raman spectroscopic apparatus, the details of which are reported elsewhere [10, 11]. Laser light from a DPSS laser (LASOS, Jena, Germany, 637.9 nm, 200 mW) was monochromated with a laser line filter, and irradiated into the notched portion of the specimen, with a spot size of 1 mm in diameter. The elongation speed was set to 1 mm/min, and the stretching temperature was 20°C . The scattered light was collected with a pair of convex lenses, where the excitation light was removed with a Raman long-pass filter. A charge-coupled device camera equipped with a monochromator (PIXIS100 and SpectraPro 2300i, Princeton Instruments, Trenton, USA, NJ) was used as the detector. For polarized Raman spectroscopy, a pair of wire-grid polarizers was inserted as the polarizer and

Figure 1. Schematic illustration of sample specimen

Figure 2. Schematic illustration of rheo-Raman spectroscopic apparatus

analyzer. The polarized spectra were collected in the zz , yz , and yy geometries and accumulated 10 times with an exposure time of 500 ms. It is noteworthy that the total exposure time of 5 s can be shortened up to ~ 1 s, with maintaining sufficient signal to noise ratio.

2.2. In situ Raman spectroscopy

Typical *in situ* polarized Raman spectra are shown in Figure 3. Assignments of the Raman bands of iPP are listed in Table 1 [13, 21]. The Raman spectra of undrawn specimens were independent of polarization, indicating that the molecular orientation was random. After elongation, the anti-symmetric (975 cm^{-1}) and symmetric (809 cm^{-1}) stretching modes were

Table 1. Vibrational and phase assignments for the Raman spectrum of iPP [13, 21]

Peak position [cm^{-1}]	Vibrational mode*	Phase	Raman tensor form
809	$\nu_s(\text{C-C}) + r(\text{CH}_2)$	Crystalline	A
830	$\nu(\text{C-C})$	Amorphous	A
840	$r(\text{CH}_2)$	Crystalline + Amorphous	A
975	$\nu_{as}(\text{C-C}) + r(\text{CH}_3)$	Crystalline	A

* ν : stretching vibration (as : anti-symmetric, s : symmetric), r : rocking vibration

strongly dependent on the polarization conditions, suggesting that highly oriented states were attained. The Raman spectra were fitted with a sum of Voigt functions using a nonlinear Levenberg-Marquardt method, and the areas for the two peaks were determined. The errors of the peak areas in the curve fitting were less than $\pm 2.0\%$ for the 809 cm^{-1} band, and $\pm 4.0\%$ for the 975 cm^{-1} band.

2.3. Orientation parameters

The orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ which represented the molecular orientation were defined as given by Equations (1) and (2):

$$\langle P_2 \rangle = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \quad (1)$$

$$\langle P_4 \rangle = \frac{35\langle \cos^4 \theta \rangle - 30\langle \cos^2 \theta \rangle + 3}{8} \quad (2)$$

where θ denotes the angle between the principal axis of the Raman tensor and the stretching axis. The orientation parameters were obtained from the intensities of the polarized Raman spectra as defined by Equations (3)–(6) [15, 19, 22–24]:

Figure 3. *In situ* polarized Raman spectra of iPP at (a) $\varepsilon = 0$ and (b) $\varepsilon = 8$. The polarization conditions are attached to each spectrum

$$I_{yy} = b \left(\frac{8a^2 + 4a + 3}{15} + 2\langle P_2 \rangle \frac{4a^2 - a - 3}{21} + 3\langle P_4 \rangle \frac{a^2 - 2a + 1}{21} \right) \quad (3)$$

$$I_{xx} = b \left(\frac{8a^2 + 4a + 3}{15} - 4\langle P_2 \rangle \frac{4a^2 - a - 3}{21} + 8\langle P_4 \rangle \frac{a^2 - 2a + 1}{35} \right) \quad (4)$$

$$I_{xy} = b \left(\frac{a^2 - 2a + 1}{15} + \langle P_2 \rangle \frac{a^2 - 2a + 1}{21} - 4\langle P_4 \rangle \frac{a^2 - 2a + 1}{35} \right) \quad (5)$$

with

$$\frac{I_{xy}}{I_{xx}} = \frac{a^2 - 2a + 1}{8a^2 + 4a + 3} \quad (6)$$

where I_{ij} denotes the integrated intensity for the i -polarized excitation and j -polarized scattered light. The terms a and b were associated with the principal elements of the Raman tensor [15, 22].

The crystalline chain of iPP has C_3 symmetry, because of its 3_1 helical conformation. Thus, the forms of the Raman tensor were classified mainly as type A or E [15]. Raman bands classified as type A can be used to calculate the orientation parameters [13, 22–24], so the Raman bands at 809 and 975 cm^{-1} were used. Both of these are classified as type A, and were sufficiently strong to calculate the orientation parameters.

2.4. Tilt-angle correction

The orientation parameters obtained by solving Equations (3)–(6) provided information on the orientation of the principal axis of the Raman tensor, but not on the orientation of the molecular chain axis. Given that 3_1 helical chains were formed in the crystalline phase of iPP, a correction for the tilt angle between the principal and molecular axes was required [13, 17, 19]. The l -th orientation parameters $\langle P_l^{\text{chain}} \rangle$ corrected for the tilt angle β can be written as shown in Equation (7) [13, 17]:

$$\langle P_l^{\text{chain}} \rangle = \frac{\langle P_l \rangle}{P_l(\cos \beta)} \quad (7)$$

where $P_l(x)$ is the l -th Legendre polynomial.

The values of the tilt-angle β of several Raman bands of iPP had been determined by using the results of the WAXD experiments [13]. They had successfully estimated the value of $\langle P_2^{\text{chain}} \rangle$ for drawn specimens of iPP for the Raman band at 998 cm^{-1} , though they had failed to use the Raman band at 810 and 1221 cm^{-1} [13]. To determine the value of β solely from the Raman spectra in a self-consistent manner, we assumed that the molecular orientation at high extension-

al ratio was described by an ideal uniaxial orientation around the stretching direction; $\langle P_4^{\text{chain}} \rangle$ and $P_4(\cos \beta)$ were assumed to be replaced by their entropically favorable values $\langle P_4^{\text{chain}} \rangle_{\text{mp}}$ and $P_{4,\text{mp}}(\cos \beta)$, respectively [11, 24]. In fact, the values of $\langle P_4^{\text{chain}} \rangle$ at high extensional ratios are very close to that of $\langle P_4^{\text{chain}} \rangle_{\text{mp}}$ for HDPE [11, 24], iPP [13], and poly(ethylene terephthalate) [24]. Then, at high extensional rates, Equation (7) for $l = 2$ and 4 can be written as Equations (8) and (9):

$$\langle P_2^{\text{chain}} \rangle = \frac{\langle P_2 \rangle}{P_2(\cos \beta)} \quad (8)$$

$$\langle P_4^{\text{chain}} \rangle = \frac{\langle P_4 \rangle}{P_{4,\text{mp}}(\cos \beta)} \quad (9)$$

respectively. The most-probable values $\langle P_4 \rangle_{\text{mp}}$ were determined to maximize the information entropy, and approximately written as the polynomials of $\langle P_2 \rangle$ as Equations (10) and (11) [24, 25]:

$$\langle P_4 \rangle_{\text{mp}} = -0.083\langle P_2 \rangle + 1.366\langle P_2 \rangle^2 - 1.899\langle P_2 \rangle^3 + 1.616\langle P_2 \rangle^4 \quad (10)$$

for positive $\langle P_2 \rangle$ values, and

$$\langle P_4 \rangle_{\text{mp}} = -0.052\langle P_2 \rangle + 1.574\langle P_2 \rangle^2 + 3.968\langle P_2 \rangle^3 + 8.058\langle P_2 \rangle^4 \quad (11)$$

for negative $\langle P_2 \rangle$ values. By combining Equations (8)–(11), the tilt angle β was estimated from the experimental $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at high extensional ratios. Thus, Equation (7) with the obtained value of β gives the tilt-angle correction for the orientation parameters. It is noteworthy that the present method provides the corrected orientation parameters from a set of polarized Raman spectra of specimens under stretching with no auxiliary experiments.

2.5. Orientation distribution function (ODF)

The ODF $N(\theta)$ which represented the angular distribution of the molecular orientation was defined as by Equation (12) [15, 25]:

$$N(\theta) = \sum_{l=0}^{\infty} \left(\frac{2l+1}{2} \right) \langle P_l^{\text{chain}} \rangle P_l(\cos \theta) \quad (12)$$

Although the polarized Raman spectrum gives only two orientation parameters ($\langle P_2^{\text{chain}} \rangle$ and $\langle P_4^{\text{chain}} \rangle$), the orientation parameters at higher ranks can also be determined by maximizing the information entropy [13, 25]. The most probable orientation distribution function was described as by Equation (13) [13, 25]:

$$N(\theta) = \frac{\exp[\lambda_2 P_2(\cos \theta) + \lambda_4 P_4(\cos \theta)]}{\int_0^\pi \sin \theta d\theta \exp[\lambda_2 P_2(\cos \theta) + \lambda_4 P_4(\cos \theta)]} \quad (13)$$

where the Lagrange multipliers λ_2 and λ_4 are determined to satisfy the following two constraints, described by Equations (14) and (15) for the experimental values of $\langle P_2^{\text{chain}} \rangle$ and $\langle P_4^{\text{chain}} \rangle$:

$$\langle P_2^{\text{chain}} \rangle = \int_0^\pi \sin \theta d\theta P_2(\cos \theta) N(\theta) \quad (14)$$

$$\langle P_4^{\text{chain}} \rangle = \int_0^\pi \sin \theta d\theta P_4(\cos \theta) N(\theta) \quad (15)$$

3. Results and discussion

Figure 4 shows the strain dependences of the orientation parameters for the principal axis of the Raman tensors of the symmetric and anti-symmetric C–C stretching modes. While the orientation parameters show similar strain dependence, the values for the 809 cm^{-1} band are substantially smaller than those for the 975 cm^{-1} band.

Table 2. Tilt angle β calculated from Raman spectroscopy and WAXD data [13]

Raman band [cm^{-1}]	β (Raman)	β (WAXD)
809	29.2	~28.0
975	16.0	16.6

In Table 2, the tilt angles β obtained by the tilt-angle correction with Equations (8) and (9) are compared with those previously determined by WAXD [13]. These values agree well with each other, suggesting that the present analysis can be safely applied for the tilt-angle correction of iPP.

In Figure 5, the orientation parameters for the molecular chain are obtained with the tilt-angle correction with Equation (7). The values of $\langle P_2^{\text{chain}} \rangle$ and $\langle P_4^{\text{chain}} \rangle$ for the Raman band at 809 cm^{-1} agree well with those for the 975 cm^{-1} band. This suggests that the apparent difference in the orientation parameters in Figure 4 is caused by the tilt angle. The slight difference in the orientation parameters between these two bands seems to result from uncertainty in the curve fitting. This is because fitting of the 809 cm^{-1} band is slightly affected by a nearby weak broad peak of the amorphous phase [9]. The consistency of the orientation parameters and the close agreement of tilt angles demonstrate that the present tilt angle correction gives $\langle P_2^{\text{chain}} \rangle$ and $\langle P_4^{\text{chain}} \rangle$ solely from a set of rheo-Raman spectra in a self-consistent method. In the elastic region, $\langle P_2^{\text{chain}} \rangle$ remains almost zero, indicating that the orientation of the crystalline chain remains random. While the macroscopic stress loaded

Figure 4. Stress–strain curves and strain dependences of the orientation parameters for the principal axis of the Raman tensor of the Raman bands at (a) 809 and (b) 975 cm^{-1}

Figure 5. Stress–strain curves and strain dependences of the orientation parameters for the molecular chain axis calculated from the Raman bands at (a) 809 and (b) 975 cm^{-1}

on the specimen sharply increases with increasing strain, no orientational change is observed for the crystalline chains. This suggests that microscopic deformation takes place only in the amorphous phase. The amorphous phase in spherulites is reportedly mainly deformed in the elastic region [26, 27]. Recent *in situ* micro-SAXS measurements indicate that the thickness of the amorphous layers in spherulites is drastically changed; thickening and thinning of the amorphous layers in the polar and equatorial zones, respectively [28]. The inhomogeneous changes in the amorphous phase in spherulites have been assigned as the dominant mechanism during elastic deformation. $\langle P_2^{\text{chain}} \rangle$ begins to increase after the first yield point (the maximum point of stress at around a strain of 0.5), and then sharply increases after the yielding region. This behavior of $\langle P_2^{\text{chain}} \rangle$ indicates that the crystalline chains are oriented toward the stretching direction after yielding. In the strain-hardening region, $\langle P_2^{\text{chain}} \rangle$ reaches an asymptotic value of ~ 0.8 . The strain dependence of $\langle P_2^{\text{chain}} \rangle$ under uniaxial stretching is in good agreement with previous results from *in situ* IR spectroscopy studies, [7, 29] and Raman spectroscopy results of drawn samples [9, 13]. While the values of $\langle P_4^{\text{chain}} \rangle$ remain constant in the elastic region, $\langle P_4^{\text{chain}} \rangle$ decreases with increasing strain and exhibits a minimum in the yielding region. This behavior of $\langle P_4^{\text{chain}} \rangle$ during yielding has also been observed for HDPE. [10, 11] After the yielding region, $\langle P_4^{\text{chain}} \rangle$ shows similar strain dependence with that of $\langle P_2^{\text{chain}} \rangle$. The values of $\langle P_4^{\text{chain}} \rangle$ at high

extensional ratios are also consistent with those of highly drawn iPP films and fibers [13, 30].

Figure 6 shows the ODF values calculated from the orientation parameters for the 975 cm^{-1} band. In the elastic region, the ODF is constant irrespective of the polar angle, indicating that the crystalline chain has a random orientation. In the yielding region, where $\langle P_4^{\text{chain}} \rangle$ shows a minimum, the ODF shows a broad peak at an intermediate angle of $\theta = 30\text{--}70^\circ$ from the stretching direction. This orientational behavior during yielding has also been observed for HDPE [10, 11, 5]. It has been interpreted as the orientation of crystalline chains being hindered by rigid and bulky stacked lamellae (lamellar cluster units) [10, 11, 5]. The interpretation of lamellar cluster units appears to also be valid for iPP, because these units have also been observed in iPP [31]. The peak of the ODF at

Figure 6. Orientation distribution functions of iPP at various strains

Figure 7. Schematic illustration of reorientation of the lamellar cluster units in the yielding region

30–70° for iPP in the yielding region is slightly shaper than that for HDPE, which may be explained by the size of their lamellar clusters (61 nm for iPP, 40 nm for HDPE) [11, 31, 32]. Reorientation of the lamellar cluster units is considered to be the dominant mechanism of molecular orientation in the yielding region, and the orientation of the crystalline chains toward the stretching direction is suppressed because one lamellar cluster units is surrounded by other cluster units as shown in Figure 7 [33]. Therefore, the reorientation of larger units for iPP is likely to be more hindered.

In the strain-hardening region, each ODF has a prominent peak at the stretching direction, and the ODF values above $\theta = 60^\circ$ are practically zero. These observations indicate that the crystalline chains are oriented towards the stretching direction. The unimodal distribution around the stretching direction is consistent with those of drawn iPP films and rod samples determined from WAXD experiments [34, 35].

4. Conclusions

The molecular orientation of the crystalline chains of iPP under uniaxial deformation was investigated by rheo-Raman spectroscopy. A new method of tilt-angle correction between the molecular chain axis and principal axis of the Raman tensor was proposed, and the real-time monitoring of the molecular orientation of iPP under stretching was performed. By using this method, the orientation parameters of the crystalline chain were calculated from the symmetric C–C stretching mode at 809 cm^{-1} , as well as the anti-symmetric C–C stretching mode at 975 cm^{-1} . The molecular orientation of the crystalline chains started after the first yield point, and proceeded rapidly in the yielding region. The ODF exhibited a broad peak in the yielding region, suggesting that molecular orien-

tation was suppressed. This was attributed to the re-orientation of bulky rigid lamellar cluster units being hindered by their large exclude volume. The assumption of entropically-favorable orientations for highly-stretched specimens seems to be valid in many polymeric systems. Thus, rheo-Raman spectroscopy combined with the present tilt-angle correction can be widely utilized to elucidate orientational behavior at the molecular level. This methodology is currently being applied to other semi-crystalline polymers in our laboratory.

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