Structural study of the ordering processes of cold drawn trans-1,4-polyisoprene samples in the heating process on the basis of wide- and small-angle X-ray scattering measurements

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Abstract. The regularization processes of the TPI glasses drawn at the various low temperatures were investigated by performing the temperature-dependent simultaneous measurements of the 2-dimensional wide-angle and small-angle X-ray scattering patterns. The glassy sample drawn below the cold crystallization temperature but above the glass transition temperature (-70°C) showed the disordered \(\beta\) form, which was found to transform to the regular \(\beta\) form at around -30°C. On the contrary, when we decreased the stretching temperature furthermore; for example -60 and -70°C, it gave the disordered \(\alpha\) form. This disordered form transforms to the regular \(\alpha\) form by heating to around 30°C. The small-angle X-ray scattering patterns were found to change in parallel with the wide-angle X-ray diffraction pattern changes, revealing a correlation between the crystalline phase transition and higher-order structure change in these regularization processes. These paracrystalline are packed in the smaller crystal cell than the regular form.

1. Introduction

Strain- or stress-induced crystallization phenomenon of some polymers has been reported in several papers, for example; polyethylene [1], natural rubber or cis-1,4-polyisoprene [2], isotactic polypropylene [3, 4], syndiotactic polypropylene [5, 6], polyethylene terephthalate (PET) [7, 8], poly(L-lactic acid) (PLLA) [9, 10], and so on. This method is quite important to study the strain effect during the crystallization process. In a lucky case, we may observe the existence of mesomorphic phase or mesophase before the appearance of crystalline phase. However, in some polymers, the mesophase was easier traced by rapid quenching over the large temperature intervals followed by applying some strain near the glass temperature point \((T_g)\) than near the melting point \((T_m)\) at high temperature. For example, in the case of PET and PLLA, nodular structure was reported as a mesophase, which is essentially amorphous with some degree of chain orientation order, by cold drawn of glassy sample above \(T_g\) [7 - 10]. Furthermore, this mesophase transforms to crystalline phase. In many cases, the crystalline phase, which formed at lower temperature, has some disordered of orientation (paracrystalline phase).

In the present paper, we will report the structural regularization of cold drawn sample of trans-1,4-polyisoprene (TPI) on the heating process. High molecular weight of TPI, well known as Gutta percha, exhibits properties that are attractive for various application fields such as root canal system, splint,

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golf ball covers, and so on according to its mechanical and physical properties [11 - 18]. Since the discoveries of TPI content in *Eucommia ulmoides* Oliv. (Tochuu cha tea) trees, this polymer becomes one of the best candidates for supporting the green plastic industry by applying this polymer in the wider application fields [19-22]. In order to do so, we have to collect all of the basic information about the crystal structure study, the structure formation process and its related physical and mechanical properties [23 - 33]. In the bulk sample, TPI shows two crystal modification; α and β forms [23,24]. According to these two forms, series number of papers have been reported which related to our research theme to clarify the not-yet-solved structure-property relationship of this polymer through the crystal structure analysis and microscopically-viewed crystallization behaviour including phase transition mechanism of these structures [34-36].

Figure 1 shows the summary of our study in the crystallization process of the α and β forms formation [34-36]. As we see from figure 1, the melt-quenched sample crystallizes into the β form with no orientation at such a low temperature of -50°C [35]. The orientation of β form is easily performed by drawing the unoriented β sample below 40°C, before the phase transition occurred. On the other hand, when the melt-quenched sample is stretched at about -70°C near *Tg*, similar X-ray pattern of α form was observed. By heating up, it changes to the high temperature phase of α form with higher crystallinity [34]. When the X-ray diffraction patterns are compared carefully between low temperature phase and high temperature phase of α form, they are found to be different from each other. In this way the structure regularization process is quite complicated. It is needed to clarify these structural changes in detail. In the present paper the temperature dependent measurements of WAXD and SAXS were performed in the TPI samples stretched at the various low temperatures to investigate the complicated structural evolution process. However, for the TPI case, it was no report about the structural regularization in the cold drawn sample at low temperature. It was unclear whether the structural regularization of strain induced crystallization grows via a mesophase or not.

![Figure 1. Schematic diagram of the formation process of the TPI α and β forms [34 - 36].](image)

2. Experimental

2.1 Sample Preparation

Synthetic TPI sample with 99% trans content was purchased from Polyscience Inc. As described in previous paper, the glassy sample was prepared by quenching the melt into liquid N₂ temperature (-196°C) [34]. The three different temperatures were chosen for stretching the glassy sample near *Tg*;
-55°C (above $T_g$), -60°C, and -70°C (at $T_g$). The stretching was carried out in the cooling bath of the mixture of liquid N₂ and methanol. The stretching temperature was monitored by inserting a thermocouple into the cooling bath with temperature fluctuation of about 3°C. The thus-stretched sample was mounted on a goniometer head, during which the sample temperature was kept constantly by blowing the cooled nitrogen gas directly to the sample [37, 38].

2.2 WAXD and SAXS Measurements

The 2-dimensional WAXD patterns of cold-drawn samples were measured using a Rigaku RAPID-II X-ray diffractometer in the heating process. A cylindrical imaging plate of 127.4 mm radius was used as a 2-D detector and an incident X-ray beam was graphite-monochromatized Mo-Kα line ($\lambda = 0.7107$ Å).

The simultaneous measurements of 2-dimensional SAXS and WAXD patterns were performed using a Rigaku Nanoviewer X-ray diffractometer, where the WAXD pattern was detected using an flat imaging plate set at 97 mm from the sample position and the SAXS pattern was detected using a Pilatus 100k detector (Dectris, Switzerland) set at 761 mm distance from the sample [37, 38]. The temperature of the sample was monitored by inserting a thermocouple into a sample.

The 00l reflections profile of the cold-drawn samples were measured in the heating process using a Rigaku RINT-TTR III diffractometer in a transmission mode. An incident X-ray beam was a graphite-monochromatized Mo-Kα ($\lambda = 0.717$ Å) in the diffraction angle (2θ) range of 5° - 60° with the 1-D scintillation counter.

2.3 SAXS Data Analysis

The 2D-SAXS data were analyzed by transforming to the 1D-SAXS profiles by the circular integration an function of scattering vector $q$, where $q = (4\pi/\lambda) \sin \theta$ and 2θ is a scattering angle. The correlation function for the stacked lamellar structure $K(z)$ was calculated using eq 1 [39].

$$K(z) = \left\langle \eta(z') - \langle \eta \rangle \right\rangle \left\langle \eta(z + z') - \langle \eta \rangle \right\rangle = 2 \int_0^{\infty} (\pi)^{-1} q^2 I(q) \cos(qz) dq$$

where $\eta(z)$ is an electron density at a position z along the direction normal to the stacked lamellar planes and $<\eta>$ is the ensemble average. The various points on the $K(z)$ curve give the various structural parameters: an invariant $Q$, a mean lamellar thickness $<d>$, a mean transition zone thickness $d_{tr}$, a mean core thickness $d_{o}$, and a long period $LP$ [39].

3. Results and Discussion

3.1. Stretching temperature above $T_g$ (-55°C)

According to figure 1, as we pointed above, that $\beta$ form starts to crystallize at -50°C. Therefore, we choose stretching temperature at -55°C. When the glassy sample was stretched at -55°C, the X-ray pattern was that of the $\beta$ form as shown in figure 2a. The 1D-profile of the WAXD pattern is shown in figure 2b. However, the diffuse scattering of layer line was observed in the WAXD pattern. By annealing above -30°C, the diffuse scatterings became more spot like. As described in previous work [36], the $\beta$-to-$\alpha$ form occurs at around 50°C via the intermediate phase. From the SAXS pattern, the lamella of $\beta$ form stood vertically along the draw axis. The scattering profiles were calculated from the 2-D SAXS patterns in figure 2a and are given in figure 3a. The SAXS pattern was of the meridional 2-points pattern, which increased in intensity steeply above 40°C, where the $\alpha$ form started to appear.
Figure 2. (a) The 2D WAXD and SAXS pattern of the oriented sample of TPI stretched at -55°C during heating, (b) The 1D-WAXD diffraction profiles of the oriented sample of TPI stretched at -55°C during heating process.

Figure 3. (a) The 1D SAXD profile of the oriented TPI sample stretched at -55°C above T_g in the heating process (refered to figure 2a). (b) Temperature effect to lattice cell of the oriented β sample of TPI stretched at -55°C (referred to figure 2b).

The unit cell parameters of the β form were estimated and plotted against temperature in figure 3b. Within the temperature region I, the parameters were almost constant. When temperatures reach at around -30°C, the b-axial length started to increase and the a-axial length decreased at the same time. These behaviours indicate that the β form in the region I is different from the β form in the region II. Let us call them the disorder β (low temperature) and regular β (high temperature), respectively. These two kinds of the β form take essentially the same chain conformation judging from the c-axial length. But, these chains are packed in a little more compacted manner in the regular β form as known from the cross-sectional area (a × b).

Figure 4 shows the temperature dependence of the 00l reflection profile measured in the transmission mode. The 002 reflection intensity of disordered β form increased and became sharper in the regular β form. According to the space group of the β form, P2_12_12_1-D_2^4, only the 00l reflections with l = even should be detected [40]. However, in the low-temperature phase of β form, the 001 reflection was observed, indicating the disorder in chain conformation from the regular 2_1 screw symmetry. The 001 reflection disappeared above 0°C and the disordered chain conformation was regularized there.

Figure 5 shows the intensity changes of the SAXS and WAXD data. In the region I (< -30°C) the β form was in the disordered state. By heating to the region II, the amorphous phase decreased and the 002 reflection of the β form increased in intensity in the region II. In this region the intensity of 120
reflection, the crystallinity (or $Q$), and long period gradually increased. In the region III the $\beta$-to-$\alpha$ transition occurred. The crystallinity (or $Q$) and long period significantly increased, where the transition to the $\alpha$ form was detected.

![Graph showing crystallinity and long period changes](image1)

**Figure 4.** The 00l profile of the oriented $\beta$ sample of TPI stretched at -55°C above $T_g$ in the heating process.

![Graph showing various parameters plotted as function of temperature](image2)

**Figure 5.** Various parameters plotted as function of temperature by calculating the correlation function from SAXS profiles and integrated intensity from WAXD profiles of the oriented TPI sample stretched at -55°C.

### 3.2. Stretching temperature at $T_g$ (-70 ~ -60°C)

The 2D-WAXD and SAXD patterns are shown in figures 6a and 6b, respectively, for the samples stretched at -70 and -60°C. The similar WAXD patterns were observed for these two, but the SAXS patterns were different. Four scattering pattern was observed for the -70°C sample while the -60°C
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sample gave the meridional two scattering pattern. The SAXS profiles obtained by an azimuthal angle scan are shown in figure 7.

![Figure 6](image)

**Figure 6.** (a) The 2D WAXD and SAXS pattern of the oriented sample of TPI stretched at -70°C during heating. (b) The 2D WAXD and SAXS pattern of the oriented sample of TPI stretched at -60°C during heating.

![Figure 7](image)

**Figure 7.** Azimuthally-scanned (β scan) of the oriented sample of TPI stretched at (a) -70°C and (b) -60°C during heating from -100°C to melting point.

The 2D-WAXD patterns given in figures 6a and 6b are those of the disorder α form as known from the diffuse layer lines and broader reflections. The β form content was negligible small. The 1D-profiles of WAXD pattern is shown in figure 8, where the data of the -70°C-stretched sample is given since the -60°C sample shows essentially the same behaviour about the WAXD pattern. By heating, the reflections became sharper and increased the intensity. On the first layer line, one broad reflection peak was split into two reflections (-111 and 111) at about 30°C, indicating the transformation to the regular α form. The lattice parameters were estimated for the disorder and regular α forms by assuming the similar crystal structure. The result is shown in figure 9a. In the temperature region of 40°C, the a- and b-axial lengths were detected to change, corresponding to the region where the layer line profiles became shaper.
The temperature dependence of the 00l reflection profile is shown in figure 9b, where the result of the -70°C-stretched sample is given as an example. The meridional reflections of the disorder α form passed were sharp up to 60°C. The intensities change of SAXS, WAXD, and 00l reflections is shown in figure 10. The meridional peak became weaker and broader in the temperature region of 65~70°C, where the equatorial line reflections were almost halo. This suggests the regular α form changes to the intermediate phase [34], before perfectly melted; that is, the phase consisting of the conformationally disordered chains but with the chain orientations kept still.

**Figure 8.** The 1D-WAXD diffraction profiles of the oriented sample of TPI stretched at -70°C during heating process.

**Figure 9.** (a) Temperature effect to lattice cell of the oriented α sample of TPI stretched at -70°C, (b) The 00l profile of the oriented α sample of TPI stretched at -70°C in the heating process.

Figure 11 shows the comparison of crystallite size ($D_{hk0}$) perpendicular to the 110 plane and lamellae thickness ($<d>$) during annealing. In the first stage, 7 monomeric units are included in the α’ form lamella along the fiber axis. After the phase transition occurs, around 14 monomeric units are included in the α form lamella which is twice than the disorder form. The crystallite size of along the $ab$ direction was also increased in 2 steps. When we viewed from this direction, the regular α form has three times bigger size than the disorder form. However when we compared to the crystallite size along the fiber axis toward the $ab$ direction, the α form has anisotropy of crystal size.
Figure 10. Various parameters plotted as function of temperature by calculating the correlation function from SAXS profiles and integrated intensity from WAXD profiles of the oriented TPI sample stretched at -70°C.

Figure 11. Crystallite size along the fiber axis and ab direction for the disorder-to-order transition of the α forms by stretching temperature at -70°C on the heating process.

4. Conclusion

In the present paper, the detailed information of the structural changes was investigated for the samples drawn at low temperatures by analyzing the temperature-dependent WAXD and SAXS. The stretching of the melt quenched sample at -55°C, which is below cold crystallization temperature but above Tg, gives the disorder β form. This disorder β form transforms to the regular β phase by heating to -30°C and to the α form at 40°C. On the contrary, when we decreased the stretching temperature of glassy sample; at -70°C and -60°C, these samples give the disordered α form which is regularized to the α form at 30°C. These two samples show the different lamellar stacking structure; tilted structure
in the -70°C-stretched sample and non-tilted structure in the -60°C sample. The SAXS pattern at the high temperature is that of the non-tilted lamellar structure. The disorder α form shows the diffuse scattering along the layer lines, indicating the disorder in the relative height between the neighbouring chains. In this way the cold-drawn TPI samples show a variety of transitions attendant with the disorder-to-order structural change. The lamellar tilting is also affected by this transition: the tilted structure is created when the sample is stretched near Tg, while the lamellae stand vertically in the sample drawn above Tg.

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