Studies on conformational changes of poly(trimethylene terephthalate) chains during uniaxially cold drawing using time-resolved polarized infrared analysis

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ABSTRACT

The conformational conversion between an extended and a helical conformation of PTT chains during uniaxially cold drawing with different draw rates at temperatures below and above glass transition temperature (T_g) was investigated by time-resolved polarized IR analysis. When the draw rate ($\dot{\gamma}$) is faster than the retraction rate ($1/\tau_b$) of chain segments, the drawing-induced extended conformation can be found. On the contrary, polymer chains can adjust to form a helical conformation. Besides, the conformation fraction, segmental orientation, inter-molecular interactions, relative mobility of the flexible and rigid segments of PTT chains and cold crystallization behavior were discussed in detail for clarifying the micro-structural changes during drawing process, and we found that the segmental orientation and the conformational changes occurred simultaneously when $T < T_g$, while the former arose prior to the latter when $T > T_g$.

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1. Introduction

Uniaxially cold drawing is a common processing to promote the micro-structural changes on polymers (e.g., conformational changes [1–6], orientation [7,8], crystallization [9,10], etc.) and involves in their polymer applications and great importance in the different grades [11–15]. Recent studies have exhibited two opposite experimental results on the conformational changes in uniaxially cold drawn polymers i.e. formation of an extended or a helical conformation. The drawn syndiotactic polypropylene (sPP) proceeded a gradual transition in chains conformation from *gauche-gauche-trans-trans* helical to all-*trans* planar conformation [1], and the higher-energy *trans* conformation of drawn isotactic polystyrene (iPS) was found to raise with increasing strain [2]. In contrast, the poly(L-lactic acid) (PLLA) showed a development of 3_1 helical conformation during drawing [3], and the increment of crystalline *gauche* of drawn poly(trimethylene terephthalate) (PTT) with increasing draw ratio was investigated [4,5]. On the other hand, the promotion and suppression of helical chains for isotactic polypropylene (iPP) were discussed at various draw ratios and temperatures [6]. However, the relationship between the

conformational conversion and the drawing conditions for polymers is still unsolved problem. To make further progress, a detail information on the micro-structural changes of polymer chains during cold drawing is indispensable.

Besides, uniaxially drawn polymers is generally considered to be accelerated its crystallization rate by acquiring the drawing-induced intra- and inter-molecular orderings [11–13], which are achieved by the formation of crystalline conformation (e.g., extended conformation) and mesophase (e.g., parallel orientated and disorder aggregated segments), respectively. Since the helical chains may be pulled to form a more extended conformation during drawing before crystallization, we were also wondering that the drawing-induced structural changes (e.g., conformational changes, segmental orientation, etc.) might be possible to accelerate or decay the crystallization rate for polymers with helical crystalline conformation in various cases.

Fourier transform infrared spectroscopy (FTIR) is a valuable and sensitive tool to measure the characteristic micro-structural changes. The absorbance and full width at the half-height (FWHH) of IR bands were used to evaluate the conformation fraction [4–7] and relative molecular mobility [16,17], while the position shift of IR bands was considered to be correlated with the formation of intra- or inter-molecular interactions [17,18]. The segmental orientation can be observed from the dichroic IR spectra

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[19—21]. The micro-structural changes during crystallization [17,22], melting [23], glass transition [24], etc. have been monitored by the time-resolved IR measurement. For revealing the structural changes of polymer during cold drawing, the time-resolved polarized IR analysis was adopted to make a thorough inquiry on the sequential ordering of polymer chains at the molecular level.

In this work, the conformation fraction, segmental orientation, inter-molecular interactions, relative mobility of the flexible and rigid segments of PTT chains during uniaxially cold drawing and its cold crystallization behavior were investigated exhaustively by time-resolved polarized IR analysis for the first time. The sequence of the conformational changes and the segmental orientation during drawing was also revealed. Specially, the conformation conversion between an extended and a helical conformation of PTT chains was clarified by the relationship among the draw rate, drawing temperature and chain dynamics.

2. Experimental methods

2.1. Materials

Poly(trimethylene terephthalate) (PTT) ($T_g \approx 45$ °C and $T_m^0 = 252$ °C [25]) pellets of specific gravity 1.34 and intrinsic viscosity 0.92 dL/g (60/40 phenol/tetrachloroethane, 160 °C) were kindly supplied by Shell Chemical. Quenched amorphous (QA) specimens were prepared by melt-pressing at 270 °C for 5 min before quenching into ice water [26,27]. The prepared PTT films with a thickness of 30 μm were cut into dog-bone shape with dimensions of 3×1 cm^2 for cold drawing under draw rates ($\dot{\gamma}$) of 6.6×10^{-3} and 0.13 s^{-1} at 30, 45 and 50 °C using Linkam TST350 hot stage. The draw ratio (DR) was estimated by taking the ratio between the marked final and the initial length. In this study, we neglected the necking effect of cold drawn specimens since the necking was very inconspicuous during cold drawing.

2.2. Fourier transform infrared spectroscopy

The infrared (IR) spectra were measured at a resolution of 1 cm^{-1} by a Nicolet 8700 FT-IR Spectrometer (Thermo Fisher Scientific Inc.) equipped with MCT detector. Polarized IR spectra were measured by using a rotation-controllable ZnSe polarizer. In this study, the parallel and perpendicular spectra were measured independently. The polarizer was fixed during single cold drawing process. All of the unpolarized and polarized experiments were carried out more than three times for confirming the reproducibility. The 1408 cm^{-1} band was used as an internal reference band for drawn spectra to calibrate the absorbance decrement by the drawing-induced thickness reduction [4,20,21]. The absorbance (A), position (V) and full width at the half-height (FWHH) of IR bands were analyzed using the Peak Resolve by OMNIC™ Series Software. The Harmen's orientation function, $P_2 \cos\theta$, for the molecular long axis (c-axis) was characterized using the following equation [28—30]:

$$P_2\langle cos\theta \rangle = \left(\frac{R-1}{R+2}\right)\left(\frac{2}{3cos^2\beta - 1}\right) \tag{1}$$

where θ is the orientation angle of c-axis distributed around the drawing direction (z), and β is the angle between the transition moment (M) and the c-axis, as shown in Fig. 1. The dichroic ratio, $R = A_{//} / A_{\perp}$, is obtained from the ratio of absorbance with the electric vector parallel and perpendicular to the drawing direction. The β is generally considered as a fixed value [28—30]. For obtaining β, the absorbance of characteristic IR bands, $A(\alpha)$, versus the polarization angle (α) of the incident radiation was measured. The
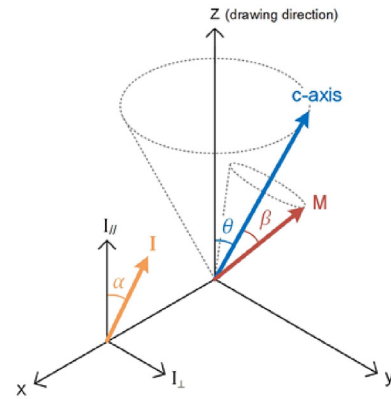

Fig. 1. Geometric representation for the nested axially symmetric distributions of the molecular long axis (c-axis) about the drawing direction (z). The transition moment (M) is distributed around the c-axis. The polarized direction (I) of the incoming IR beam at 0° and 90° polarizer settings is marked as $I_{//}$ and $I_{\perp}$, respectively.

normalized absorbance, $A_n(\alpha)$, was defined as:

$$A_n(\alpha) = \frac{A(\alpha) - A_{\min}(\alpha)}{A_{\max}(\alpha) - A_{\min}(\alpha)} \tag{2}$$

where $A_{\min}$ and $A_{\max}$ are the minimum and maximum of $A(\alpha)$. With perfect molecular alignment in the drawing direction, $A_{//} / A_{\perp} = cot^2\beta$. When $cot^2\beta = 0.5$ ($\beta = 54.7°$), the system is a perfectly isotropic state since $A_{//} = A_{\perp}$. Therefore, the $A_n(\alpha)$ for $\beta < 54.7°$ was suggested as [33]:

$$A_n(\alpha) = \frac{1 + (1/A_{\perp})\ln\left[e^{-2A_{\perp}cot^2\beta}cos^2(\alpha - \theta) + e^{-A_{\perp}}sin^2(\alpha - \theta)\right]}{1 - cot^2\beta} \tag{3}$$

and for $\beta > 54.7°$:

$$A_n(\alpha) = \frac{2cot^2\beta + (1/A_{\perp})\ln\left[e^{-2A_{\perp}cot^2\beta}cos^2(\alpha - \theta) + e^{-A_{\perp}}sin^2(\alpha - \theta)\right]}{2cot^2\beta - 1} \tag{4}$$

A curve fitting procedure by a least squares method was applied for obtaining the β and θ of characteristic IR bands.

3. Results and discussion

3.1. Conformational changes and segmental orientation of cold drawn PTT film

The IR spectra of undrawn (DR = 1) and cold drawn (DR = 4) PTT films with $\dot{\gamma} = 6.6 \times 10^{-3}$ s^{-1} at 30 °C in the wavenumber range of 960—800 cm^{-1} were shown in Fig. 2a. The cold crystallized (CC) spectra were acquired from separately isothermal treating the DR = 1 and DR = 4 quenched amorphous (QA) PTT films at 50 °C for 6 h. The flexible and rigid segments of PTT chains were sorted by characteristic IR bands. For QA spectra, the bands at 933 and 818 cm^{-1}, which were assigned to the CH$_2$ rocking mode of gauche and trans conformer of the inner two C—C bonds of trimethylene glycol unit of PTT chains [4,19,31,32], showed absorbance decreasing and increasing after cold drawn, respectively. The relative gauche fraction, $G(t)$, of DR = 1 and DR = 4 QA specimens were estimated by previous assumption [4,26]: $G(t) = A_{933}/(A_{933} + 4.9A_{818})$, as 29% and 20%. It indicates that part of chain conformation changed from gauche to trans for stretched sample.