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Strain-Induced Enthalpy Relaxation in Poly(lactic acid)

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Introduction. Annealing of amorphous polymers below the glass transition temperature (T_g), i.e., sub-T_g annealing, induces a decrease in enthalpy, which is called enthalpy relaxation. The decreased enthalpy is recovered as an endotherm in the glass transition region on reheating to above T_g. Since the first observation of the endothermic enthalpy recovery,[1] the relaxation behavior of a lot of polymers has been investigated by measuring the recovered enthalpy.[2−6]

Poly(lactic acid) (PLA) is well-known as an eco-friendly and biodegradable polymer, produced from renewable biomass such as corn and sugar beet. There has been several studies[7−10] on enthalpy relaxation behavior in PLA, mostly focused on the changes of enthalpy, glass transition behavior, and mechanical properties during the annealing process. Meanwhile, many literatures show an endotherm in the glass transition region on the differential scanning calorimetry (DSC) heating curves for PLA fibers and oriented films.[11−14] This endotherm shown in deformed PLA has also been considered to be attributed to the annealing effect below T_g during the fabrication process or storage and has drawn little attention. Solarski et al.[15] just mentioned that the endothermic peak can be caused by chain relaxation from a nonstable conformation frozen in at the glassy state to a more stable conformation.

On drawing the amorphous polymers, the chain conformations change to the statistically unfavorable states, resulting in a decrease in entropy. On the other hand, the enthalpy change due to stretching is usually positive, even small in magnitude.[16] It is reported that drawn atactic polystyrene exhibits an exotherm just above T_g on reheating, which simultaneously undergoes shrinkage.[17] Contrary to the polystyrene case, we expect that stretching the amorphous PLA chains induces a decrease in enthalpy, which phenomenon is, for the first time, named as "strain-induced enthalpy relaxation" in this report. The endotherm in the glass transition region shown for deformed PLA in previous papers[11−14] may be a recovery of enthalpy decreased mainly by straining, not solely by annealing. Hence, in this study, the effect of uniaxial drawing on enthalpy relaxation in amorphous PLA was investigated by DSC. In addition, the conformational change with drawing was determined by the method using Raman spectroscopy, developed by Yang et al.[18] The origin of strain-induced enthalpy relaxation was discussed in terms of conformational distribution change caused by deformation. To our knowledge, this is the first report containing both the experimental evidence and the origin of strain-induced enthalpy relaxation.

Experimental Section. PLA pellets with 10% D-isomer content were supplied from NatureWorks LLC. The intrinsic viscosity of PLA sample was 1.3 dL/g in chloroform solution at 25 °C, which corresponds to the viscosity-average molecular weight of 4.3×10^4 g/mol. PLA films were prepared by compression-molding at 180 °C for 5 min and subsequently quenched into ice water. Before compression-molding, the pellets were dried at 80 °C in vacuum for at least 48 h. Drawing experiments were carried out on a universal testing machine (Instron series 4467) equipped with a temperature-controlled chamber. The films were stretched uniaxially at a strain rate of 0.033 s^{-1} with two draw ratios of 2 and 3 at 65 °C, just above T_g, to minimize plastic deformation. Subsequently, the drawn films were cooled to room temperature at a rate of 15 °C/min under constant length condition. The undrawn film was also heat-treated in the same process with drawn films. Before all measurements, all the films were stored in a refrigerator of −80 °C to avoid the sub-T_g annealing effect on enthalpy relaxation.

One undrawn film and two drawn ones were characterized through the following experiments. A calorimetric measurement was performed on a differential scanning calorimeter (DSC Q2000, TA Instruments) at various heating rates of 5, 10, 20, and 40 °C/min. Two-dimensional X-ray diffraction photographs were obtained using a DIP-2030 X-ray system (MAC Science Co.) with an imaging plate detector. Nickel-filtered Cu Kα radiation was generated at 45 kV and 90 mA. Polarized Raman spectra were recorded on a Raman microscope spectrometer (inVia Raman microscope, Renishaw plc), with a Nd:YAG laser as an excitation source. Two polarized spectra were taken by adjusting the polarization of incident radiation parallel and perpendicular to the drawing direction. Each spectrum was collecting 200 scans at a 4 cm^{-1} resolution. Film density was measured with a density gradient column using a mixture of *n*-hexane and CCl_4 at 25 °C.

To investigate the effect of dimensional constraint of a drawn PLA sample on enthalpy change appearing at glass transition region of DSC heating curve, PLA monofilament was produced by melt-extruding the pellets at 190 °C using a capillary rheometer (D8052B, Kayeness Inc.) with an orifice diameter of 0.75 mm, since a filament is more convenient to be endowed with the dimensional constraint than a film. DSC measurement for a drawn monofilament with draw ratio of 3, prepared by the same method as above drawn films, was carried out under two types of dimensional constraints. First, in order to restrain the longitudinal shrinkage of the drawn filament during DSC heating run, the filament was rolled up with a thin aluminum sheet, and then both ends were pressed. This aluminum cylinder containing the ends-fixed filament was loosely made to have empty space. Second, in addition to constraint of fixed ends, the filament was tightly rolled up with an aluminum sheet without empty space within cylinder, which is a more effective way to prevent dimensional change of a filament, i.e., longitudinal shrinkage accompanying lateral expansion.

Results and Discussion. DSC heating curves for PLA films are shown in Figure 1. While the undrawn film exhibits the representative shape of glass transition, the endothermic peak is clearly seen in the temperature region just above

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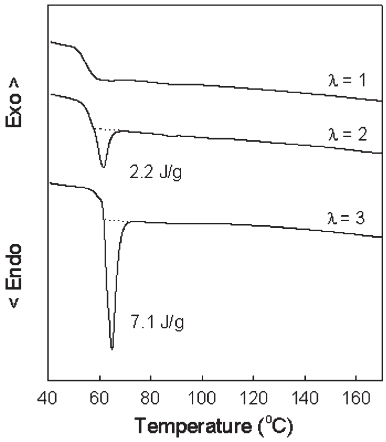

Figure 1. DSC heating curves for PLA films with various draw ratios (λ). Heating rate was 10 °C/min.

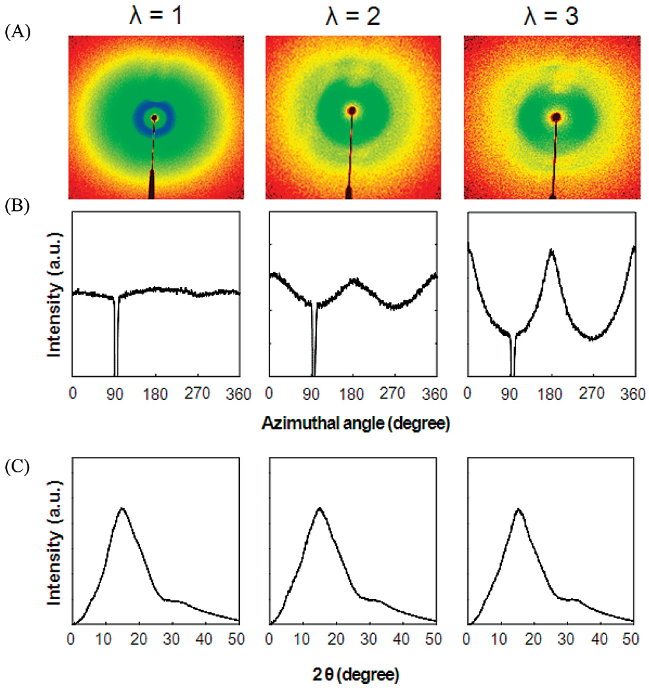

Figure 2. Two-dimensional X-ray photographs (A), azimuthal scans (B), and circularly averaged scattering patterns (C) for PLA films with various draw ratios (λ).

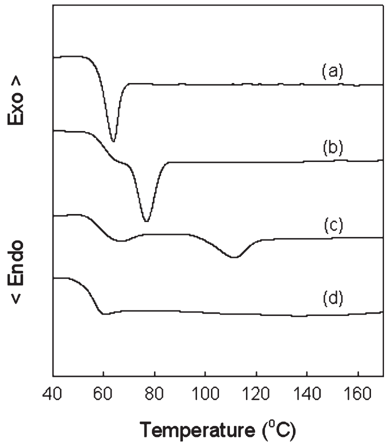

Figure 3. DSC heating curves for a drawn PLA monofilament (λ = 3) under various dimensional conditions: (a) free; (b) ends-fixed; (c) ends-fixed and tightly rolled-up; (d) ends-fixed and very tightly rolled-up. Heating rate was 10 °C/min.

glass transition for the drawn films and the peak area increases with the draw ratio (λ). This behavior looks same as the recovery of decreased enthalpy due to the sub-T_g annealing. However, it is obvious that this endotherm is caused by stretching the PLA film, not by annealing below T_g. All the films have no endothermic peak corresponding to the crystal melting (around 160 °C), which means that both undrawn and drawn films are totally amorphous. This is also confirmed from two-dimensional X-ray photographs (Figure 2A), which have no sharp diffraction rings and just show the arcing of the broad ring for the drawn films, indicating the chain orientation in the amorphous state. This result is supported by the azimuthal scans for the amorphous hallow scattering and the circularly averaged scattering patterns, as shown in parts B and C of Figure 2, respectively. It was found that the degree of chain orientation in amorphous state increases with the draw ratio (Figure 2B), although there appears no diffraction peaks due to strain-induced crystals (Figure 2C).

To obtain further information on the nature of this endothermic transition, DSC measurement was carried out on a drawn monofilament with draw ratio of 3 under two types of dimensional constraints, as shown in Figure 3. The endothermic peak for an ends-fixed filament (Figure 3b) moves to higher temperature apart from the glass transition and becomes broader than that for a filament free to shrink (Figure 3a). For a filament ends-fixed and tightly rolled up with aluminum sheet, both the peak temperature and the broadness depend strongly on how tightly to be rolled up a filament with aluminum sheet. Two typical data are presented in Figure 3c,d. A filament with severe dimensional constraint exhibits a very broad endotherm from about 90 °C, as seen in Figure 3d. This change of the endothermic peak with dimensional constraint suggests that the endotherm is directly associated with shrinkage and also rules out the possibility that the endotherm is melting of small crystal produced during the drawing process. Therefore, it is considered that the stretching of amorphous PLA chains induces a decrease in enthalpy, contrary to the fact that the enthalpy of stretched chains is higher than that of isotropically relaxed chains in some polymeric systems.[16,17] The decreased enthalpy is recovered as an endotherm, when a drawn sample shrinks.

Based on a rotational isomeric state approximation, a conformational energy map for PLA chain predicts four distinct energy minima, corresponding to four conformers: I(gg), I′(tg), III(gt), and III′(tt).[19] Although the energy values and populations of four conformers estimated in several studies[19−21] are divergent, it is in common that the III(gt) conformer is the lowest energy state and most dominant in amorphous phase. In addition, it is reported that the deformation of amorphous PLA films increases the population of the most favorable III(gt) conformer.[18] This result means that the conformational energy state of PLA chain is lowered by deformation, which may be a main origin of strain-induced enthalpy relaxation in PLA amorphous phase. In order to obtain the quantitative information about the content of the predominant III(gt) conformer for the undrawn and drawn films, we used, in this study, a Raman spectroscopic method developed by Yang et al.[18] In this method, just by measuring the intensity ratio (R) of the 1128 to 1044 cm^{-1} Raman bands, the

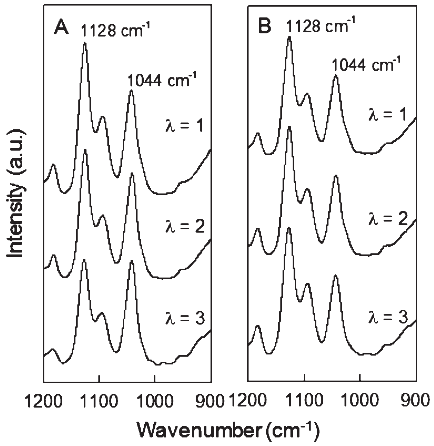

Figure 4. Parallel (A) and perpendicular (B) polarized Raman spectra for PLA films with various draw ratios (λ).

Table 1. Recovered Enthalpy (ΔH_r), the Mole Fraction of III(gt) Conformer (f_{gt}), the Conformational Energy Change (ΔE_{conf}), and Density for PLA Films with Various Draw Ratios (λ)

λ	ΔH_r (J/g)	f_{gt}	ΔE_{conf} (J/g)	density (g/cm^3)
1	0	0.69	0	1.258
2	2.2	0.73	2.7	1.252
3	7.1	0.79	6.7	1.250

content of III(gt) conformer can be calculated from the calibration line of R to f_{gt}

$$R = -1.3f_{gt} + 2.4 \tag{1}$$

where f_{gt} is the mole fraction of III(gt) conformer. Figure 4 shows the polarized Raman spectra of PLA films in the range of 1200−900 cm^{-1} at room temperature. In parallel polarized spectra, the intensity of the 1128 cm^{-1} band, relative to that of the 1044 cm^{-1} one, decreases with increasing the draw ratio, while the relative intensity of the 1128 cm^{-1} band in perpendicular polarized spectra slightly increases with the draw ratio. In order to average the Raman intensities dependent on polarization direction, assuming cylindrical symmetry for uniaxially drawn film, the isotropic intensity (I_{iso}) was obtained by the following equation

$$I_{iso} = (I_{\parallel} + 2I_{\perp})/3 \tag{2}$$

where $I_{\parallel}$ and $I_{\perp}$ are the intensities with the polarization of the incident beam parallel and perpendicular to the draw direction, respectively. The R values, calculated from the isotropic intensity ratios of 1128 to 1044 cm^{-1} band, were 1.50, 1.45, and 1.38 for the PLA films with draw ratios of 1, 2, and 3, respectively. The quantity f_{gt}, obtained from eq 1, increases with the draw ratio (Table 1), which is consistent with a previous report.[18] The increase in the content of III(gt) conformer, which also corresponds to the only conformer in the crystalline state, can be caused by both the chain stretching in amorphous phase and the strain-induced crystallization, and this Raman spectroscopic method is not able to discriminate III(gt) conformer in amorphous phase from the one in crystalline phase. Hence, in previous studies,[11,18] the content of III(gt) conformer in amorphous phase was calculated by subtracting the content in crystalline phase (eq 8 in ref 18 and eq 2 in ref 11), in which the degree of crystallinity was determined from the sum of cold crystallization and melting enthalpies on DSC heating curve. However, in the present experimental condition for PLA with 10% D-isomer content, there is no evidence indicating the existence of strain-induced crystallinity on both DSC and X-ray results. Therefore, it is valid to conclude that the increase of the quantity f_{gt} with the draw ratio in Table 1 stems from the conformational change in amorphous phase. In addition, the relaxed films were prepared by annealing the drawn films at 80 °C for 5 min and cooling into the glassy state to get the conformational information in the rubbery state after glass transition and enthalpy recovery. The relaxed films have almost same spectra with undrawn film, which represents that the conformational state returns to the undrawn state via shrinkage above T_g. Hence, the f_{gt} decrements of enthalpy recovery in two drawn films are calculated to be 0.04 and 0.10, respectively. Assuming that this excess content of III(gt) conformer in the glassy state caused by chain stretching turns into I(gg) conformer in the rubbery state, the conformational energy change (ΔE_{conf}) for the transition of enthalpy recovery can be calculated. This assumption is reasonable, recalling that the I(gg) conformer has the second lowest energy level, and the other two conformers I′(tg) and III′(tt) are energetically unfavorable and rare in population. In the calculation of ΔE_{conf} for two drawn films, the value of 1.148 kcal/mol is used as the energy difference between two conformers I(gg) and III(gt), determined by Yang et al.[20] As shown in Table 1, the values of recovered enthalpy (ΔH_r) measured by DSC are comparable to those of conformational energy change (ΔE_{conf}) calculated from the population change of conformers, which means that the recovered enthalpy mainly stems from the conformational distribution change due to the chain stretching. Besides the conformational energy change, the other factor to contribute the recovered enthalpy is $P\Delta V$ work, where P is pressure and ΔV is the specific volume difference between isotropic rubbery state and oriented glassy one. The values of $P\Delta V$ for two drawn films, estimated from the density values in Table 1, are in the order of ~10^{-4}, which is negligibly small.

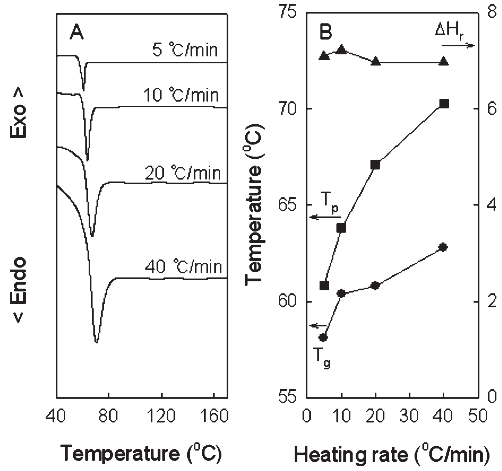

Figure 5. DSC heating curves with various heating rates (A) and the effect of heating rate on T_g, T_p, and recovered enthalpy (B) for a drawn PLA film (λ = 3).

The influence of heating rate on thermal data was investigated for a drawn PLA film (λ = 3), as shown Figure 5A. For the enthalpy relaxation by sub-T_g annealing, it is well-known that T_g shift to higher temperature at high heating rate leads to the enthalpy increase at rubbery state, resulting in the increase of recovered enthalpy.[6] On the other hand, in this study, the recovered enthalpy does not change with the heating rate, while the increase of heating rate brings about increases of both T_g and T_p, as can be seen in Figure 5B. Here, T_g and T_p were taken as onset temperature of glass transition and peak temperature of endotherm, respectively. Accepting that the recovered enthalpy originates from conformational energy change between isotropic rubbery state and oriented glassy one, the constancy of recovered enthalpy with the heating rate is reasonable because the conformational change in rubbery state is very small in the temperature range from 60 to 70 °C.[21]

In conclusion, we observed the endotherm concurrent with shrinkage just above the glass transition on DSC heating scan for drawn and amorphous PLA films, which is direct experimental evidence of the strain-induced enthalpy relaxation. It was also proved that the origin of strain-induced enthalpy relaxation is associated with an increase in population of the III(gt) conformer with the lowest energy level due to the chain stretching.

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