Supporting Information for

Dominant β-Form of Poly($_L$-lactic acid) Obtained Directly from Melt under Shear and Pressure Fields

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EXPERIMENTAL SECTION

Fourier Transform Infrared (FTIR) Spectroscopy. In order to verify the PLLA crystalline modifications of sample at various shear rates, FTIR measurements were performed by using Nicolet 6700 (Thermal Scientific, USA) in the transmission mode. The scanning range was from 4000 to 400 cm^{-1}, and a total of 64 scans were collected at a resolution of 0.5 cm^{-1}. All spectra were baseline corrected.

Rheo-Stress Measurements during Shear Pulse. Rheo-stress measurements were performed on a rotational rheometer (TAAR2000EX, TA Instruments, New Castle, DE). First, the PLLA sample was held at 200 °C for 5 min to erase any memory effects. Second, the sample was cooled to the crystallization temperature (T_c) of 140 °C rapidly. When T_c was reached, a desired shear flow was applied to the PLLA melt for a short shearing time. Third, the instrument recorded the variation of stress during the shear pulses.

Melt Rheological Properties. Rheological measurements were performed on a rotational rheometer (TAAR2000EX, TA Instruments, New Castle, DE) with a parallel plate geometry of 25 mm in diameter and a gap of 0.7 mm at 160 °C in a nitrogen atmosphere. Dynamic frequency sweep measurements were carried out in the linear viscoelastic regime from frequency of 100 to 0.01 Hz for PLLA melt.

RESULTS

The Existence of PLLA β-Form by FTIR

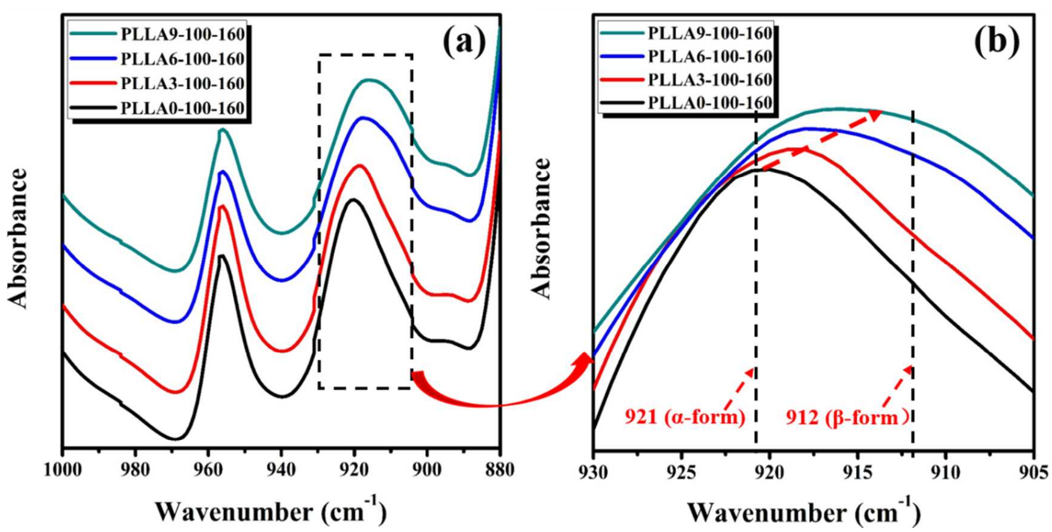

Figure S1. (a) IR spectra in the selected range 1000-880 cm^{-1} of sample PLLA-100-160 obtained at different radial positions (shear rates) as indicated. (b) Enlarged IR spectra in the range 930-905 cm^{-1} as the dotted rectangle shows in (a).

The PLLA crystal modifications were also characterized by IR spectroscopy. Cohn et al.[1] reported an absorption band at 921 cm^{-}1 characteristic of α crystal and Sawai et al.[2] concluded that the band at 912 cm^{-1} found in the β-form was assigned to the CH_3 rocking mode for β crystal. Figure S1 shows infrared spectra measured for a $\dot{\gamma}$ series of sample PLLA-100-160. The band at ca. 920 cm^{-1} deviated to lower frequency as the shear rate raised (Figure S1 (a)). Moreover, It is clearly that a new band at ca. 912 cm^{-1} was exhibited for PLLA9-100-160 compared to a band at 921 cm^{-1} for PLLA0-100-160, suggesting β crystal dominated at $\dot{\gamma}$ of 19.9 s^{-1} yet α crystal dominates at $\dot{\gamma}$ of 1.0 s^{-1} (Figure S1 (b)), which is in consistent with the results of WAXD.

Crystalline Structure of the Static Samples.

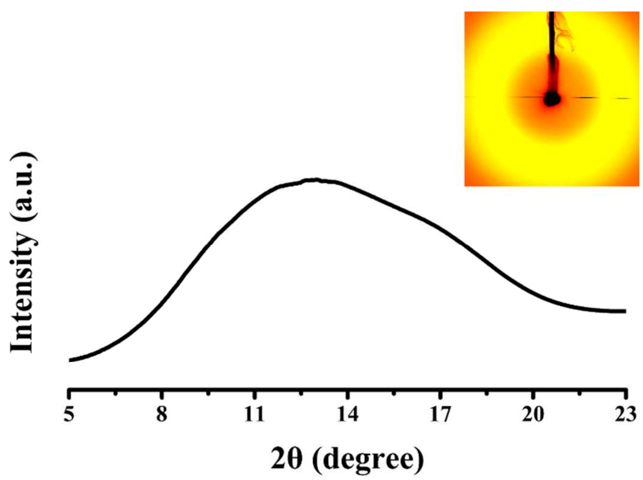

Figure S2. 1D-WAXD diffraction profile and related 2D-WAXD image of the sample quiescently crystallized under pressure of 100 MPa and temperature of 160 ºC (PLLA-100-160).

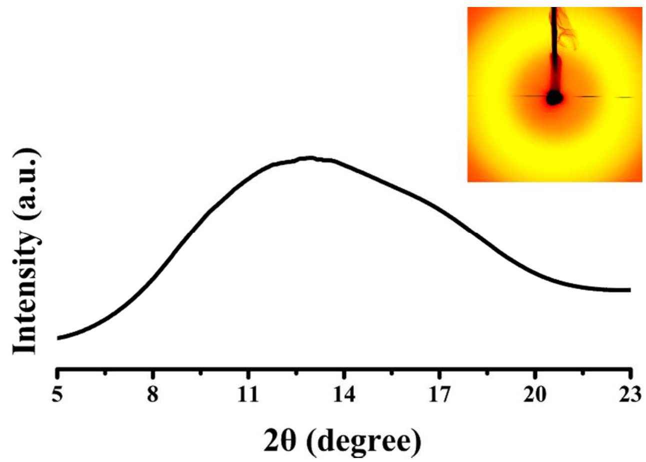

Figure S3. 1D-WAXD diffraction profile and related 2D-WAXD image of the sample quiescently crystallized under atmospheric pressure and temperature of 140 ºC (PLLA-0-140).

The 1D-WAXD diffraction profiles of samples PLLA-100-160 and PLLA-0-140 crystallized quiescently exhibited a unimodal curve, and related 2D-WAXD images illustrate amorphous diffraction signal. Therefore, it can be considered that these two samples are nearly amorphous and the contents of α- and β-form are ca. 0.

Rheo-Stress Measurements during Shear Pulse

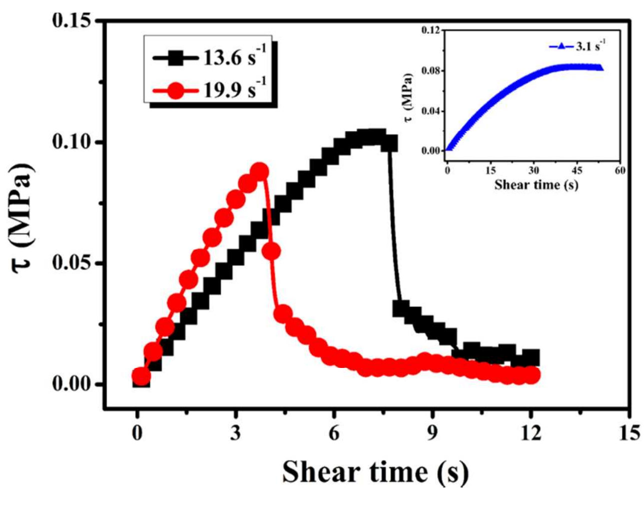

Figure S4. Stress response during steady shear. Data were measured at $\dot{\gamma}$ of 13.6 s^{-1} and 19.9 s^{-1} and 140 ºC, where shearing lasts 12 s. The inset was measured at $\dot{\gamma}$ of 3.1 s^{-1} and 140 ºC, where shearing lasts 53 s.

Dynamic Frequency Sweep Measurements

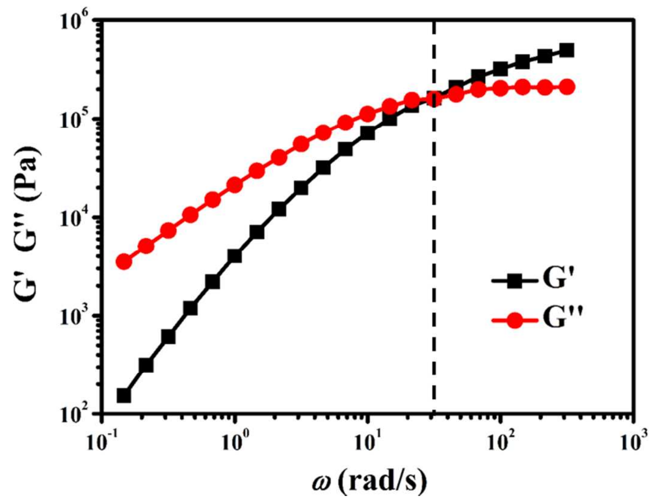

Figure S5. Small-amplitude oscillatory shear measurements of storage and loss moduli for PLLA melt at 160 ºC.

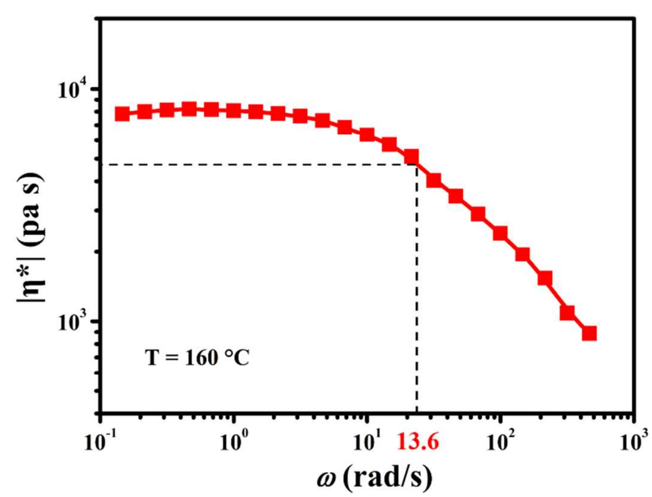

Figure S6. The complex viscosity |η*| vs angular frequency *ω* for PLLA melt at 160 °C measured by rotational rheometer.

Calculation of Weissenberg Number (W_e)

For flow-induced crystallization, the Weissenberg number (W_e) is often used to quantify the strength of applied shear flow, which is defined as the product of shear rate ($\dot{\gamma}$) and stretch relaxation time (τ_d), namely, $W_e = \dot{\gamma}\tau_d$. Considering the contribution of pressure and temperature, the pressure and temperature shift factors (a_P and a_T) are introduced, that is, $W_e = \dot{\gamma}\tau_d a_P a_T$.[3,4] In this work, for sample PLA-100-160, while the shear rate increased continuously from 0 to 20.9 s^{-1} along the radial direction, W_e ranged from 0 to 3.02.

REFERENCES

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