

Supporting Information

Preferential Formation of β -Form Crystals and Temperature-Dependent Polymorphic Structure in Supramolecular Poly(L-lactic acid) Bonded by Multiple Hydrogen Bonds

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Materials. L-lactide (> 99%) were purchased from Purac Co. (Gorinchem, the Netherlands) and purified by recrystallization from ethyl acetate. Tin(II) 2-ethylhexanoate, Sn(Oct)₂, was purchased from Aldrich and purified by distillation under reduced pressure. 1,6-Hexanediol (Aldrich-Sigma), trimethylolpropane (Aldrich-Sigma), and dibutyltin dilaurate (J&K Chemical) were used without further purification. 2(6-Isocyanatohexylaminocarbonyl-amino)-6-methyl-4[1*H*] pyrimidinone (UPy-NCO) was synthesized according to a reported method.¹

Synthesis of Hydroxyl-Terminated 2 and 3-Arm PLLA Precursors. Hydroxyl-terminated 2 and 3-arm PLLAs were obtained by the ring-opening polymerization of L-lactide using 1,6-hexanediol and trimethylolpropane as the bi- and trifunctional initiators, respectively. A typical procedure to synthesize the 2-arm PLLA precursor with an expected M_n of 4.0 kg/mol is shown as follows. Dried L-lactide (30.0 g, 0.21 mol), 1,6-hexanediol (0.73 g, 0.006 mol), and Sn(Oct)₂ (0.09 g, 0.22 mmol) were added into a Schlenk flask and further dried at 65 °C for 1 h under the reduced pressure. The flask was degassed with argon, heated to 130 °C and the polymerization was allowed to proceed at this temperature for 5 h. The crude product was dissolved into chloroform and precipitated into excess of ethanol, filtered off and finally dried under vacuum at 80 °C for 6 h. Trimethylolpropane was used as the initiator for synthesizing the hydroxyl-terminated 3-arm star-shaped PLLA precursor.

Synthesis of UPy End-Functionalized 2 and 3-Arm PLLAs. A typical procedure to synthesize UPy end-functionalized PLLAs is shown as follows. 3.0g of hydroxyl-terminated 2-arm PLLA precursor ($M_{n,NMR}=26.8\text{kg/mol}$) and UPy-NCO (10-fold molar excess of with respect to the terminal hydroxyl groups) were added into a dried Schlenk flask, which was further dried at 65 °C for 1 h under a reduced pressure. Then, 120 mL of toluene and 0.09 g (0.22 mmol) of Sn(Oct)₂ catalyst were

added under the argon atmosphere, and the resulting solution was stirred at 110 °C for 12 h. After removal of the solvent under reduced pressure, the obtained product was dissolved in 200 mL of chloroform and treated with silica (5.0 g) and dibutyltin dilaurate (20.0 mg) at 60 °C for 1 h. Finally, the suspension was filtered off and the filtrate was precipitated in ethyl alcohol. The precipitate was finally dried at 80 °C *in vacuo* for 6 h.

Measurements

NMR Analysis. ^1H NMR spectra were carried out on a Bruker AVANCE II NMR spectrometer (Bruker BioSpin Co., Switzerland) operating at 400 MHz for the ^1H nucleus with CDCl_3 as the solvent. Chemical shifts (δ) were recorded in parts per million (ppm) and referenced to residual protonated solvent (CDCl_3 , 7.26 ppm).

Gel Permeation Chromatography. Molecular weight were measured on a Waters gel permeation chromatography (GPC, Waters Co., Milford, MA, USA) consisting of a PL-gel 10 μm MIXED-BLS column and a Waters 2414 refractive index (RI) detector at 30 °C with tetrahydrofuran (THF) as the mobile phase and polystyrene as the standard.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed on a Pyris 1 TGA instrument (PerkinElmer, Waltham, MA, USA). The sample was heated from 50 to 600 °C at a heating rate of 10 °C under a nitrogen atmosphere.

Calculation of Crystallization Half-Time ($t_{1/2}$)

Based on the assumption that the evolution of crystallinity is linearly proportional to the evolution of heat released during the crystallization, the relative degree of crystallinity (X_t) at any given time can be calculated according to the following equation:

$$X_t = \frac{\int_{t_0}^t (dH_c / dt) dt}{\int_{t_0}^{\infty} (dH_c / dt) dt} \quad (S1)$$

where dH_c denotes the measured enthalpy of crystallization during an infinitesimal time interval dt . The limits t_0 and ∞ denote the times corresponding to the starting and end points of the crystallization process, respectively. A straight line from the starting to ending points in the DSC curves was used as the baseline for integration. The plot of X_t vs t can be attained by processing the DSC isothermal crystallization results by eq. S1, as shown in Figure S1. $t_{1/2}$ was evaluated from the time with $X_t = 50\%$.

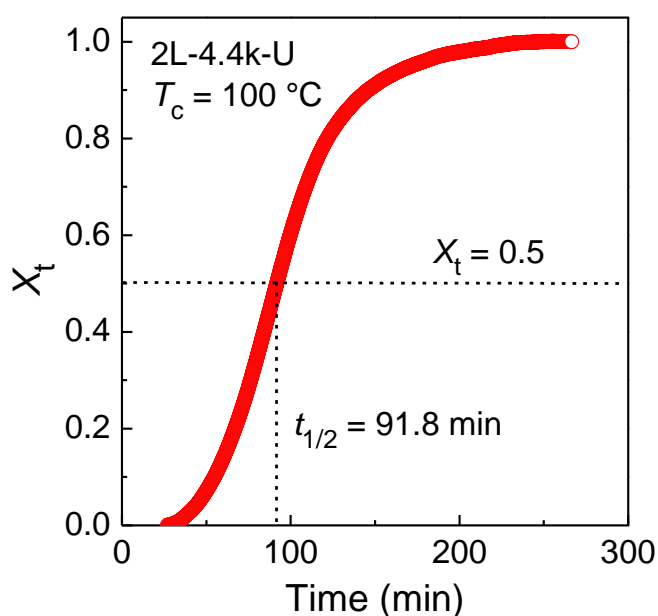


Figure S1. Determination of $t_{1/2}$ from the $X_t \sim t$ plot.

References

- (1) Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt J. A. J.; Meijer, E. W. Supramolecular Polymer Materials: Chain Extension of Telechelic Polymers Using a Reactive Hydrogen-Bonding Synthon. *Adv. Mater.* **2000**, *12*, 874–878.

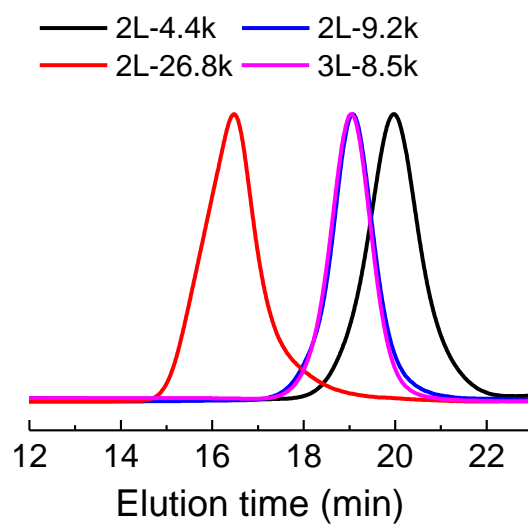
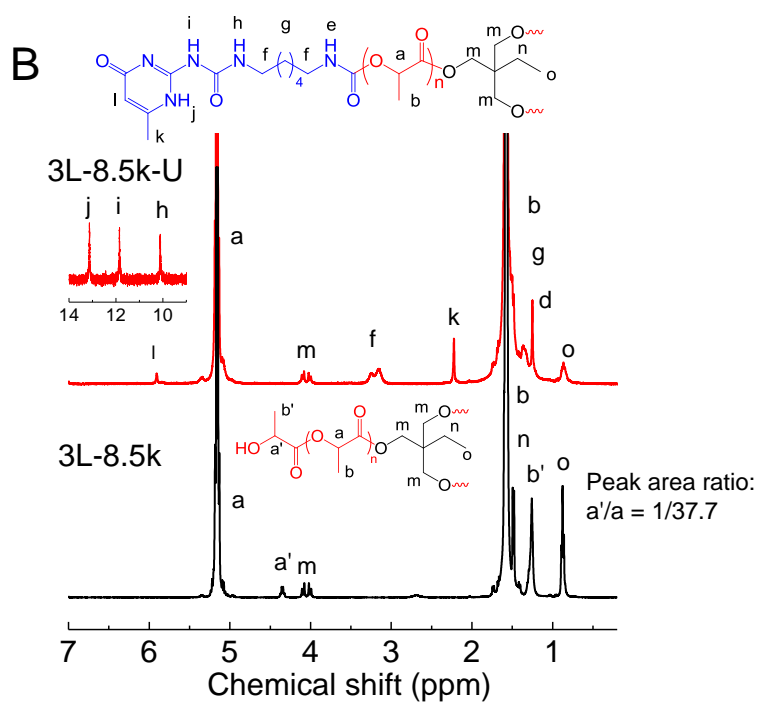


Figure S2. GPC traces of 2 and 3-arm PLLA precursors with different molecular weights.



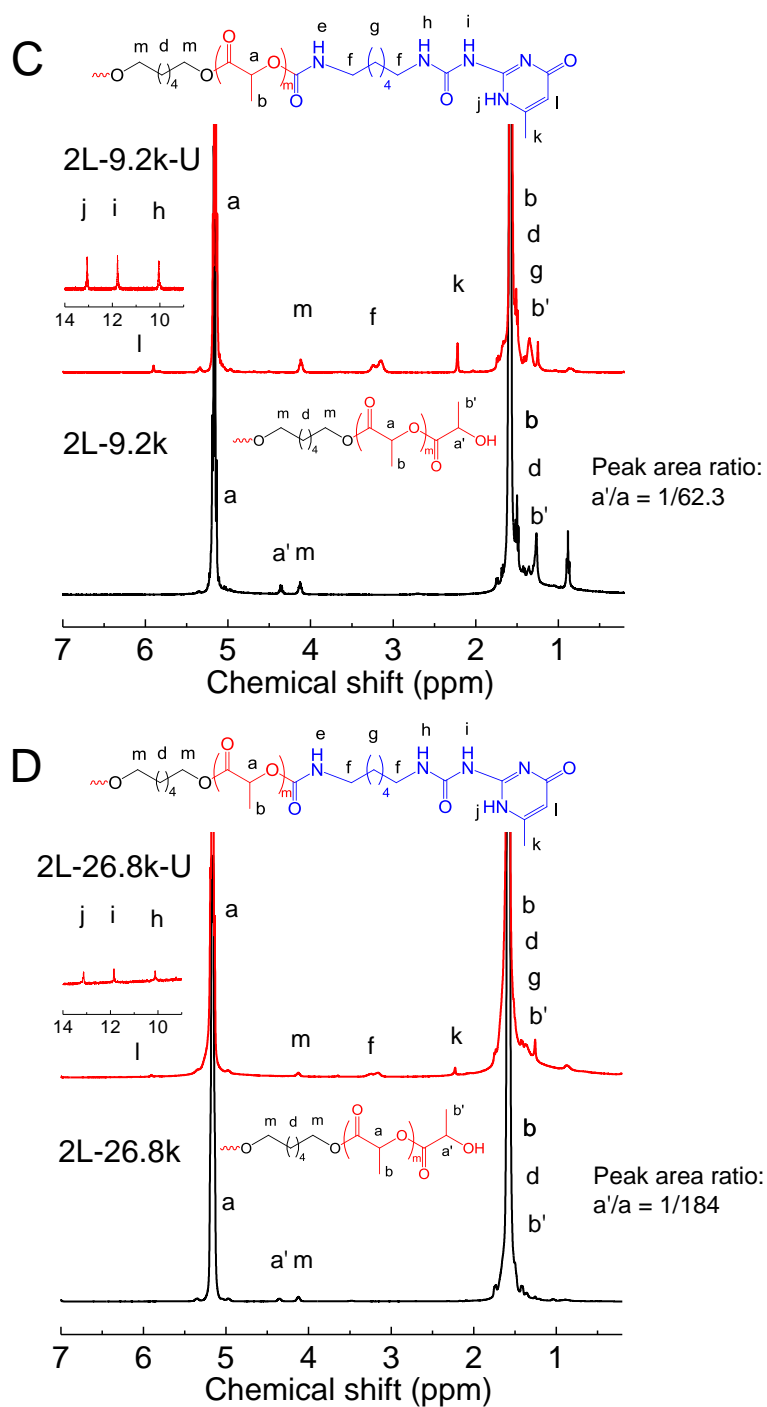


Figure S3. ^1H NMR spectra of synthesized PLLAs with and without UPy end groups.

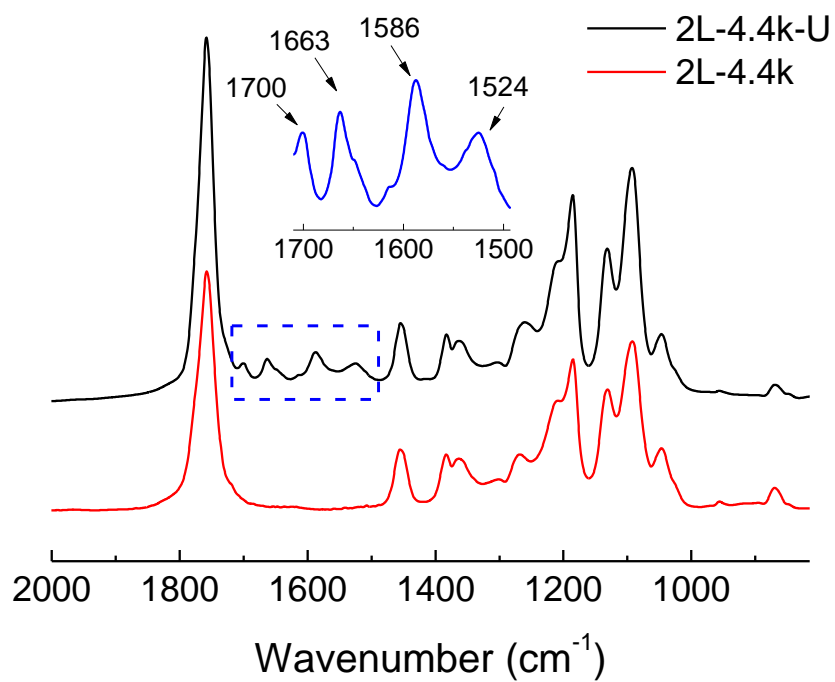


Figure S4. FTIR spectra of 2L-4.4k-U SM-PLLA and 2L-4.4k PLLA precursor.

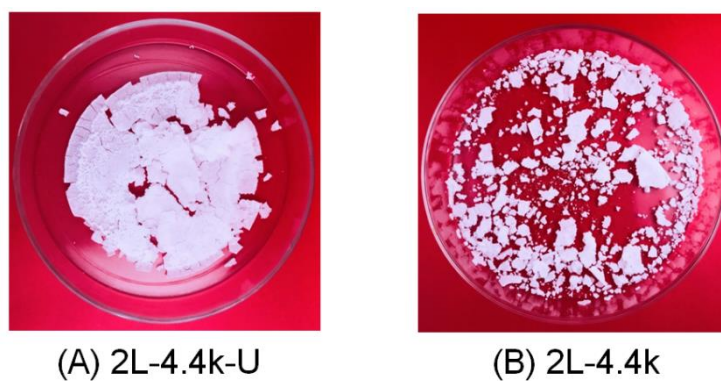


Figure S5. Representative images of the solution-cast samples. (A) UPy-terminated PLLA. (B) PLLA precursor.

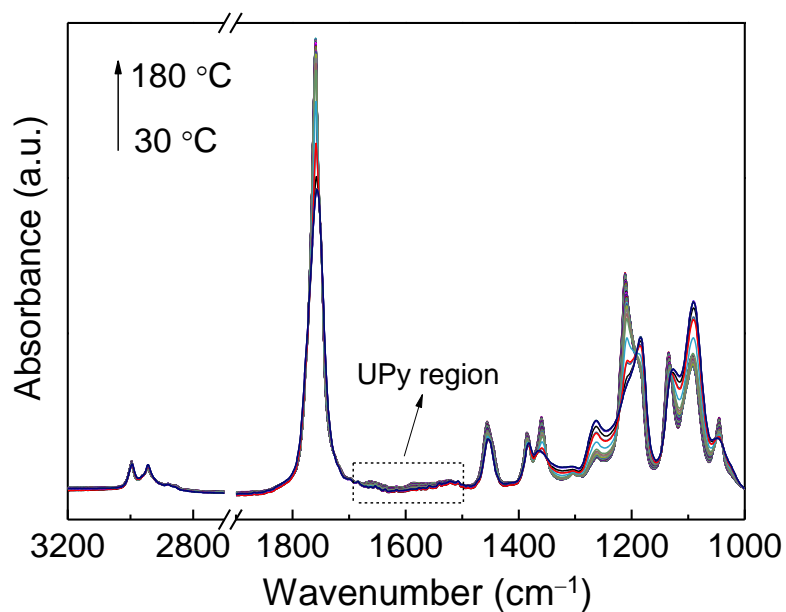


Figure S6. Temperature-dependent FTIR results of 2L-9.2k-U SM-PLLA ($T_c = 130\text{ }^{\circ}\text{C}$) collected upon heating from 30 to 180 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$. The spectra were shown with a 2 $^{\circ}\text{C}$ interval.

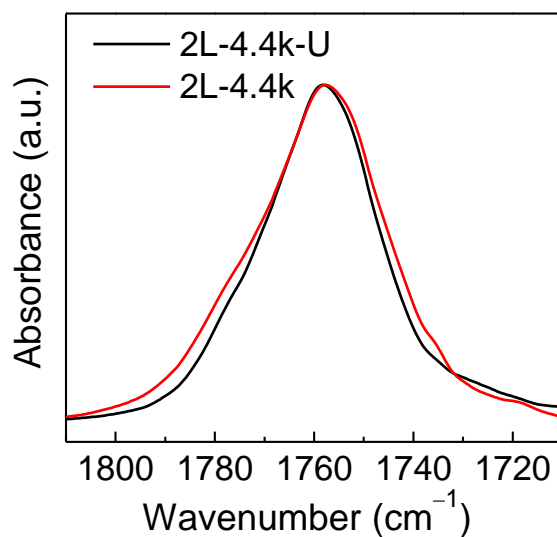


Figure S7. FTIR spectra of melt-quenched SM-PLLA and 2L-4.4k PLLA precursor in the carbonyl stretching region.

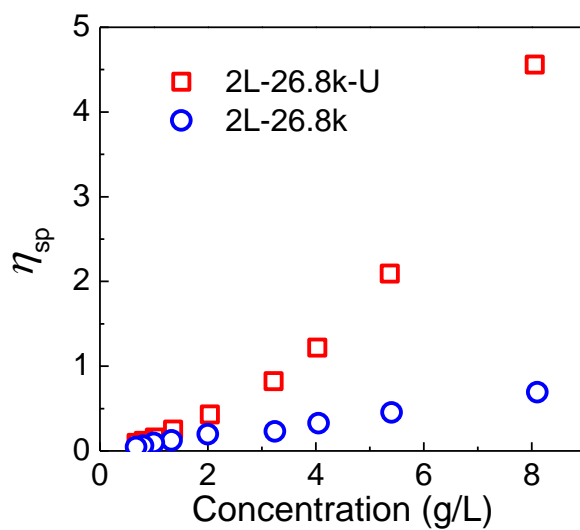


Figure S8. Relationship between specific viscosity (η_{sp}) and concentration for 2-arm UPy-terminated PLLA and PLLA precursor and in chloroform at 30 °C.

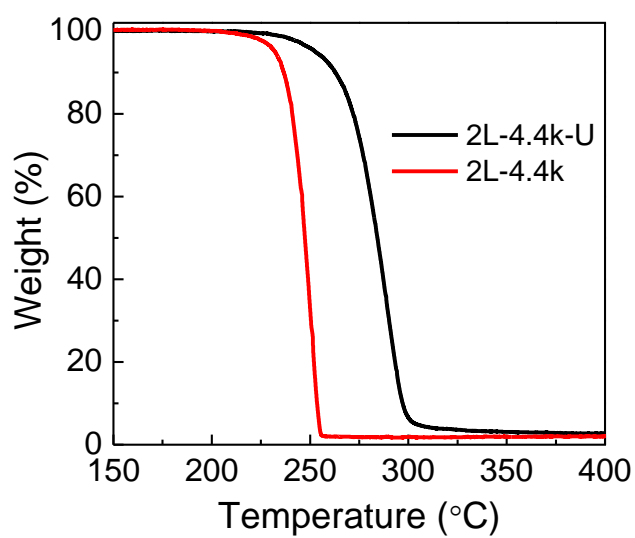


Figure S9. TGA curves of 2L-4.4k-U SM-PLLA and 2L-4.4k PLLA precursor.

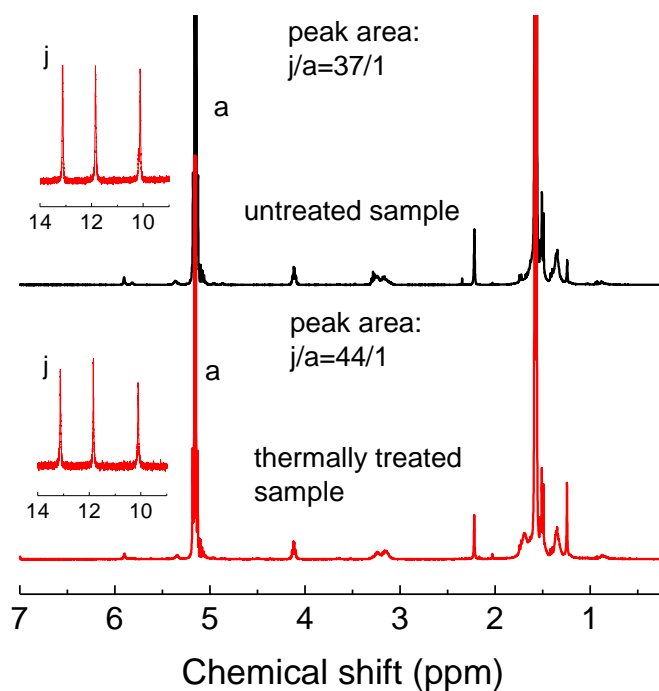


Figure S10. ^1H NMR spectra of untreated and thermally-treated 2L-4.4k-U SM-PLLA. In the thermal treatment, the sample was first heated to 180 $^{\circ}\text{C}$ and held at this temperature for 2 min on a hot stage. It was then cooled to 0 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$.

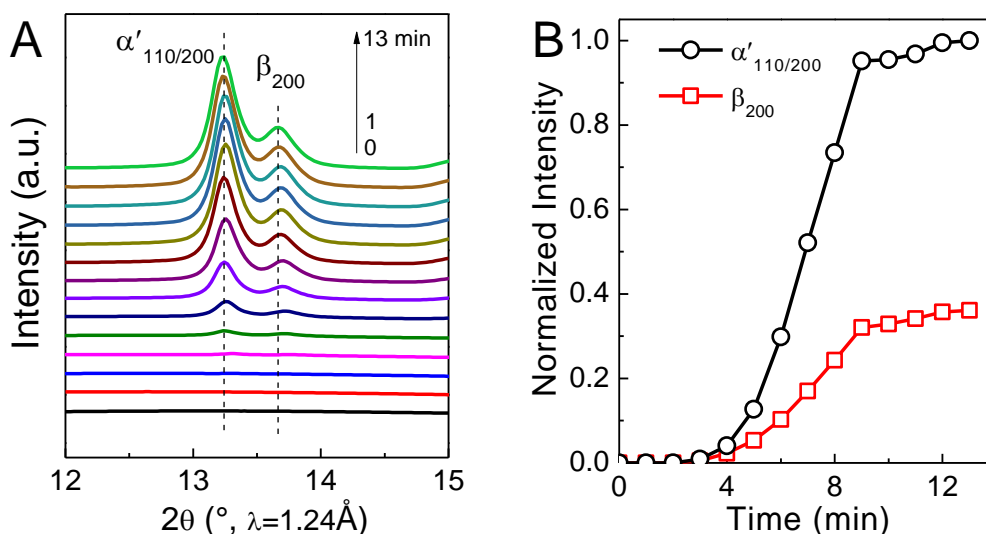


Figure S11. WAXD results of 2L-9.2k-U SM-PLLA collected during isothermal cold crystallization at $T_c = 90$ $^{\circ}\text{C}$. (A) WAXD patterns in the range of $2\theta = 12\sim 15^{\circ}$ with a time interval of 1 min. (B) Intensity changes of $\alpha'_{110/200}$ and β_{200} diffractions with the crystallization time. In the *in-situ* WAXD analysis, the melt-quenched sample, sandwiched by two polyimide films, was heated to 90 $^{\circ}\text{C}$ at 50 $^{\circ}\text{C}/\text{min}$ and held at this temperature for isothermal crystallization. WAXD pattern was collected every 1 min during the isothermal crystallization process.

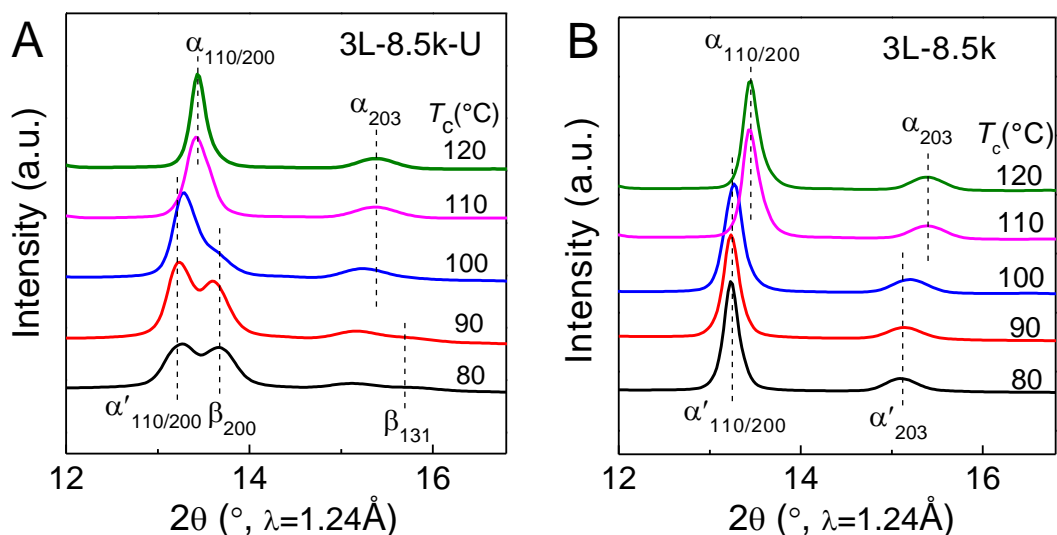


Figure S12. WAXD patterns of SM-PLLAs and PLLA precursors after isothermal melt crystallization at different T_c 's. (A) 3L-8.5k-U SM-PLLA. (B) 3L-8.5k PLLA precursor. To prepare the crystallized samples for WAXD analysis, the samples were first melted at 180 °C for 2 min and then transferred to an oven preset at a given T_c for crystallization.

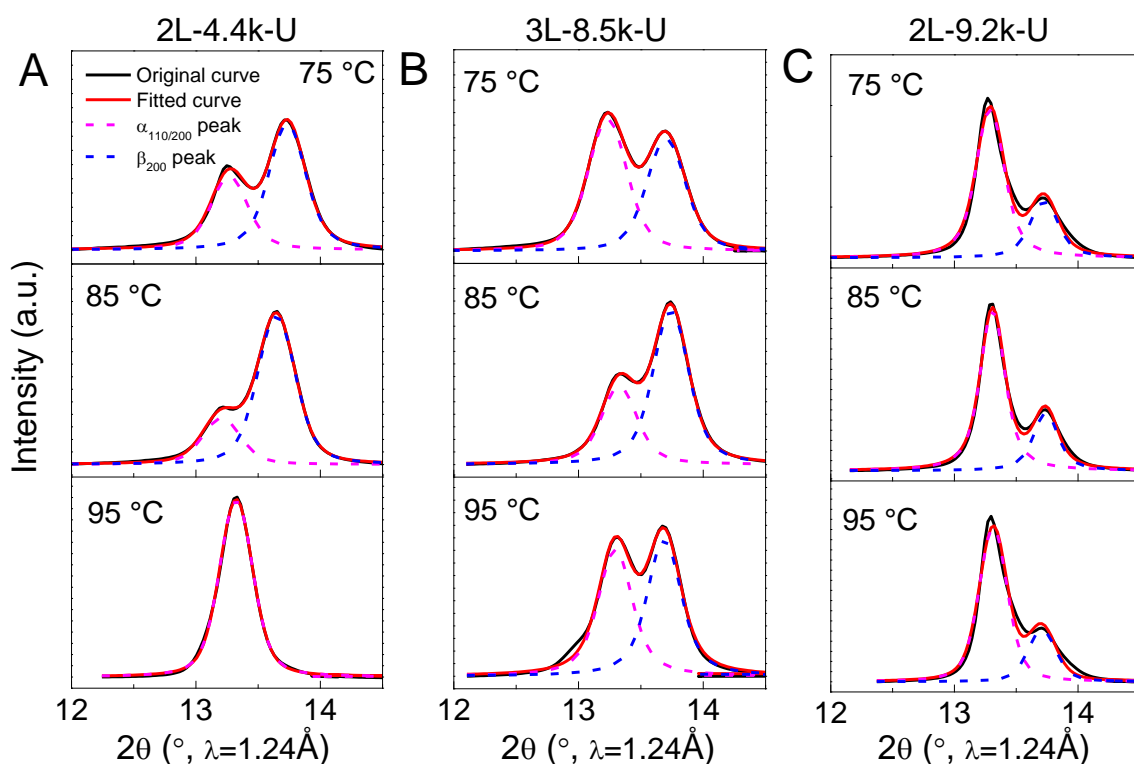


Figure S13. Multiple peak splitting/fitting of WAXD patterns in the 2θ range of 12.5~14.5 ° for SM-PLLAs crystallized at various T_c 's. (A) 2L-4.4k-U, (B) 3L-8.5k-U, (C) 2L-9.2k-U.

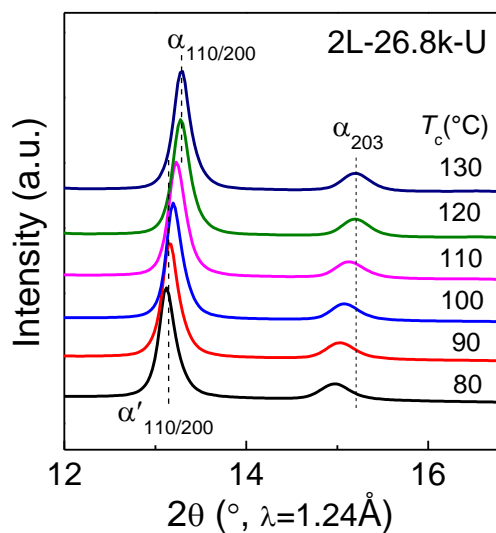


Figure S14. WAXD patterns of 2L-26.8k-U SM-PLLA after isothermal cold crystallization at different T_c 's.

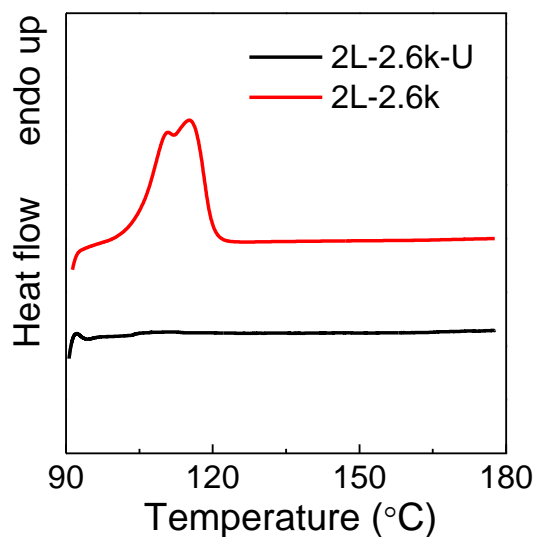


Figure S15. DSC heating curves (10 °C/min) of 2L-2.6k-U SM-PLLA and 2L-2.6k PLLA precursor after isothermal cold crystallization at 90 °C for 10 h.

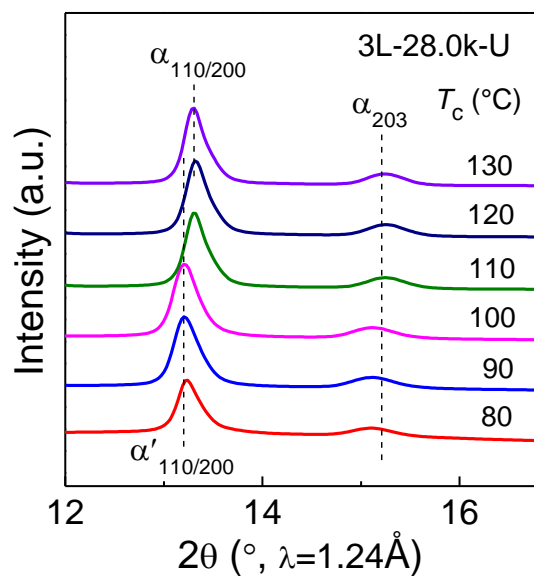


Figure S16. WAXD patterns of 3L-28.0k-U SM-PLLA after isothermal cold crystallization at different T_c 's.

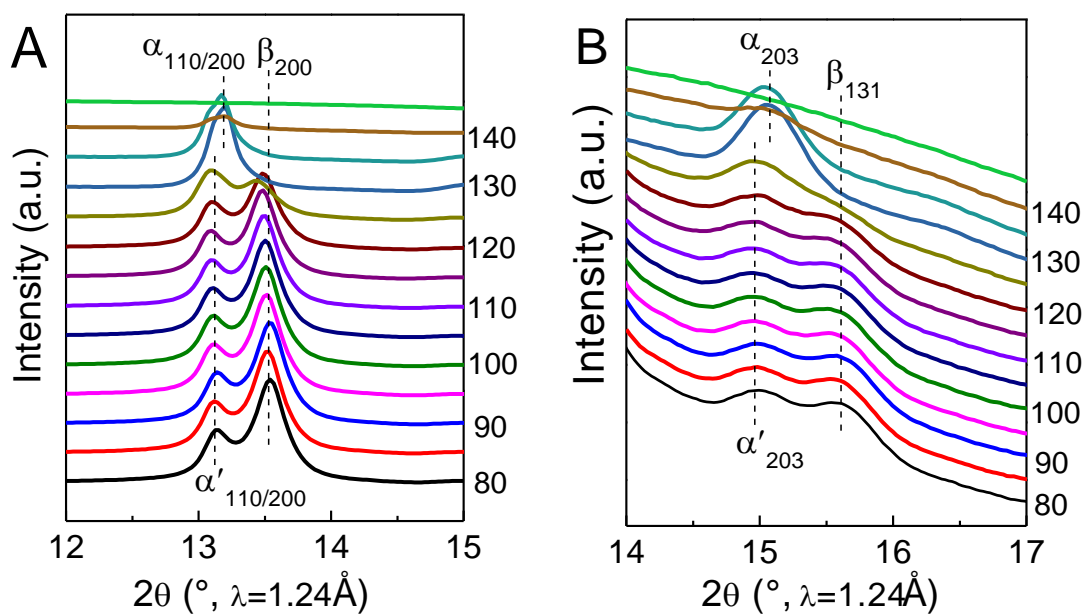


Figure S17. Temperature-variable WAXD patterns collected upon heating of 3L-8.5k-U SM-PLLA ($T_c = 90$ °C). (A) WAXD patterns in $2\theta = 12\sim 15$ ° region. (B) Enlarged patterns in $2\theta = 14\sim 17$ ° region.

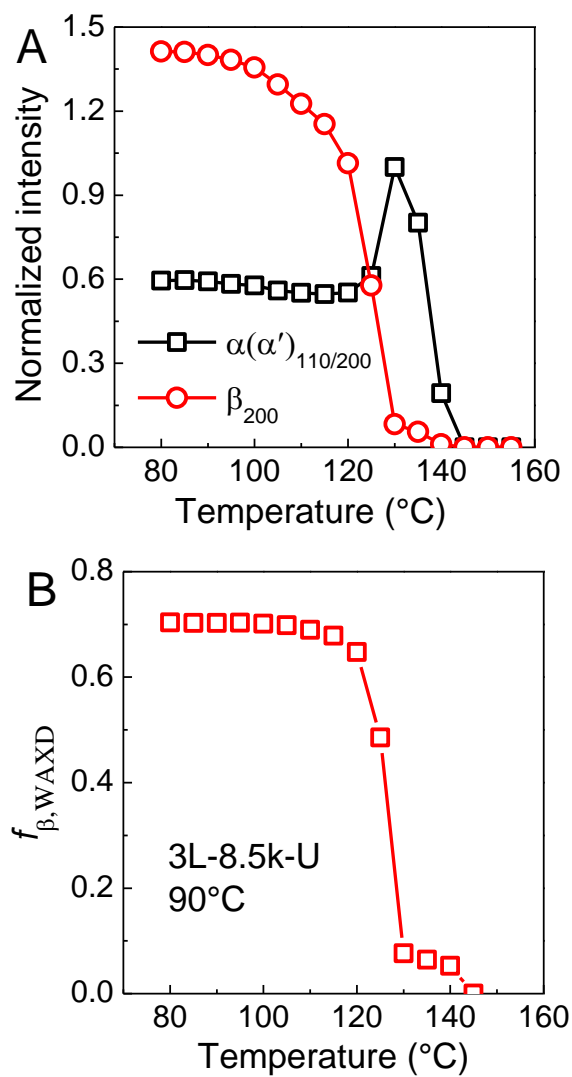


Figure S18. Temperature-variable WAXD results derived from Figure S17 for the 3L-8.5k-U SM-PLLA ($T_c = 90$ °C). (A) Intensity changes of $\alpha_{110/200}$ (or $\alpha'_{110/200}$) and β_{200} diffractions during heating. (B) Changes of β -form fraction during heating.

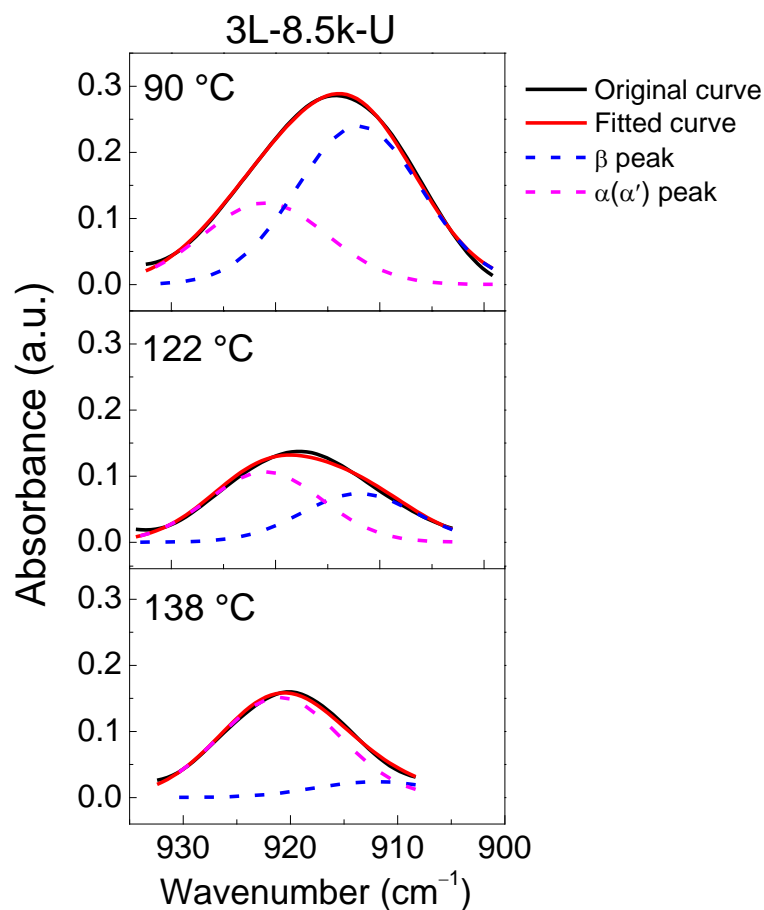


Figure S19. Peak splitting and fitting of FTIR spectra in the wavenumber region of 935~900 cm^{-1} for 3L-8.5k-U SM-PLLA ($T_c = 90\text{ }^{\circ}\text{C}$) collected during heating to different temperatures. In the peak splitting/fitting process, FTIR absorption peak was split into two peaks, whose positions were fixed at 921 (α or α' phase) and 912 cm^{-1} (β phase), respectively.

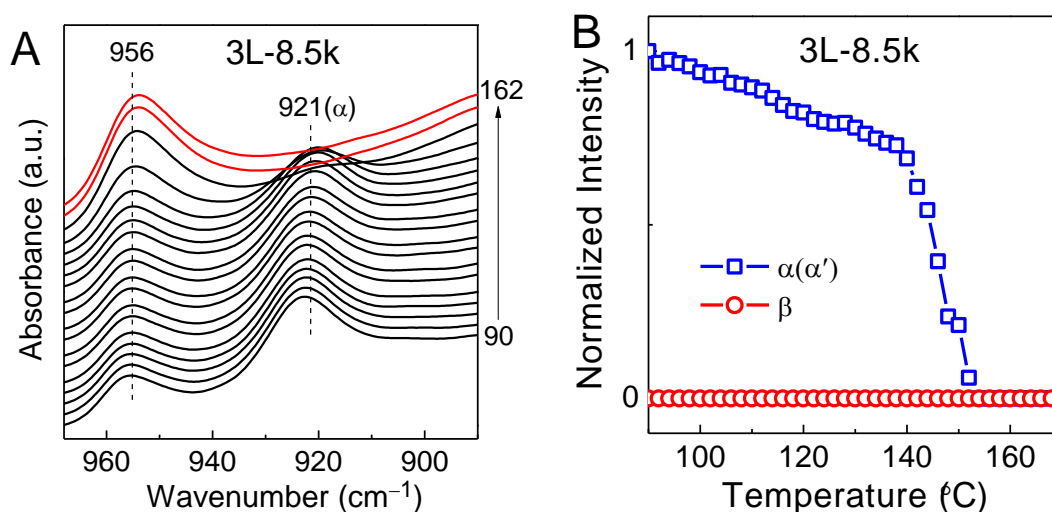


Figure S20. Temperature-variable FTIR results in the wavenumber range of 970~890 cm^{-1} for 3L-8.5k PLLA precursor ($T_c = 90$ $^{\circ}\text{C}$) collected during heating (5 $^{\circ}\text{C}/\text{min}$). (A) Temperature-variable FTIR spectra collected in 90~162 $^{\circ}\text{C}$ (shown with a 4 $^{\circ}\text{C}$ interval). (B) Intensity changes of 921 and 912 cm^{-1} bands during heating. In panel B, the intensities were normalized by the maximum intensity of 921 cm^{-1} band.