Supporting Information

Figures S1–S15.

Mesophase-Mediated Crystallization of Poly(L-lactide): Deterministic Pathways to Nanostructured Morphology and Superstructure Control

Qiaofeng Lan, and Yong Li*

Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences (CAS), Ningbo 315201, China

* Corresponding authors.

E-mail address: lanqf@nimte.ac.cn or lanqf2016@gmail.com (Q.L.).

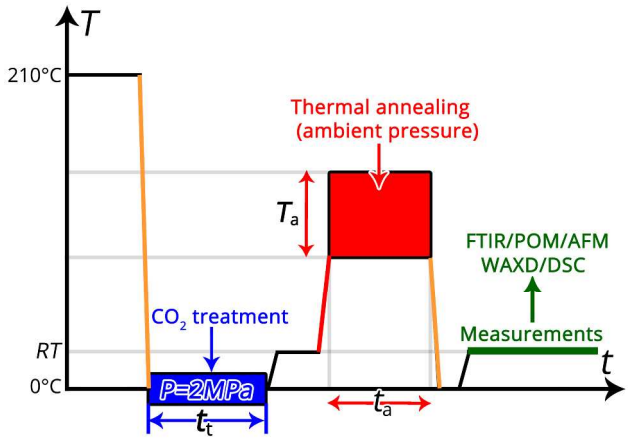

Figure S1. Temperature-time protocol for the CO_2 treatment at 2 MPa/T_t = 0 °C for t_t = 15 s−360 min and/or subsequent thermal annealing at T_a = 78−135 °C under atmospheric pressure for t_a = 5 s−1 h.

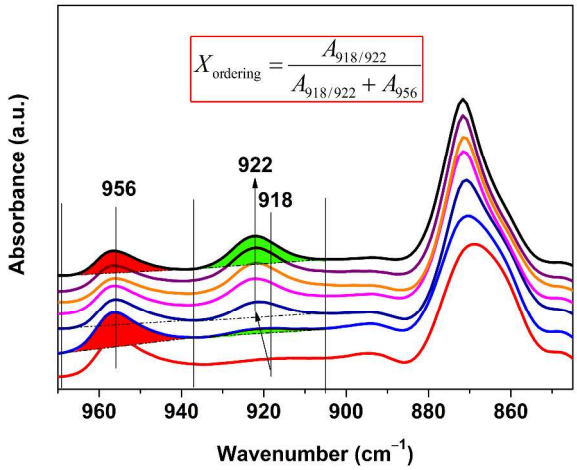

Figure S2. Calculation of the overall fraction of the structural ordering (X_{ordering}) including the crystal (with 922 cm^{-1} band) (X_{crystal}) and/or mesophase (with 918 cm^{-1} band), and intermediate (with band at range of 918−922 cm^{-1}) structure having degree of conformational ordering between mesophase and crystal, were performed according to the equation (inset)[1, 2] as follows

$$X_{\text{ordering}} = \frac{A_{918/922}}{A_{918/922} + A_{956}}$$

where $A_{918/922}$ and A_{956} are the integrated intensities (as shown by the representative shadows) of the IR bands at around 918 to 922 cm^{-1} and 956 cm^{-1}, respectively. The equation was applied to the calculation for the FTIR spectra in Figures 1−3, Figure 9b, and Figure 11. When the crystalline phase (showed 922 cm^{-1} band) was exclusively and definitely present in the PLLA sample, the X_{ordering} was expressed as X_{crystal}.

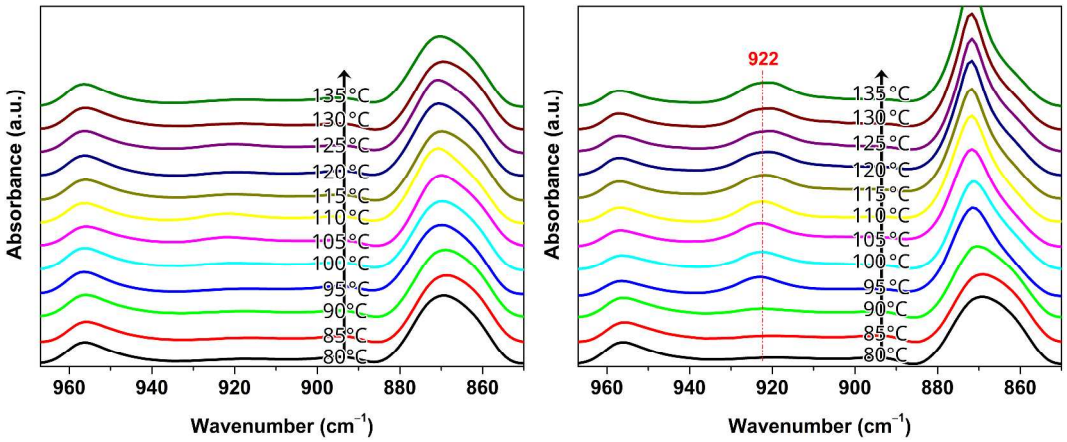

Figure S3. FTIR spectra in the wavenumber range of 970−850 cm^{-1} for PLLA films that treated under 2 MPa CO_2 at T_t = 0 °C for different t_t = 0 s (melt-quenched) (left) and t_t = 30 s (right), and then thermally annealed at T_a = 80−135 °C for t_a = 1 min.

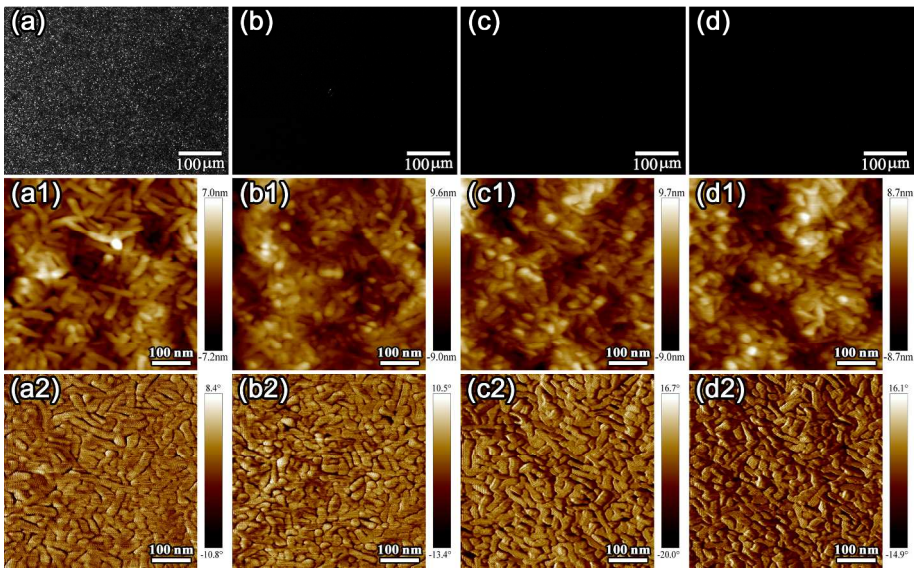

Figure S4. POM (a−d) micrographs and AFM height (a1−d1) and phase (a2−d2) images for PLLA films that treated under 2 MPa CO_2 at T_t = 0 °C for t_t = 2 min (a, a1, a2), t_t = 10 min (b, b1, b2), t_t = 45 min (c, c1, c2), t_t = 180 min (d, d1, d2), and then thermally annealed at T_a = 130 °C for t_a = 1 h.

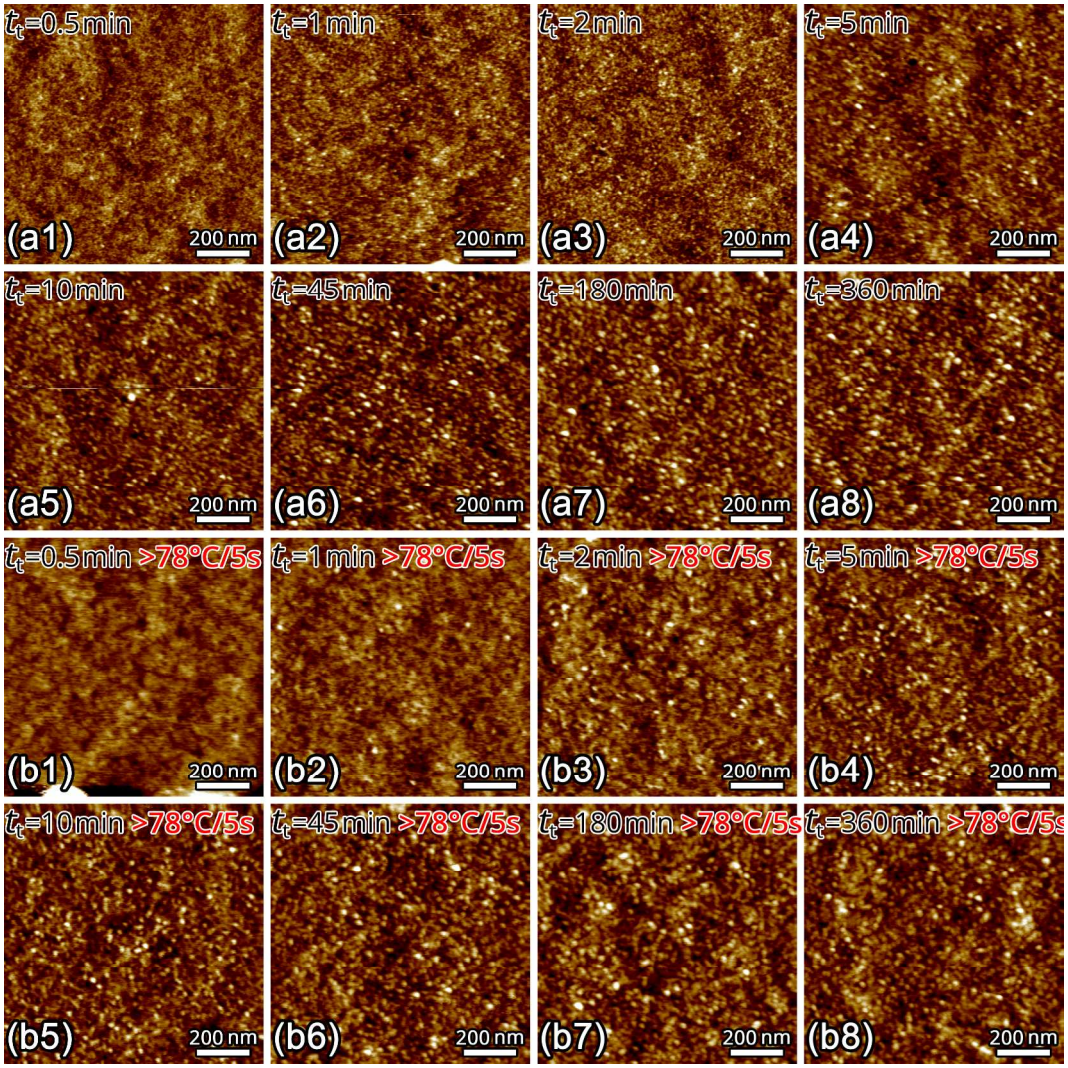

Figure S5. AFM height images for CO_2-treated PLLA (mesophase) before (a1−a8) and after (b1−b8) annealing at T_a = 78 °C for t_a = 5 s. The CO_2 treatments were conducted at 2 MPa and T_t = 0 °C for different t_t (0.5−360 min) as indicated. After annealing, in contrast to the samples with t_t = 5−360 min (b4−b8), whose morphologies remained substantially unchanged, a change in morphology can be seen in those with t_t = 0.5−2 min (b1−b3), indicating that the samples with t_t = 0.5−2 min had relatively low viscosity.

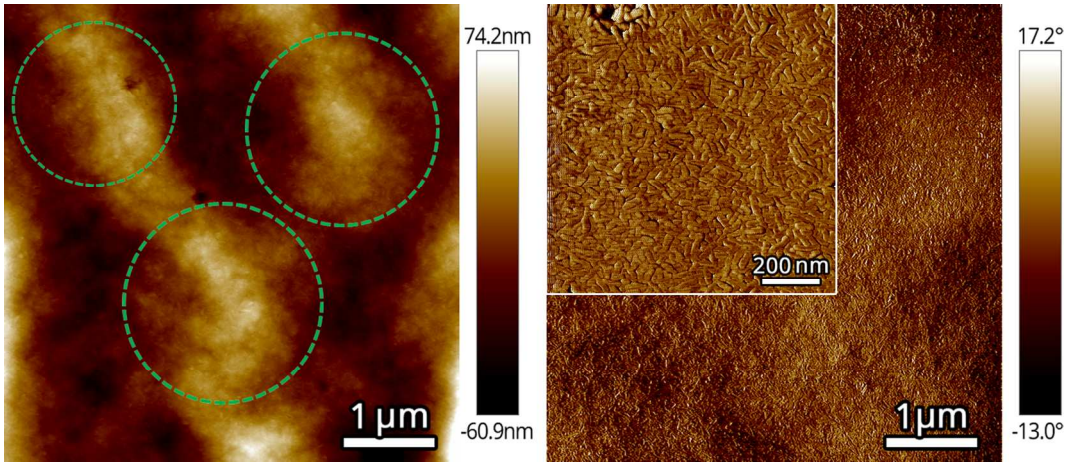

Figure S6. AFM height (a) and phase (b) images for PLLA film that treated under 2 MPa CO_2 at T_t = 0 °C for t_t = 2 min and then thermally annealed at T_a = 130 °C for t_a = 1 h. The dashed circles in panel (a) imply the grains observed in POM of Figure 4; the inset in panel (b) shows a high-magnification phase image.

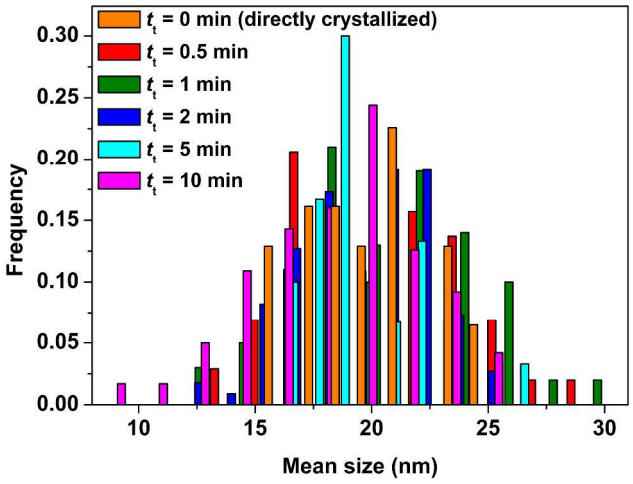

Figure S7. The size distribution of lamellae (directly crystallized) and nanorods determined from the PLLA films that treated under 2 MPa CO_2 at T_t = 0 °C for different t_t (0.5−10 min) and then thermally annealed at T_a = 130 °C for t_a = 1 h.

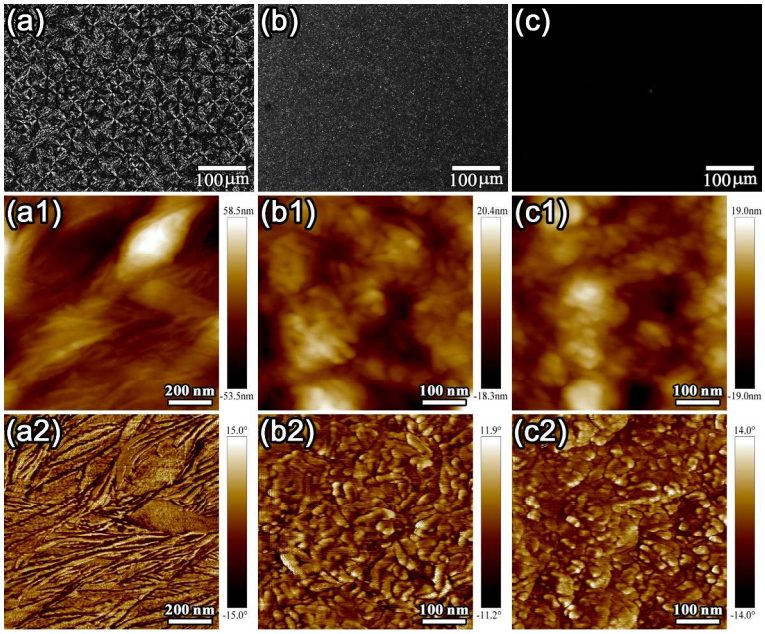

Figure S8. POM (a−c) micrographs and AFM height (a1−c1) and phase (a2−c2) images for PLLA films that treated under 2 MPa CO_2 at T_t = 0 °C for t_t = 2 min (b, b1, b2) and t_t = 10 min (c, c1, c2), and then thermally annealed at T_a = 90 °C for t_a = 1 h. For comparison, panels (a, a1, a2) show the results for the sample that directly melt-crystallized at 90 °C (cooled from 210 °C).

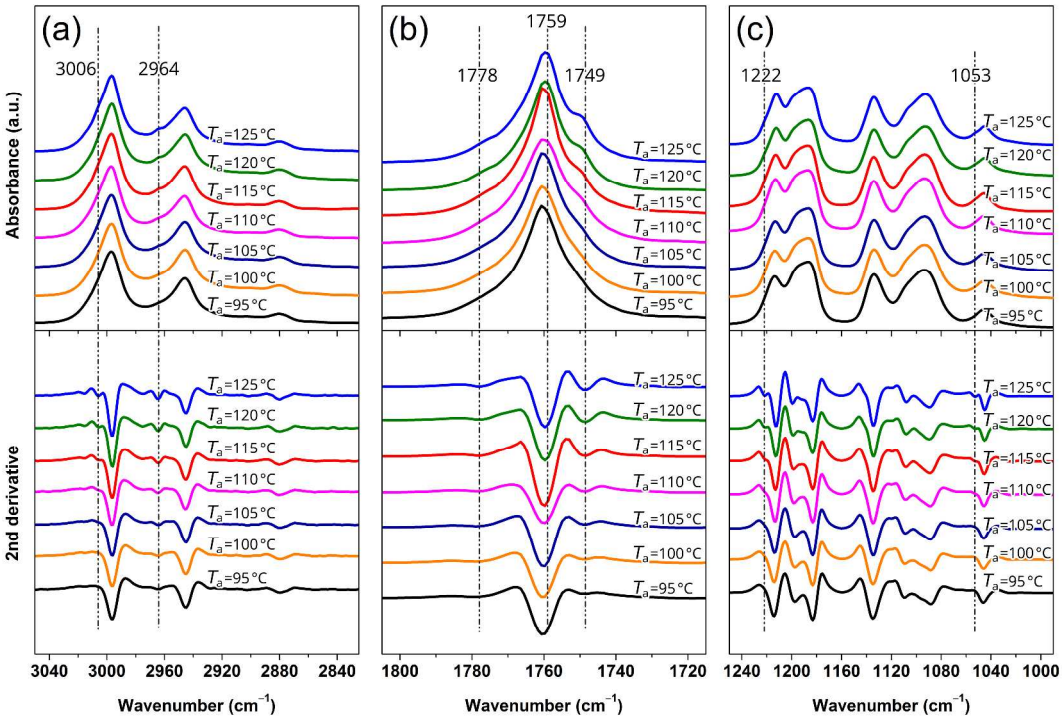

Figure S9. FTIR and corresponding second derivative spectra in the wavenumber ranges of 3050−2850 (a), 1800−1720 (b), and 1250−1000 cm^{-1} (c) for PLLA samples that treated under 2 MPa CO_2 at T_t = 0 °C for t_t = 30 min, and then thermally annealed at T_a = 95−125 °C for t_a = 1 h.

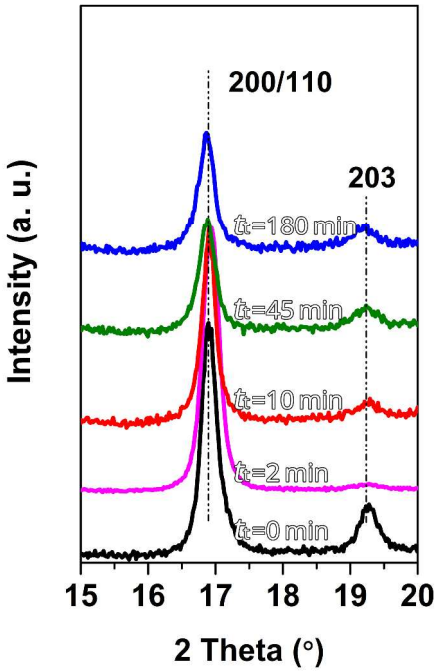

Figure S10. WAXD patterns for PLLA samples that treated under 2 MPa CO_2 at T_t = 0 °C for t_t = 0−180 min (b), and then thermally annealed at T_a = 130 °C for t_a = 1 h.

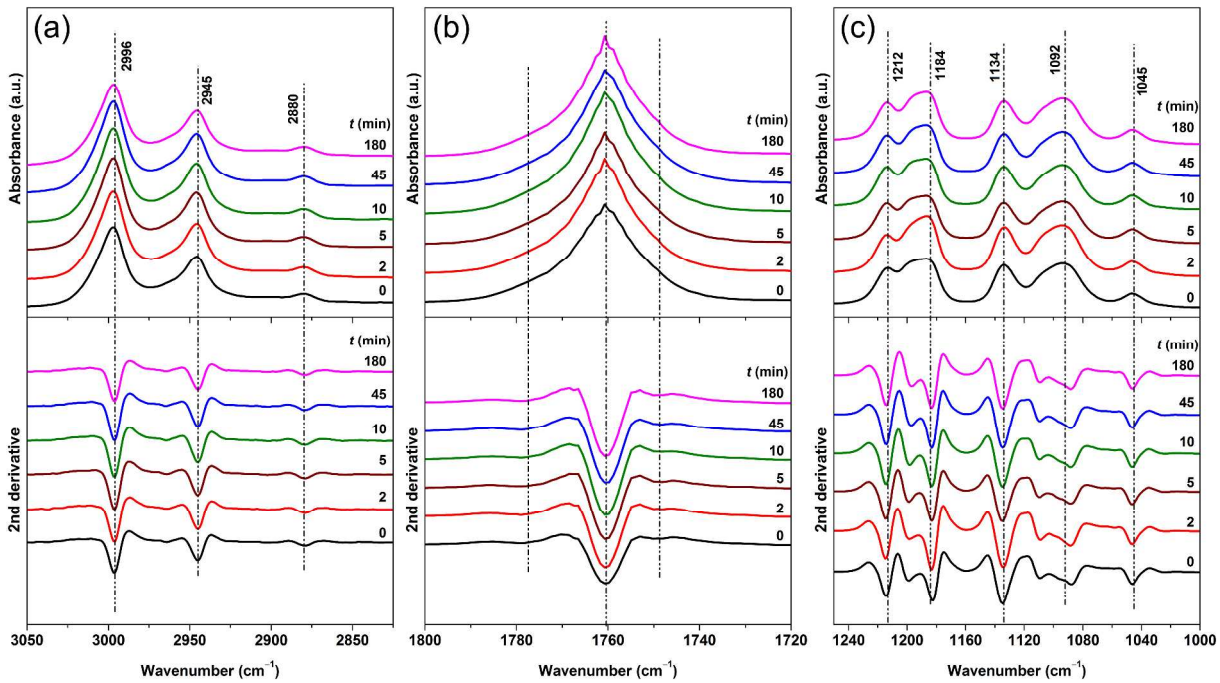

Figure S11. FTIR and corresponding second derivative spectra in the wavenumber ranges of 3050−2850 (a), 1800−1720 (b), and 1250−1000 cm^{-1} (c) for PLLA samples that treated under 2 MPa CO_2 at T_t = 0 °C for t_t = 0−180 min as indicated, and then thermally annealed at T_a = 90 °C for t_a = 1 h.

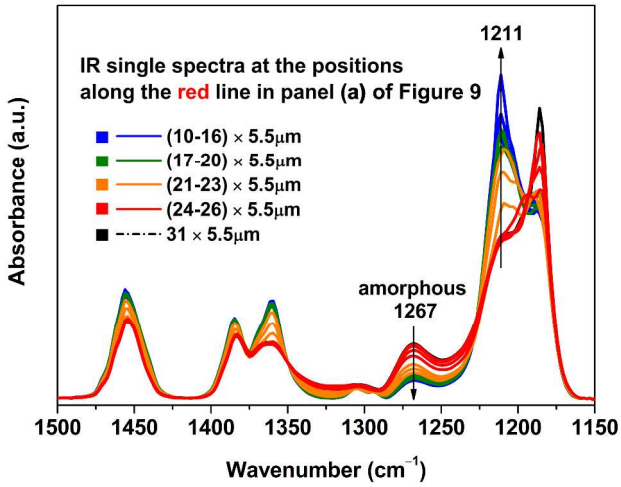

Figure S12. FTIR spectra in the wavenumber range of 1500−1150 cm^{-1} at the positions marked along the red line in panel (a) in Figure 9.

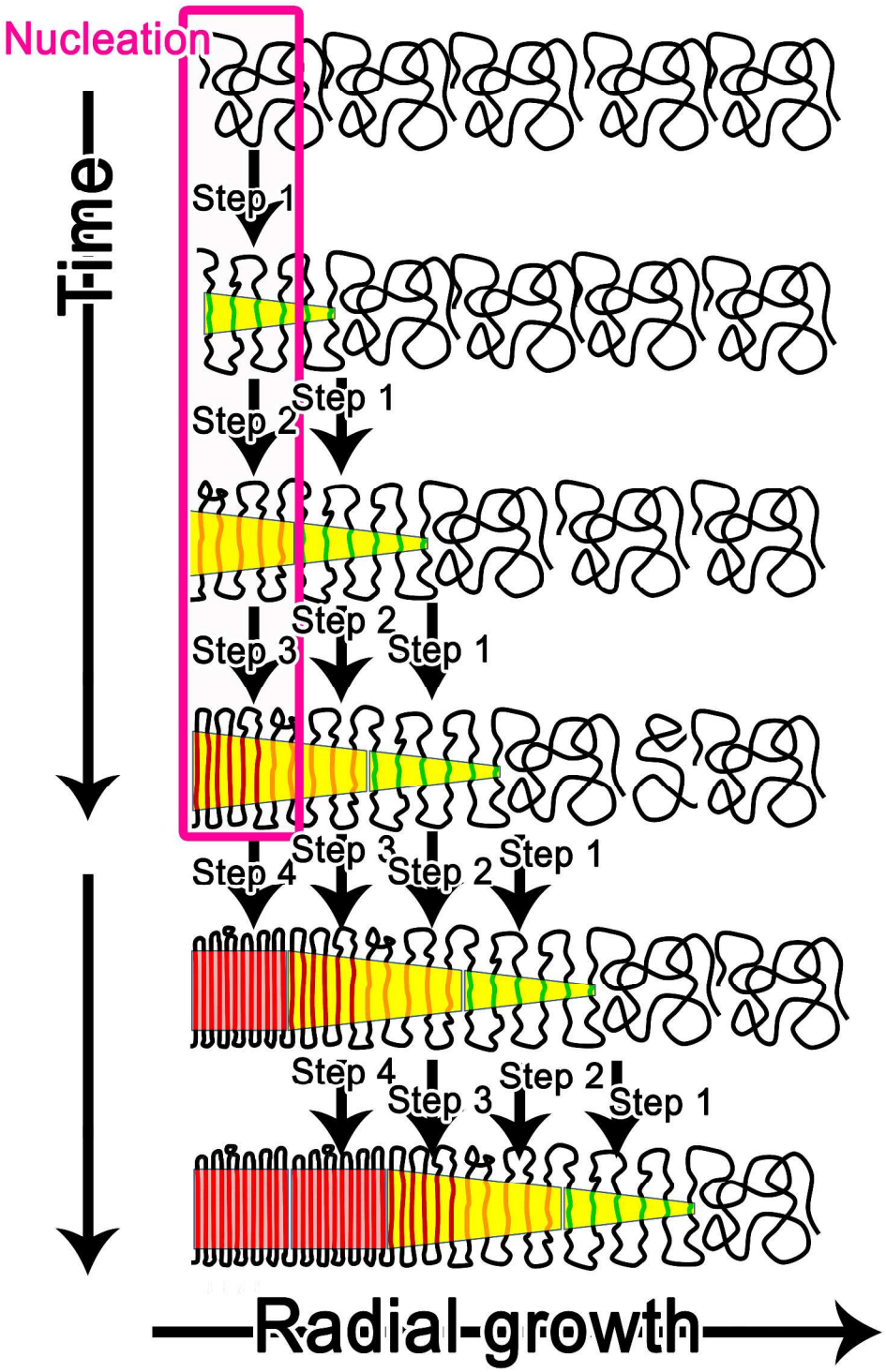

Figure S13. Schematic representation (replotted from Figure 10 for easier visualization) of multistage model proposed for the formation of the PLLA crystals (spherulites). The Steps 1-3 represent the multistep nucleation process. The figure is not to scale.

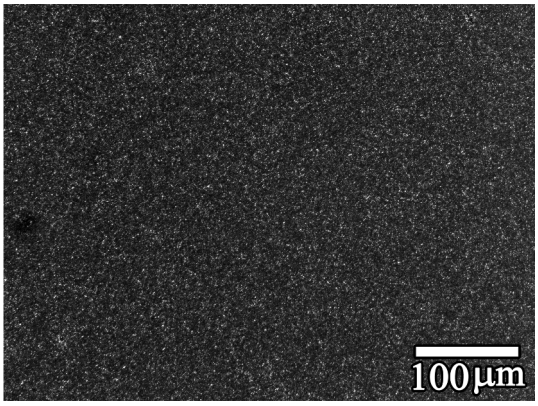

Figure S14. POM micrograph for PLLA film that treated under 2 MPa CO_2 at T_t = 0 °C for t_t = 30 s and then thermally annealed at T_a = 130 °C for t_a = 1 min.

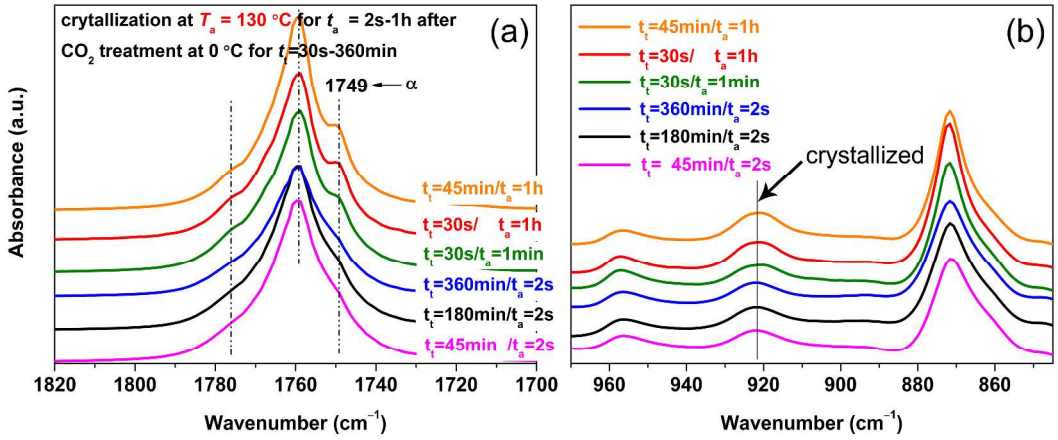

Figure S15. FTIR spectra in the wavenumber ranges of (a) 1820-1700 and (b) 970−850 cm^{-1} for PLLA films that treated under 2 MPa CO_2 at T_t = 0 °C for different t_t as indicated and then thermally annealed at T_a = 130 °C for t_a = 2 s−1 h as indicated.

References

(1) Zhang, T. P.; Hu, J.; Duan, Y. X.; Pi, F. W.; Zhang, J. M. Physical Aging Enhanced Mesomorphic Structure in Melt-Quenched Poly(L-lactic acid). *J. Phys. Chem. B* **2011**, *115*, 13835−13841.

(2) Lan, Q. F.; Li, Y.; Chi, H. T. Highly Enhanced Mesophase Formation in Glassy Poly(L-lactide) at Low Temperatures by Low-Pressure CO_2 That Provides Moderately Increased Molecular Mobility. *Macromolecules* **2016**, *49*, 2262−2271.