Electronic Supplementary Information

Hierarchical Ordering and Multilayer Structure of Poly(ε-caprolactone) End-functionalized by a Liquid Crystalline Unit: Role of Polymer Crystallization

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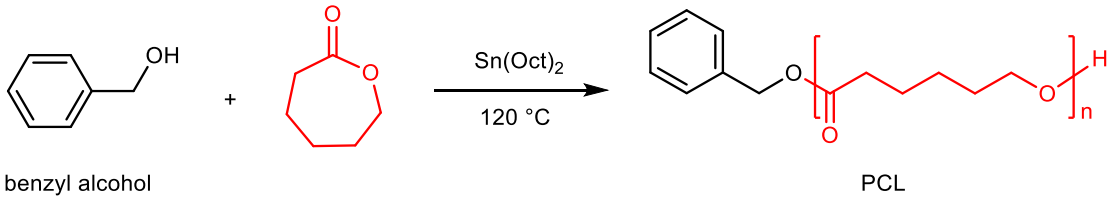
Experimental

Synthesis of Nonfunctionalized PCL. Typical procedure for synthesizing the nonfunctionalized PCL is shown as follows (Scheme S1). Benzyl alcohol (0.24 g, 2.2 mmol), ε-CL (2.0 g, 17.5 mmol), and $Sn(Oct)_2$ (14.0 mg, 0.04 mmol) were added into a flask and further dried at 50 °C for 1 h under reduced pressure. The mixture was then purged with dry argon and heated to 120 °C for 6 h for polymerization. After reaction, the crude product was dissolved in chloroform and then precipitated into excess of hexane to remove the unreacted monomer. The isolated product was dried at 30 °C under vacuum for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 7.39-7.31 (m, 5H, Ar-H), 5.11 (s, 2H, Ar-CH_2-O), 4.05 (t, 18H, CH_2-CH_2-O), 3.64 (t, 2H, CH_2-OH), 2.30 (m, 20H, CO-CH_2), 1.63 (m, 40H, CH_2-CH_2-CH_2-CH_2-CH_2), 1.37 (m, 20H, CH_2-CH_2-CH_2-CH_2-CH_2).



Scheme S1. Synthesis of nonfunctionalized PCL

Molecular weight and chemical structure of nonfunctionalized PCL were characterized by GPC (Table 1) and ^{1}H NMR (Figure S2), confirming the successful synthesis of the PCL with well-defined end-functionality, controlled molecular weight, and narrow molecular-weight distribution ($Đ \leq 1.19$). According to the ^{1}H NMR spectra, the molecular weight of nonfunctionalized PCL was calculated by comparing the resonance peak area of the methylene proton beside ester group (peak c, Figure S2) with that of the terminal methylene proton (peak d, Figure S2). The peak area of methylene proton in the initiator side (peak b, Figure S2) was almost the same as that of the terminal methylene proton (peak d, Figure S2), implying that the nonfunctionalized PCL was initiated by benzyl alcohol.

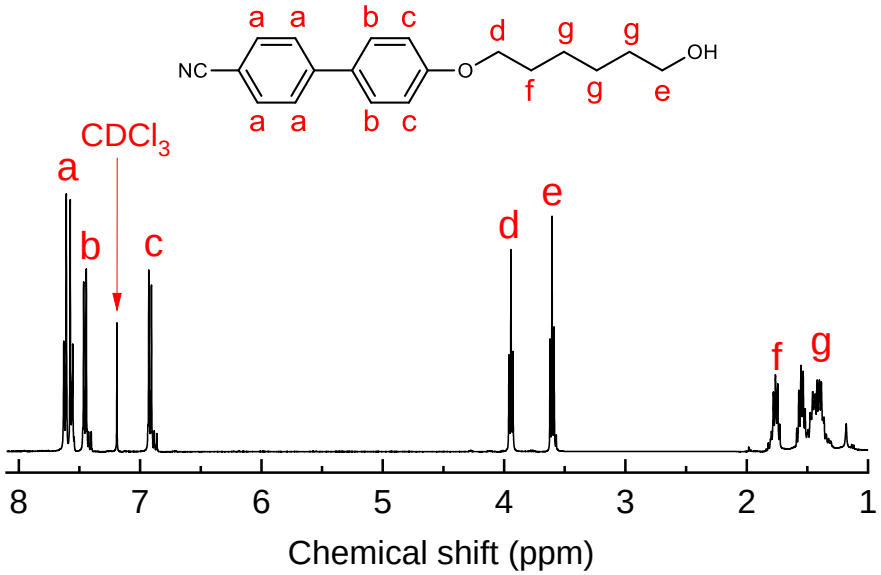


Fig. S1. ^{1}H NMR spectra of H6CBP in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 7.65-7.53 (q, 4 aromatic H *ortho* and *meta* to CN), 7.49-7.43 (d, 2 aromatic H *meta* to O-CH_2), 6.95-6.89 (d, 2 aromatic H *ortho* to O-CH_2), 3.97-3.90 (m, 2H, O-C$\underline{H}_2$), 3.63-3.56 (m, 2H, C$\underline{H}_2$-OH), 1.84-1.71 (m, 2H, O-CH_2-C$\underline{H}_2$), 1.61-1.28 [m, 6H, O-$(CH_2)_2$-(C$\underline{H}_2$)$_3$].

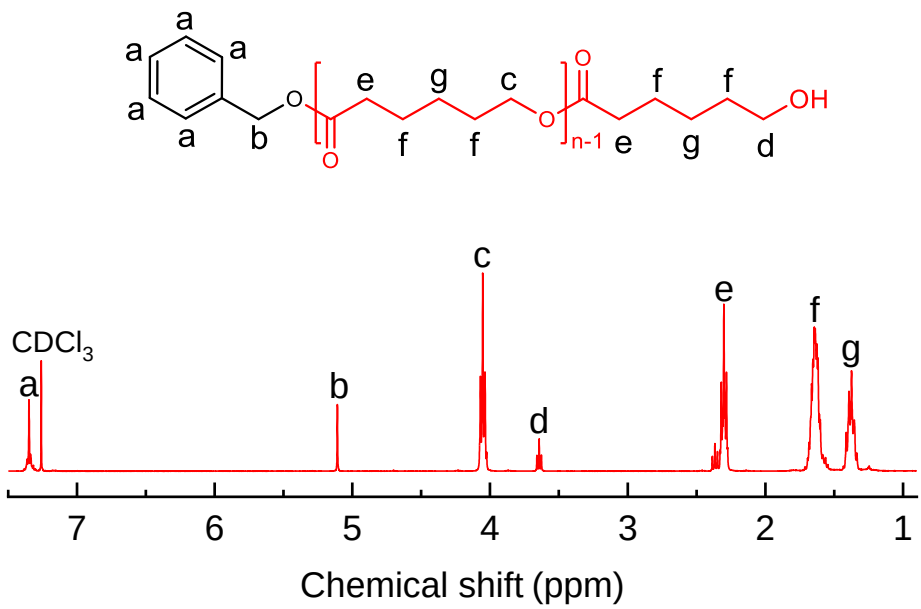


Fig. S2. ^{1}H NMR spectra of nonfunctionalized $PCL_{0.79k}$ in $CDCl_3$.

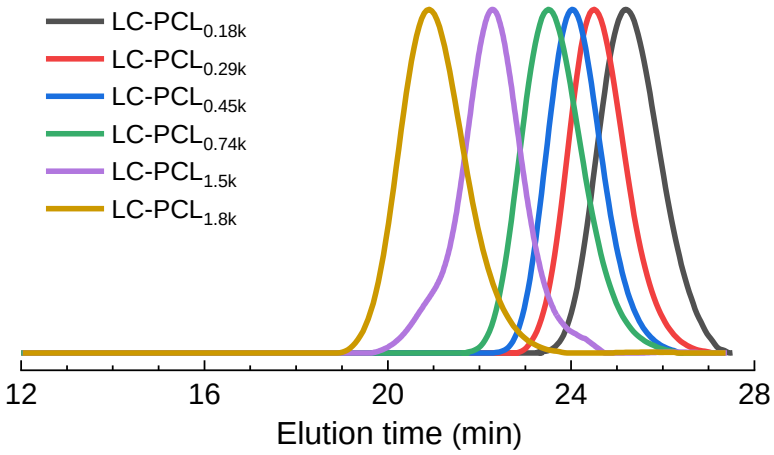


Fig. S3. GPC traces of the synthesized LC-PCL with different molecular weights. LC-PCL shows the narrow and single elution peak, indicating the narrow molecular weight distribution. The GPC curves has no elution peak of unfunctionalized PCL or H6CBP, indicating that the synthesized samples are functionalized PCL but not a mixture of PCL/functionalized PCL/H6CBP.

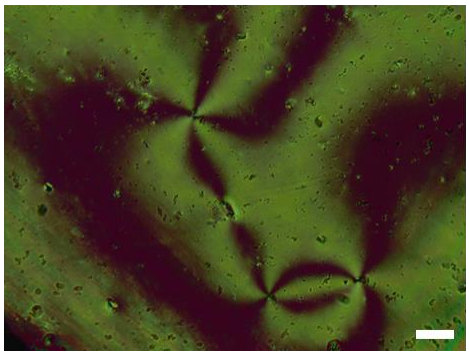


Fig. S4. POM image of H6CBP after cooling from 120 to 90 °C. Scale bar: 20 μm.

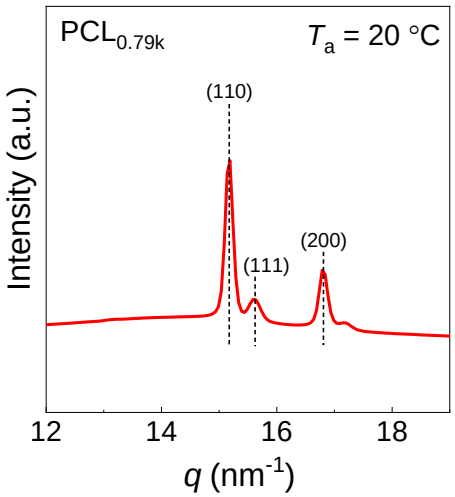


Fig. S5. WAXS pattern of nonfunctionalized $PCL_{0.79k}$ measured at 20 °C. Thermal history of the measured sample is: i) melting at 80 °C for 3 min; ii) cooling to 20 °C at 100 °C/min; iii) annealing at 20 °C for 6 h.

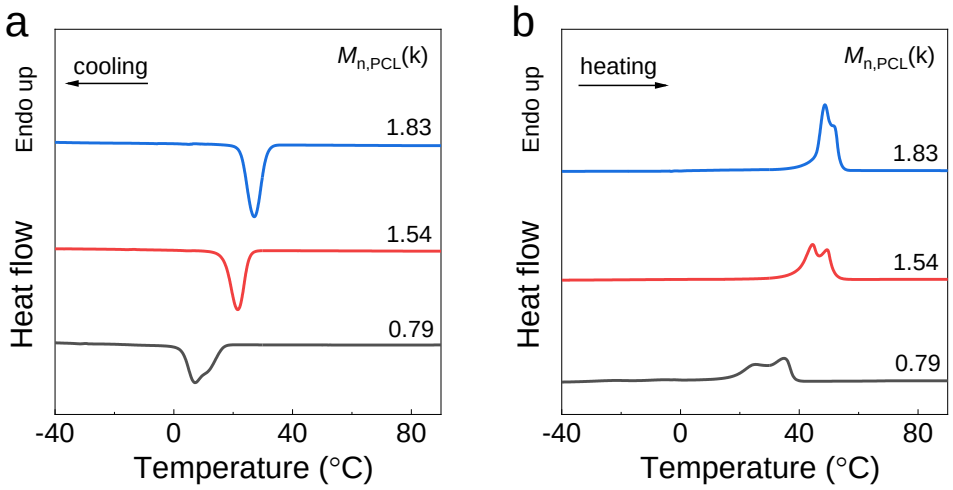


Fig. S6. DSC curves of nonfunctionalized PCLs with various $M_{n,PCL}$ values: (a) collected during cooling (10 °C/min) from 80 to –70 °C; (b) collected upon subsequent heating (10 °C/min) from –70 to 80 °C.

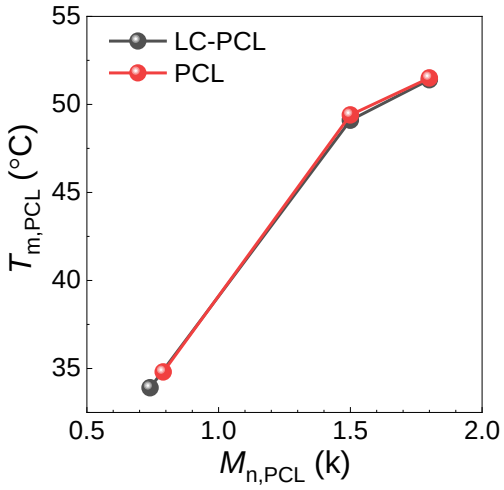


Fig. S7. Plot of the melting temperature ($T_{m,PCL}$) of PCL crystals in LC-PCLs and nonfunctionalized PCLs against $M_{n,PCL}$.

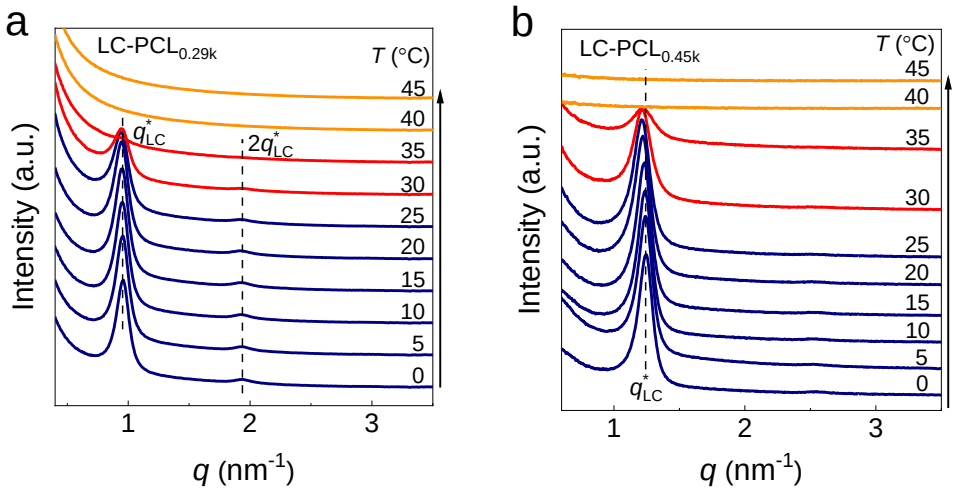


Fig. S8. Temperature-variable SAXS profiles of LC-PCL collected during heating from 0 °C at 10 °C/min: (a) LC-PCL$_{0.29k}$, (b) LC-PCL$_{0.45k}$. Thermal history of the measured sample is: i) melting at 80 °C for 3 min; ii) cooling to 20 °C at 100 °C/min; iii) annealing at 20 °C for 6 h.

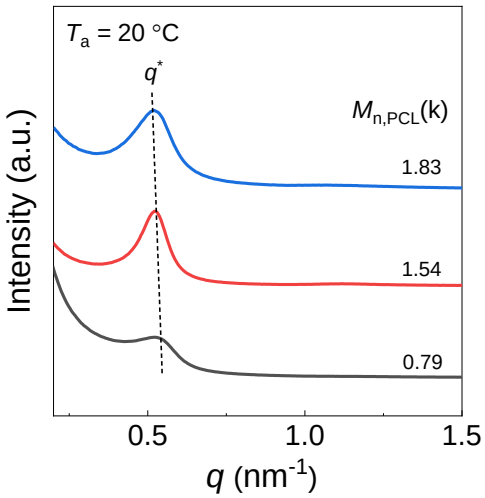


Fig. S9. SAXS patterns of nonfunctionalized PCLs with various $M_{n,PCL}$ values measured at 20 °C. Thermal history of the measured sample is: i) melting at 80 °C for 3 min; ii) cooling to 20 °C at 100 °C/min; iii) annealing at 20 °C for 6 h.

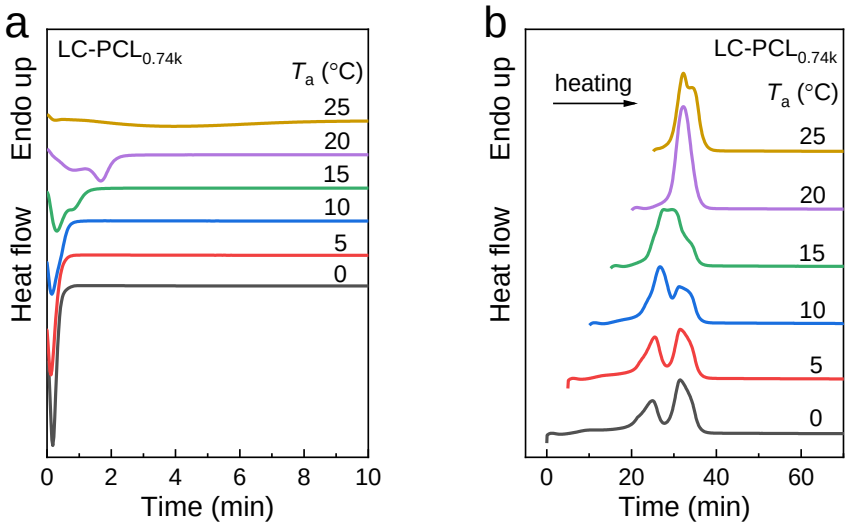


Fig. S10. DSC results of LC-PCL$_{0.74k}$ after annealing at various T_a values from the melt state: (a) DSC curves collected during annealing; (b) DSC curves collected upon subsequent heating at 10 °C /min.

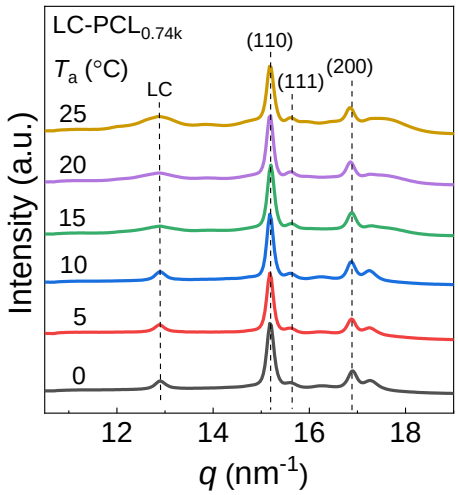


Fig. S11. WAXS patterns of LC-PCL$_{0.74k}$ annealed at various T_a values. Thermal history of the measured sample is: i) melting at 80 °C for 3 min; ii) cooling to indicated T_a at 100 °C/min; iii) annealing at indicated T_a values for 6 h.

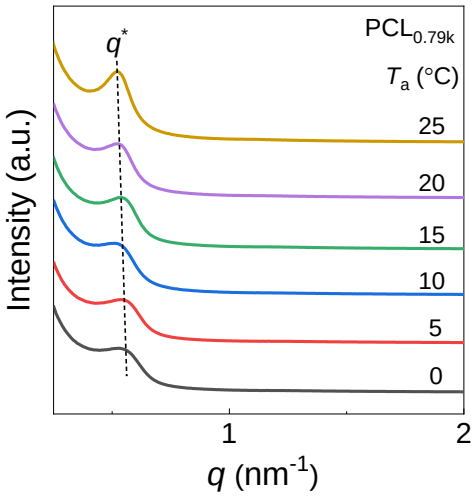


Fig. S12. SAXS pattern of nonfunctionalized PCL$_{0.79k}$ annealed at various T_a values. Thermal history of the measured sample is: i) melting at 80 °C for 3 min; ii) cooling to indicated T_a at 100 °C/min; iii) annealing at indicated T_a values for 6 h. All SAXS profiles were measured at 20 °C.