Supplementary Information

The role of entanglement in crystallization and melting of cyclic poly(ϵ-caprolactone)s

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1. Materials

Materials-Synthesis of PCL

ε-Caprolactone (ε-CL) (99%), purchased from ACROS. 9-anthracene methanol (98%), dibutyldimethoxytin (98%), 1,4-butanediol (99%), p-nitrobenzoyl chloride (98%), and stannous octoate $Sn(Oct)_2$ (95%) were purchased from Aladdin (China). Toluene (99.5%), methanol (99.5%), and methylene chloride (99%) were from Huadong Reagent Plant (China). All reagents were purified before use.

2. Experimental Techniques

1H nuclear magnetic resonance（1H NMR）Spectroscopy Measurement

After the sample was dissolved in $CDCl_3$ at room temperature, the 1H NMR spectrum was tested on a Bruker AV400 NMR spectrometer (400 MHz for 1H, Bruker BioSpin Co., Switzerland). The tetramethylsilane (TMS) internal standard is used as a reference for chemical shift and is set to 0 ppm.

Gel Permeation Chromatography (GPC) Measurement

Tetrahydrofuran (THF) was used as the mobile phase (flow rate, 1.0 mL/min) at 30 °C, after calibration with polystyrene as the standard, the PL-GPC 220 device (Agilent, Germany) was used to determine molecular weight and dispersibility.

3. Synthesis of cyclic PCLs

Cyclic PCLs with different molecular weights were synthesized with reference to Kricheldorf's protocol[1,2], as shown in the synthetic route (Scheme S1).

3.1 Preparation of 2,2-Dibutyl-2-stanna-I,3-dioxepane(DSDOP)

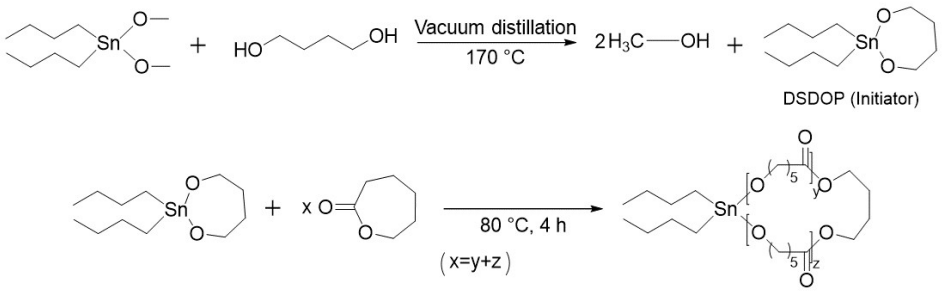
A mixture of 19.17 g (65 mmol) dibutyldimethoxytin and 5.86 g (65 mmol) 1,4-butanediol was heated to 170°C with stirring. Methanol was distilled off continuously. After cooling, the purified product was obtained by distillation under reduced pressure at 170°C.

3.2 Preparation of cyclic PCLs

Different ratios of caprolactone and DSDOP were placed in a 50 ml reaction tube at 80 °C for 4 h. After the reaction, the product was dissolved in CH_2Cl_2 (50 mL), then precipitated into cold methanol (5-6 °C), isolated by filtration and then dried under vacuum at 40 °C.

The sample information is shown in Table S1. The molecular structure information was tested by 1H NMR spectroscopy, molecular weight and dispersibility of the samples are tested by GPC.

4. Figures and tables



Scheme S1. Synthetic routes of cyclic PCLs.

Table S1. Molecular properties of PCLs

Sample	$M_{n,GPC}$[a] (KDa)	PDI[b]
c-PCL-8	8.09	1.30
c-PCL-11	10.98	1.42
c-PCL-16	15.97	1.49
c-PCL-19	19.07	1.38
c-PCL-32	32.46	1.39
c-PCL-37	36.59	1.48

[a]M_n of polymer measured by GPC. [b]polydispersity index (PDI) of polymer measured by GPC.

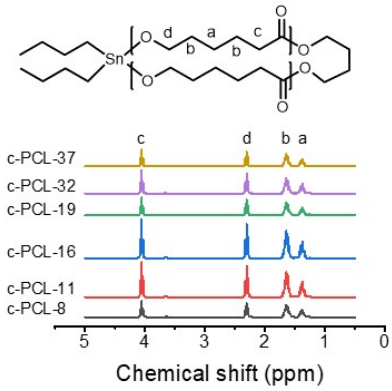


Fig. S1. 1H NMR spectrum of cyclic PCLs.

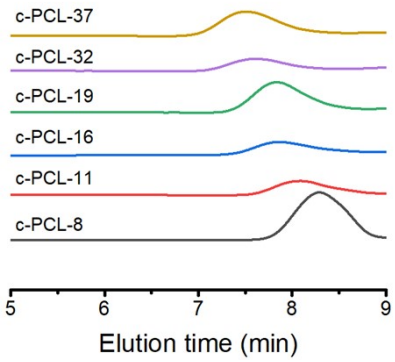


Fig. S2. GPC traces of cyclic PCLs.

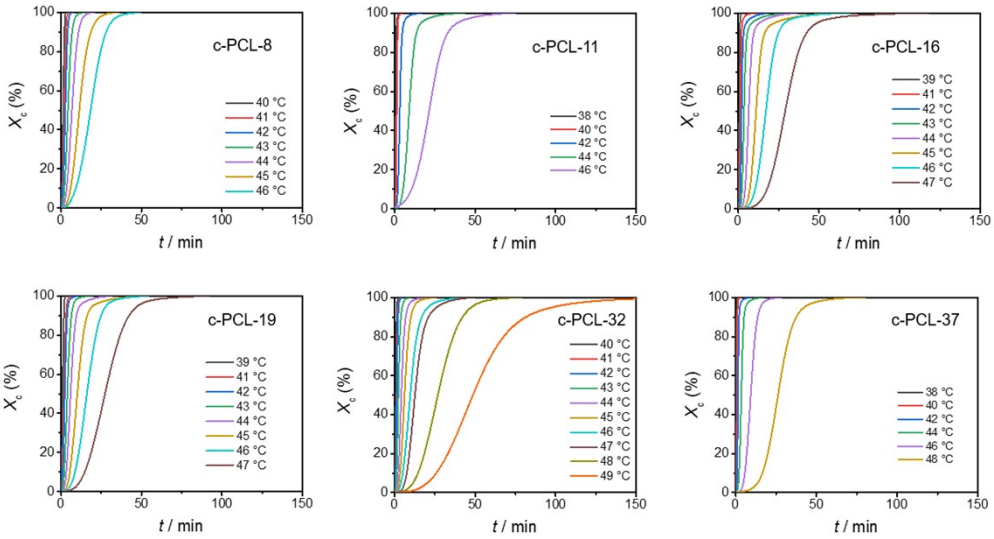


Fig. S3. Development of the crystallinity of the indicated samples over time.

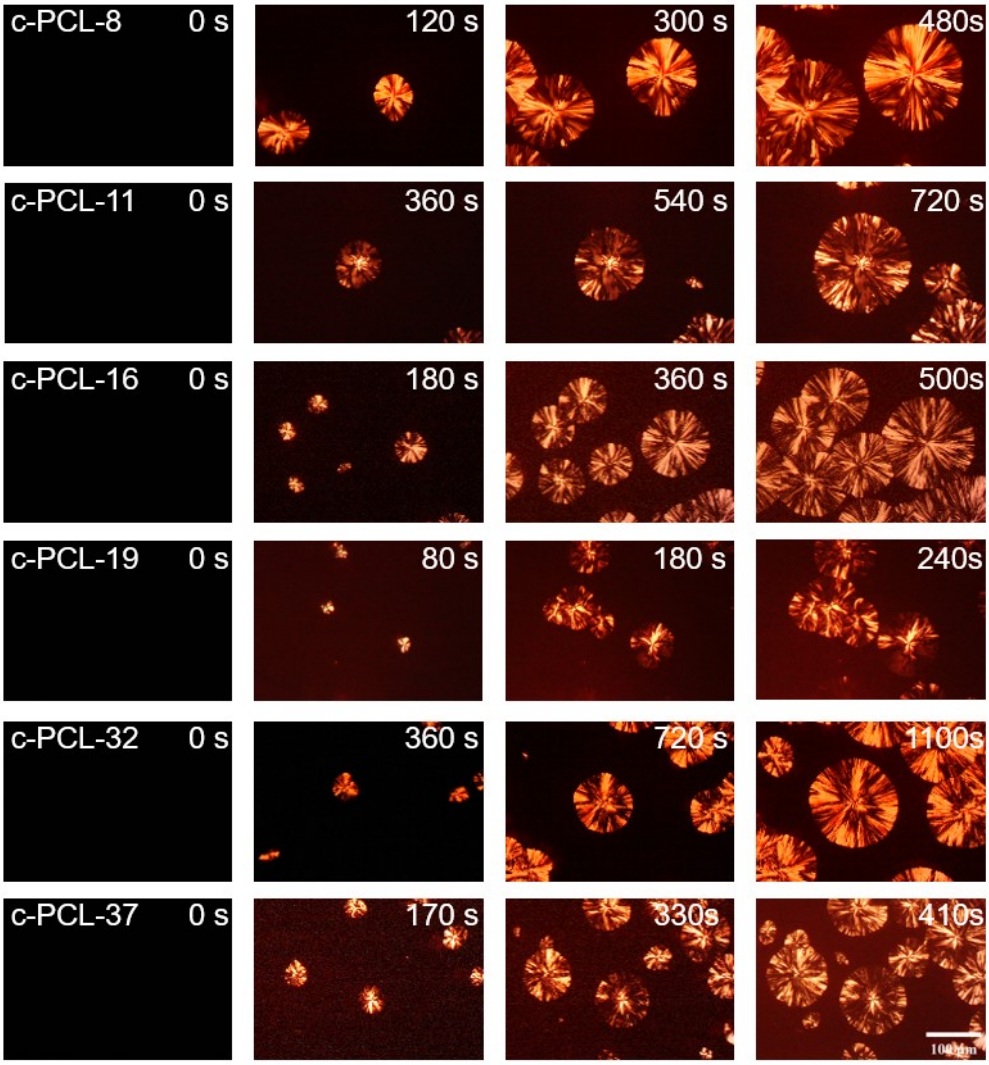


Fig. S4. POM images of the indicated samples in isothermal crystallization at 40 °C. Scale bar, 100 μm.

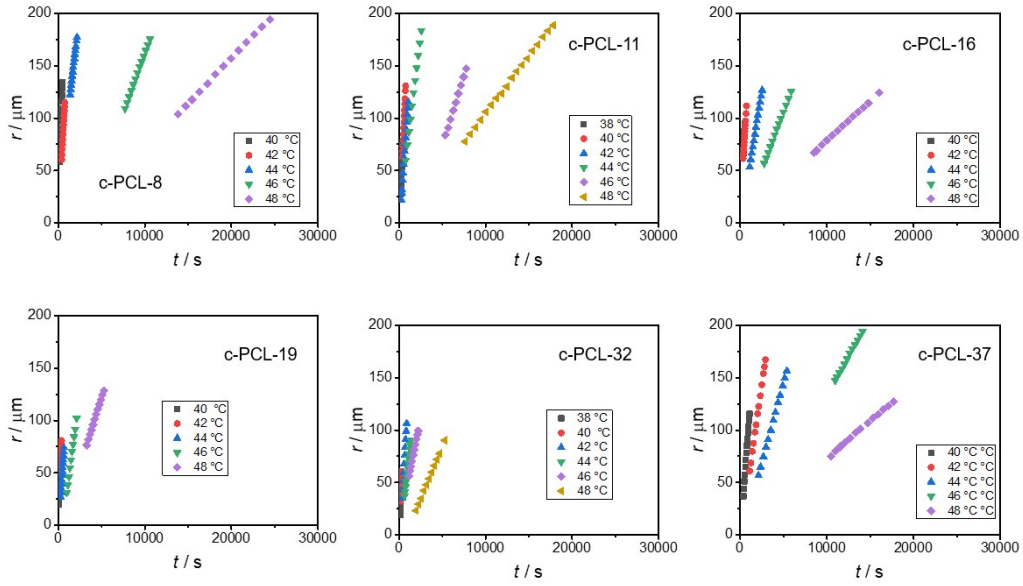


Fig. S5. Spherulite growth of cyclic PCLs in isothermal crystallization.

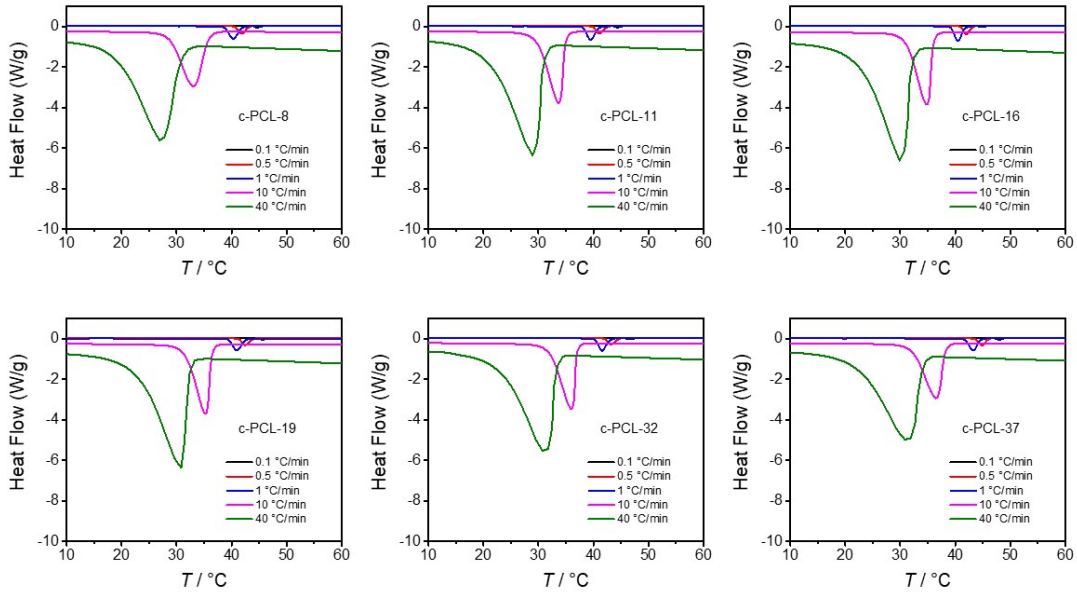


Fig. S6. DSC exothermic curves of cyclic PCLs under different cooling rates.

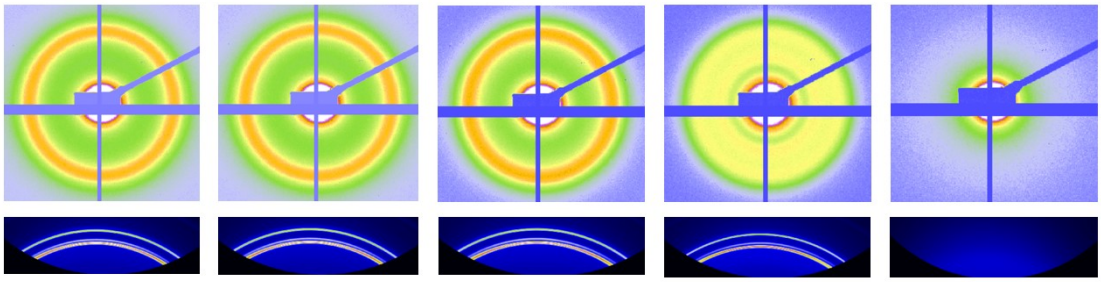


Fig. S7. 2D profiles of c-PCL-8 detected by time-dependent simultaneous SAXS/WAXS after isothermal crystallization at 40 °C.

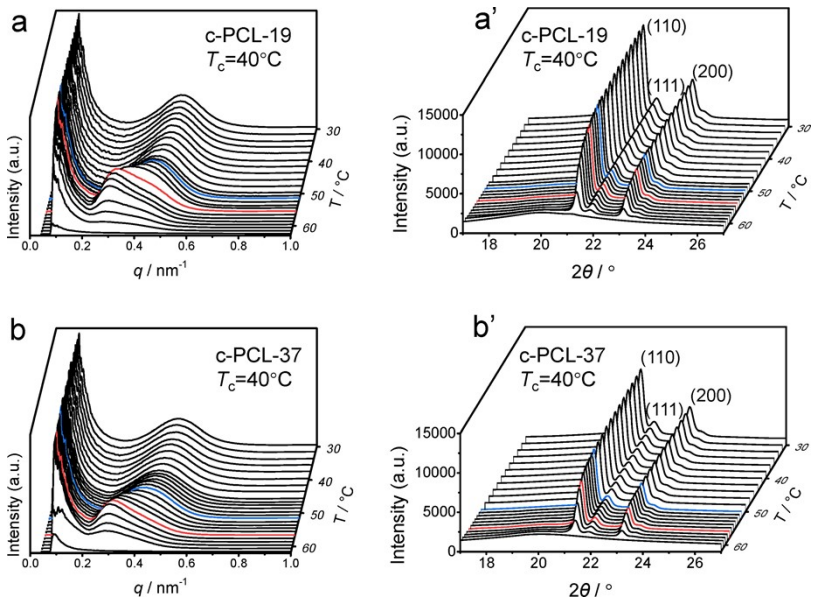


Fig. S8. SAXS and WAXS profiles recorded simultaneously during heating (2 ◦C/min) of the indicated samples after isothermal crystallization at the indicated temperatures.

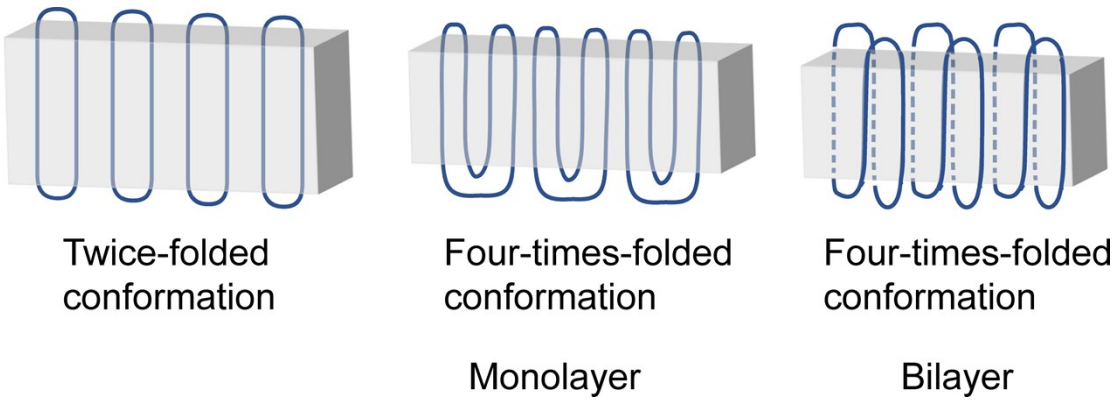


Fig. S9. Schematic drawing to show possible conformations of cyclic polymers.

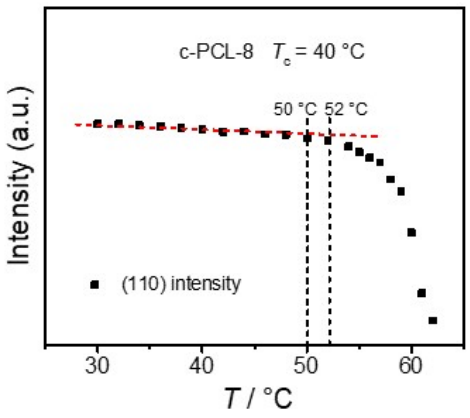


Fig. S10. (110) intensity of the indicated samples in heating after isothermal crystallization at 40 °C.

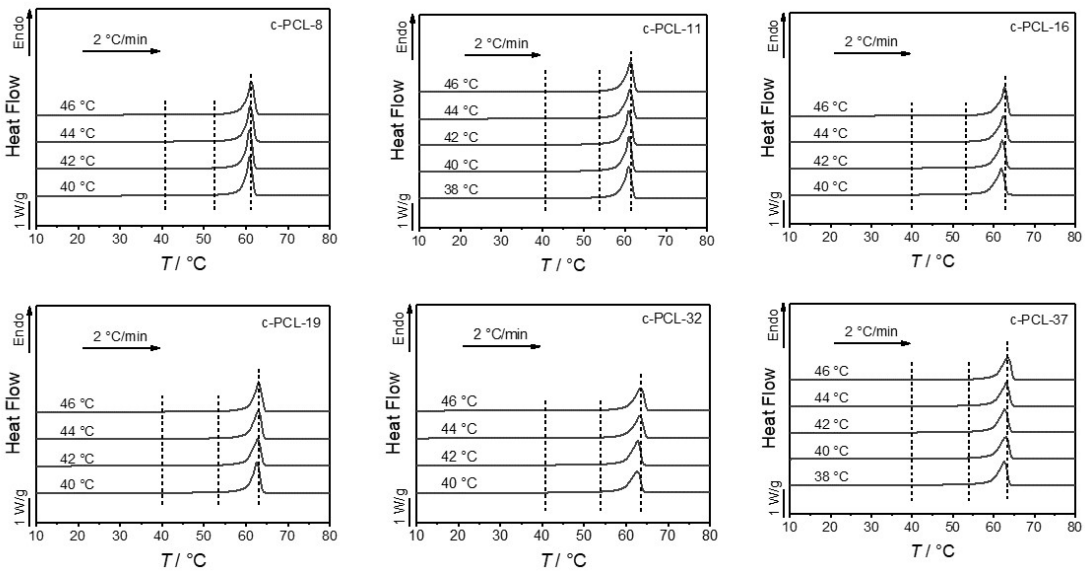


Fig. S11. DSC curves of the indicated samples heated at 2 °C/min.

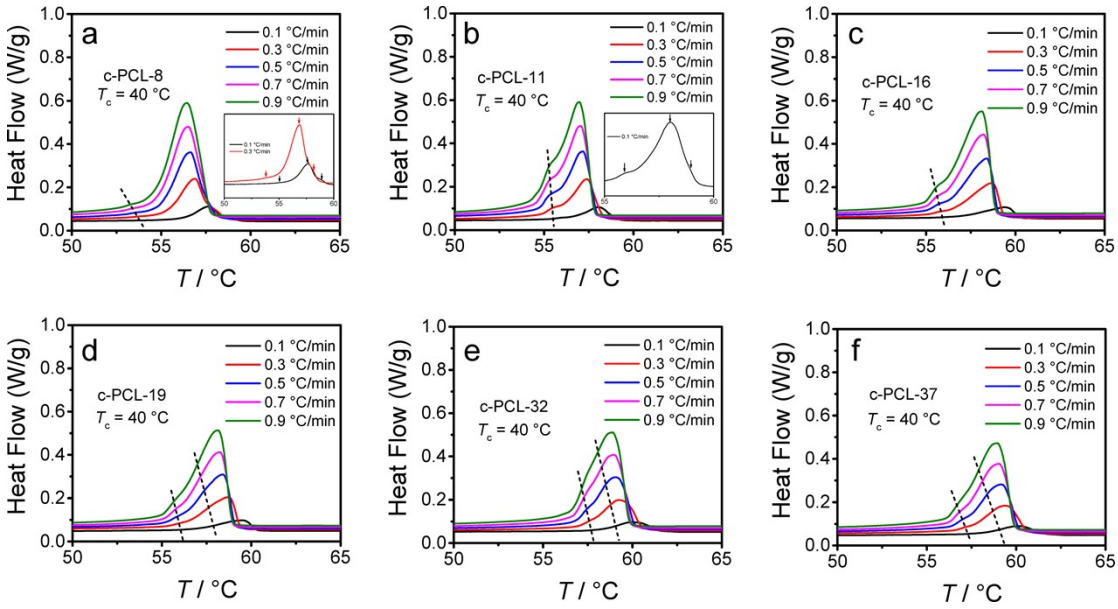


Fig. S12. DSC curves of the indicated samples in slow heating. Endothermic upward.

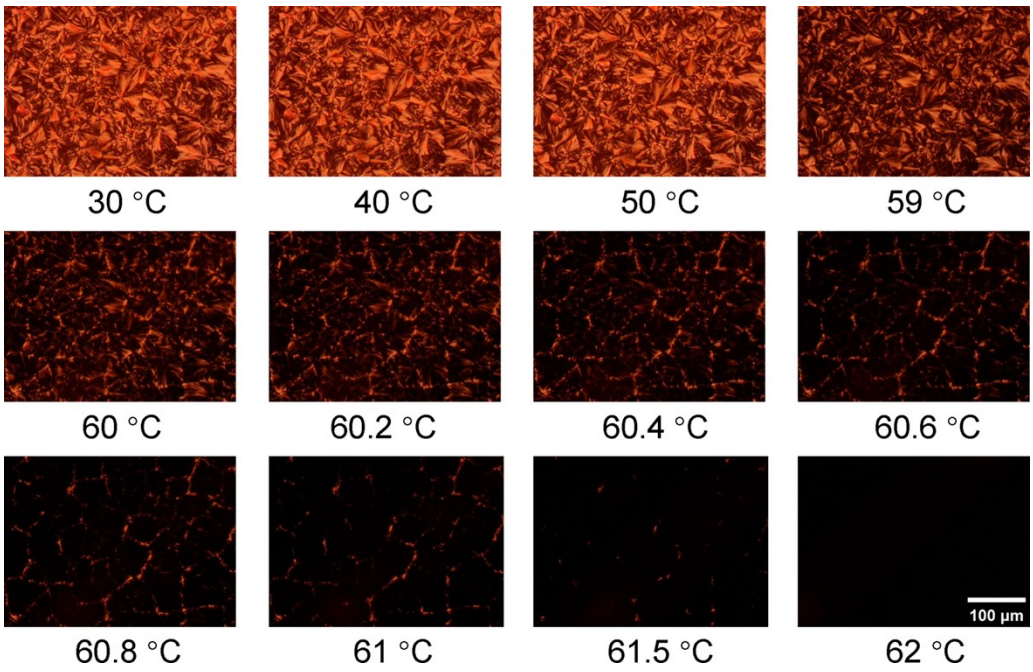


Fig. S13. POM images of c-PCL-32 under heating (2 °C/min) after isothermal crystallization at 40 °C.

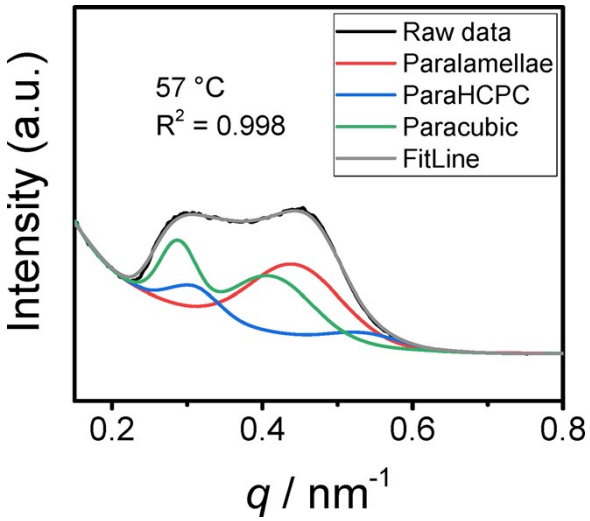


Fig. S14. Fitting results of SAXS data of c-PCL-8.

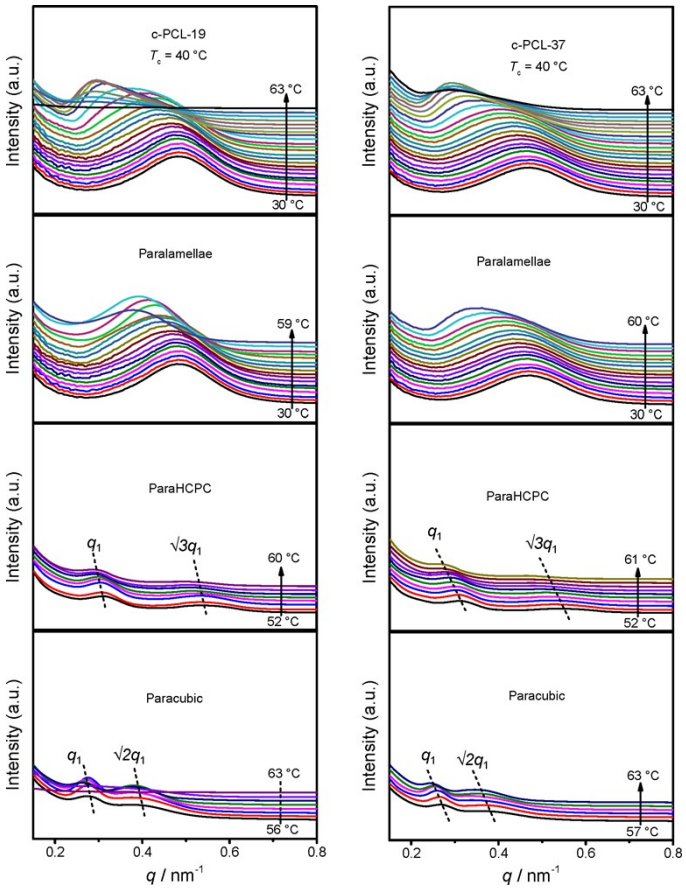


Fig. S15. Fitting scattering profiles based on the recorded SAXS data indicate structure evolution during heating: paralamellae, paraHCPC and paracubic structures.

References

1 H. R. Kricheldorf and S. Eggerstedt, *Macromol. Chem. Phys.*, 1998, **199**, 283–290.

2 H. R. Kricheldorf and K. Hauser, *Macromolecules*, 1998, **31**, 614–620.