Supplementary information for

Effects of end groups and entanglements on crystallization and melting behaviors of poly(ϵ-caprolactone)

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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 CDCl3 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 PCLs with different end groups

Synthesis of anthracenyl-modified PCLs

Refer to the methods of Wang[1] and Yamamoto[2] to synthesize PCLs with anthracenyl end groups, as shown in synthetic route 1 (Scheme S1). In a 25 mL reaction tube, add the initiator 9-anthracene methanol and caprolactone under argon protection, and finally, add the catalyst Sn(Oct)2 and solvent toluene. After reacting at 110 °C for 24 hours, the experiment was stopped. Argon was passed into the reaction tube and cooled to room temperature. After the product was precipitated in methanol (200 mL), the product was dissolved in dichloromethane and precipitated in methanol again. The dissolution and precipitation steps are repeated to fully remove impurities, and the solid obtained by suction filtration through the filter membrane is then dried in a vacuum oven (30 °C, 12 h), and finally a powdered polymer sample is obtained.

Synthesis of Nitrophenyl Modified PCLs

Nitrophenyl-modified PCLs were synthesized regarding Kricheldorf's protocol[3,4], as shown in the synthetic route 2 (Scheme S1).

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

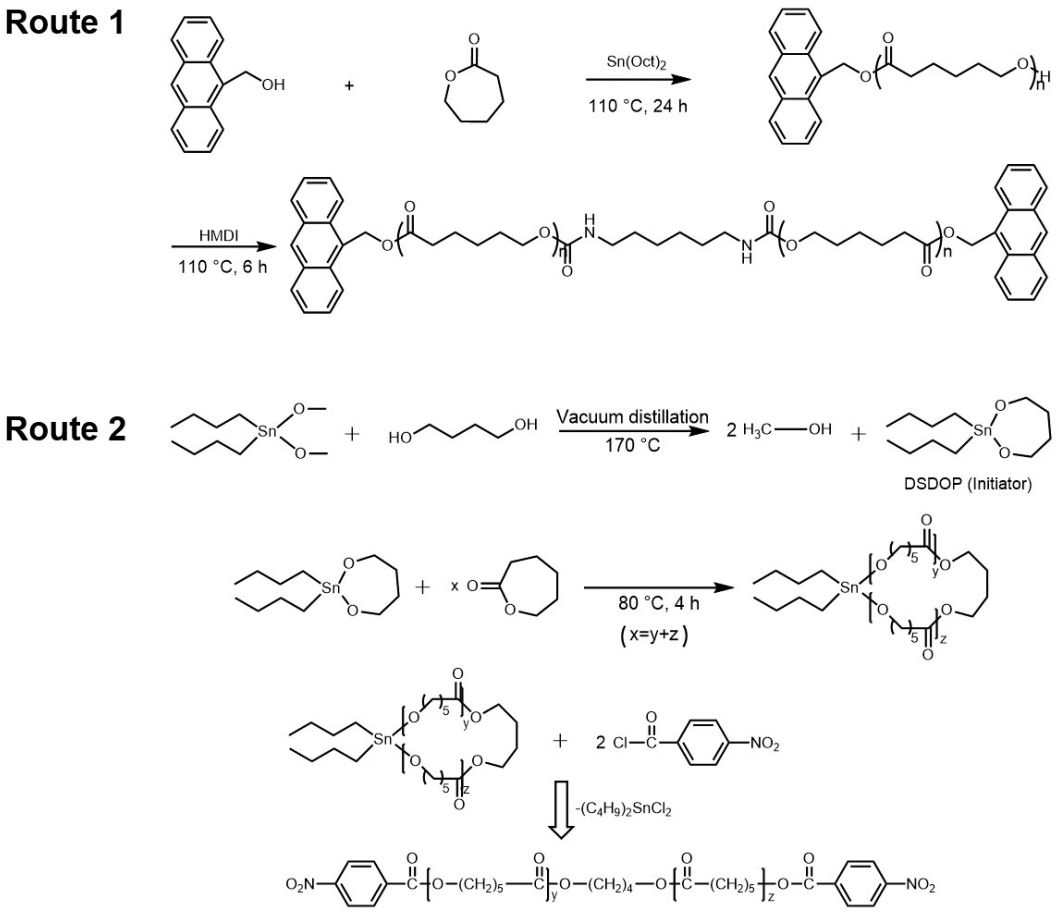
A mixture of 19.17 g (65 mmol) dibutyldimethoxytin and 5.86 g (65 mmol) 1,4-butanediol was heated to 170°C with stirring. Methanol was distilled continuously. After cooling, the purified product was obtained by distillation under reduced pressure

at 170°C.

Preparation of PCLs with nitrophenyl end groups
Different ratios of caprolactone and DSDOP were placed in a 50 ml reaction tube at 80 °C for 4 h. After the reaction, excess p-nitrobenzoyl chloride was added and the mixture continued to react at 80 °C for 6 h. Finally, the reaction 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 PCLs.

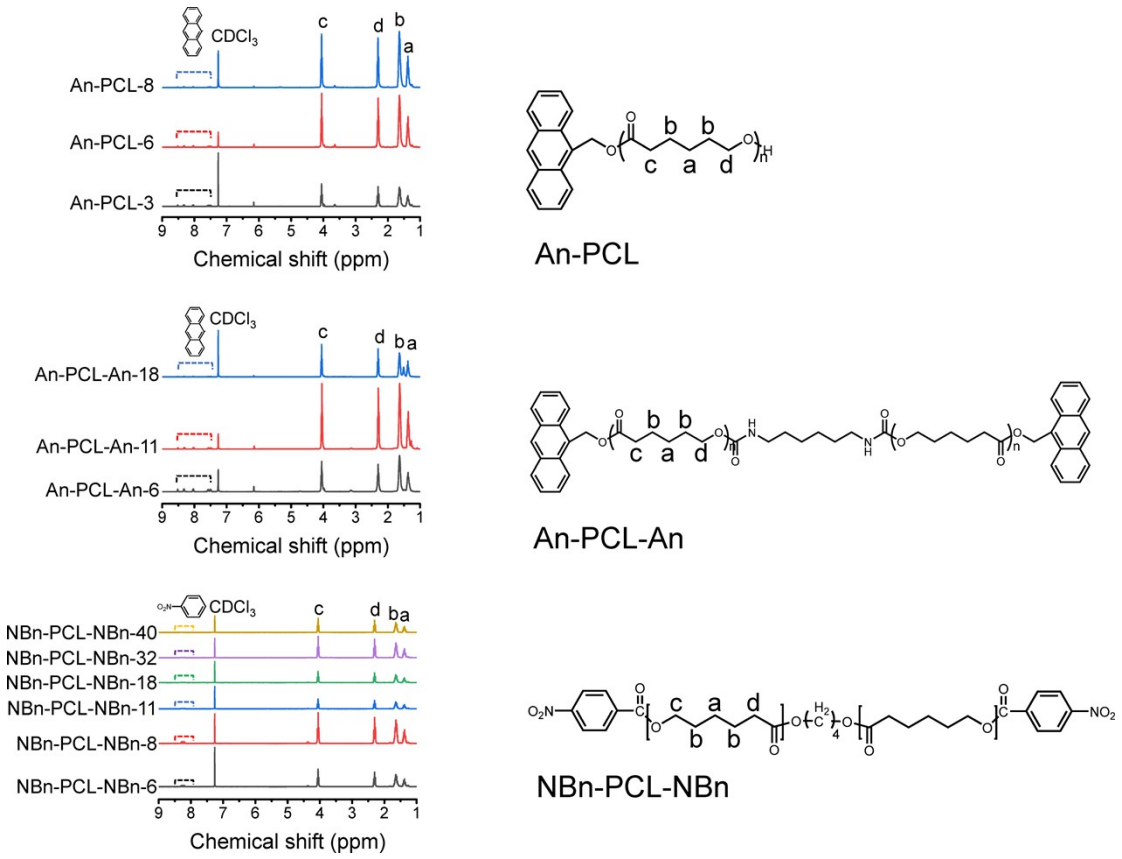


Fig. S1 1H NMR spectrum of PCLs.

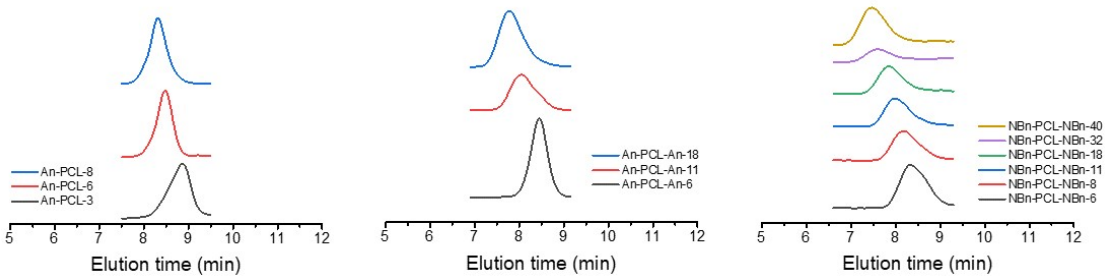


Fig. S2 GPC traces of PCLs.

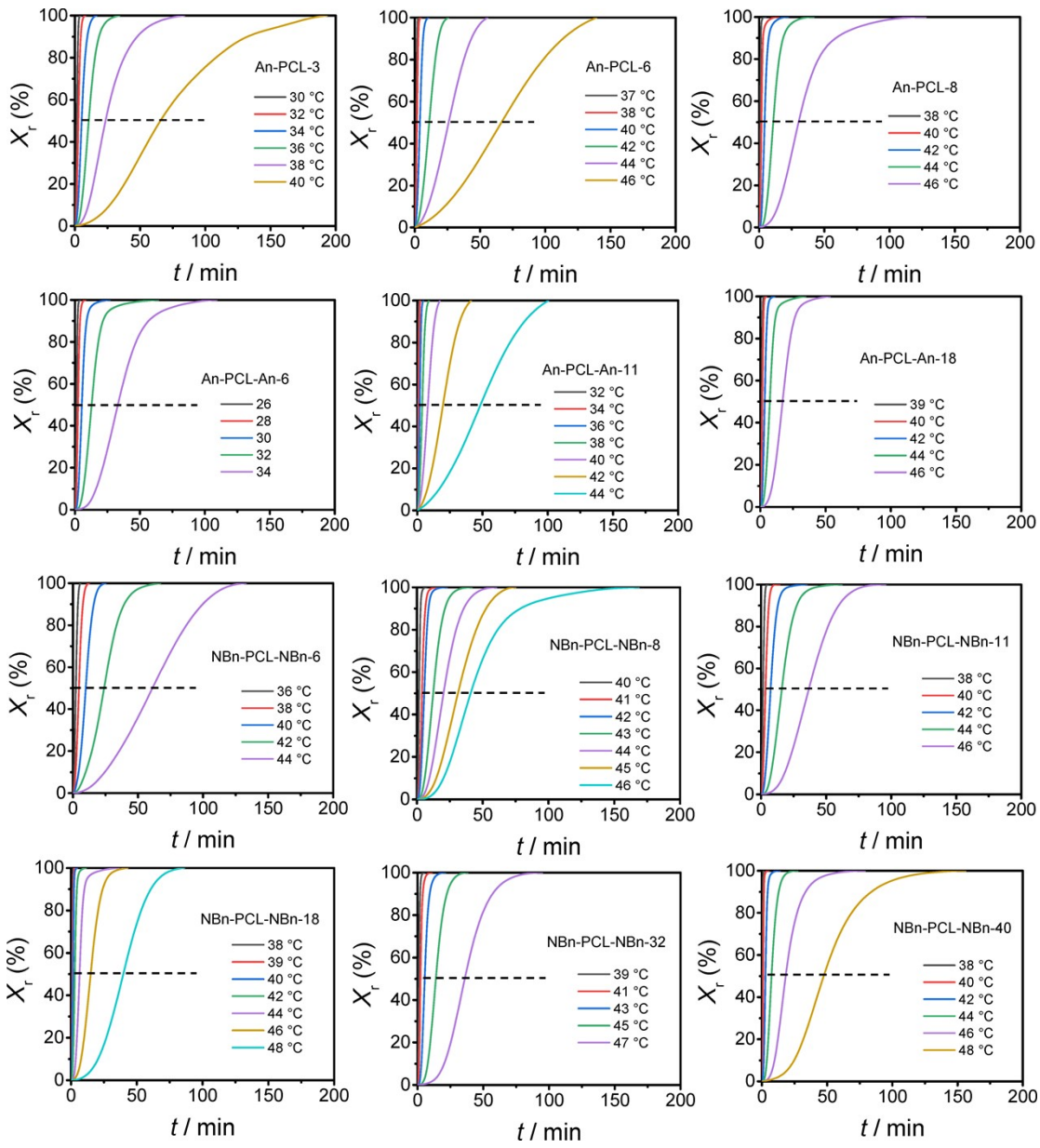


Fig. S3 Development of the relative crystallinity X_r of the indicated samples over time.

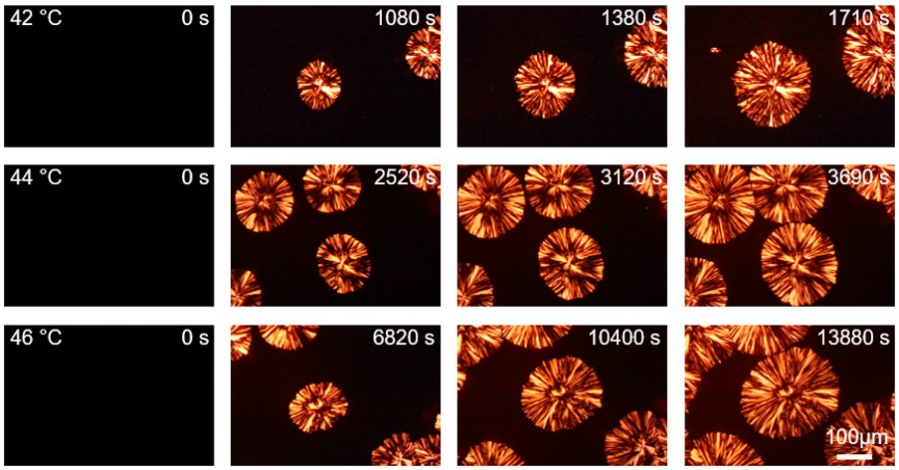


Fig. S4 Spherulite growth images of An-PCL-6 in isothermal crystallization at the indicated temperatures. The length of the scale bar is 100 μm.

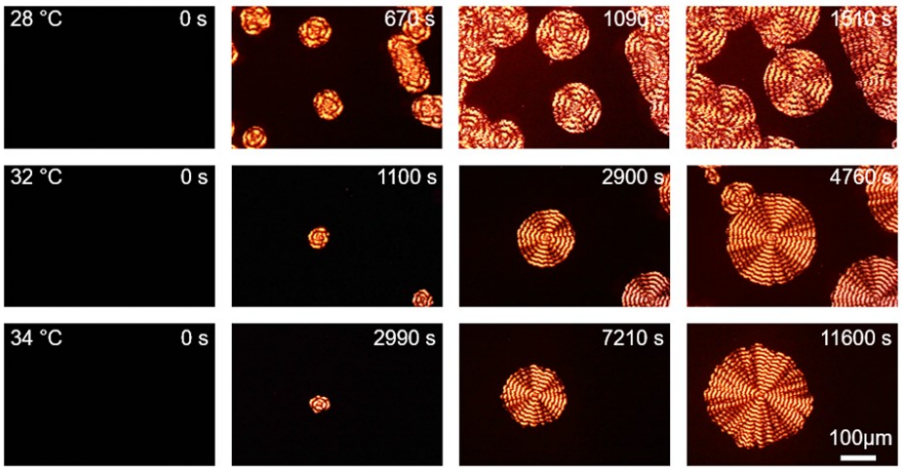


Fig. S5 Spherulite growth images of An-PCL-An-6 in isothermal crystallization at the indicated temperatures. The length of the scale bar is 100 μm.

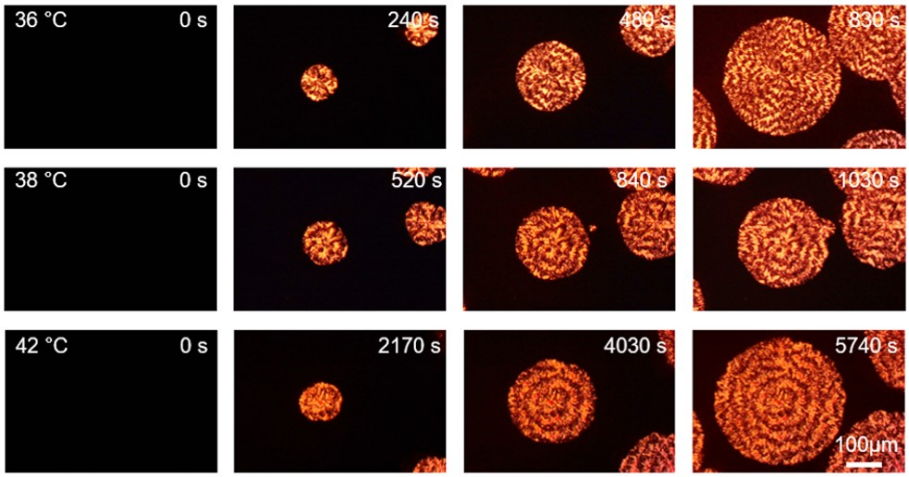


Fig. S6 Spherulite growth images of NBn-PCL-NBn-6 in isothermal crystallization at the indicated temperatures. The length of the scale bar is 100 μm.

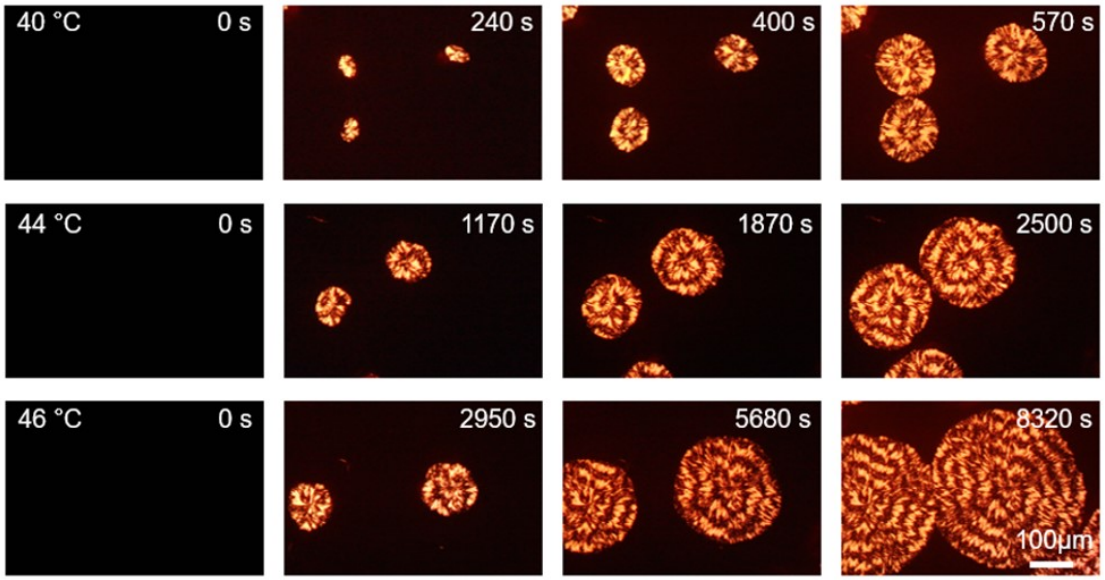


Fig. S7 Spherulite growth images of NBn-PCL-NBn-11 in isothermal crystallization at the indicated temperatures. The length of the scale bar is 100 μm.

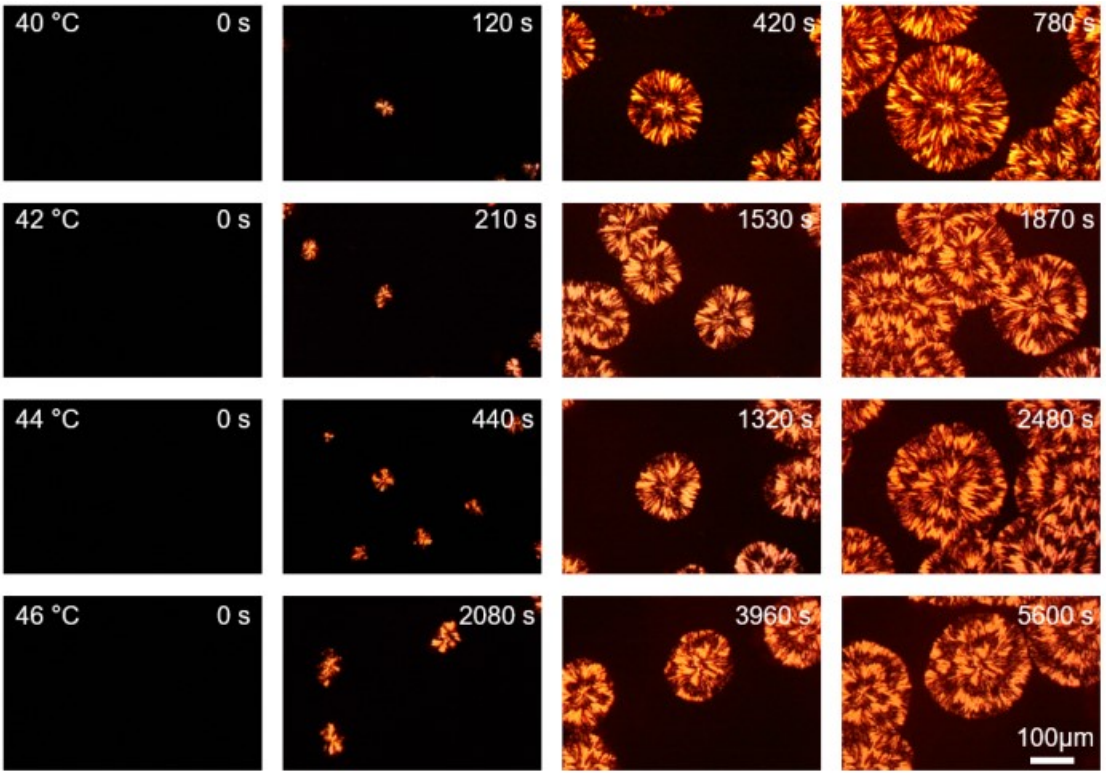


Fig. S8 Spherulite growth images of NBn-PCL-NBn-18 in isothermal crystallization at the indicated temperatures. The length of the scale bar is 100 μm.

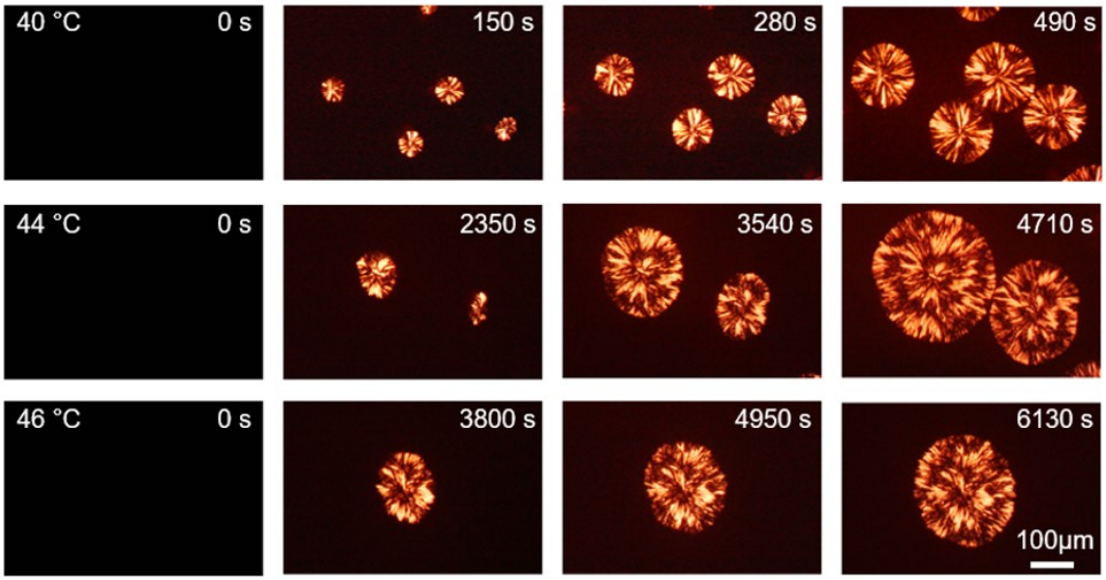


Fig. S9 Spherulite growth images of NBn-PCL-NBn-32 in isothermal crystallization at the indicated temperatures. The length of the scale bar is 100 μm.

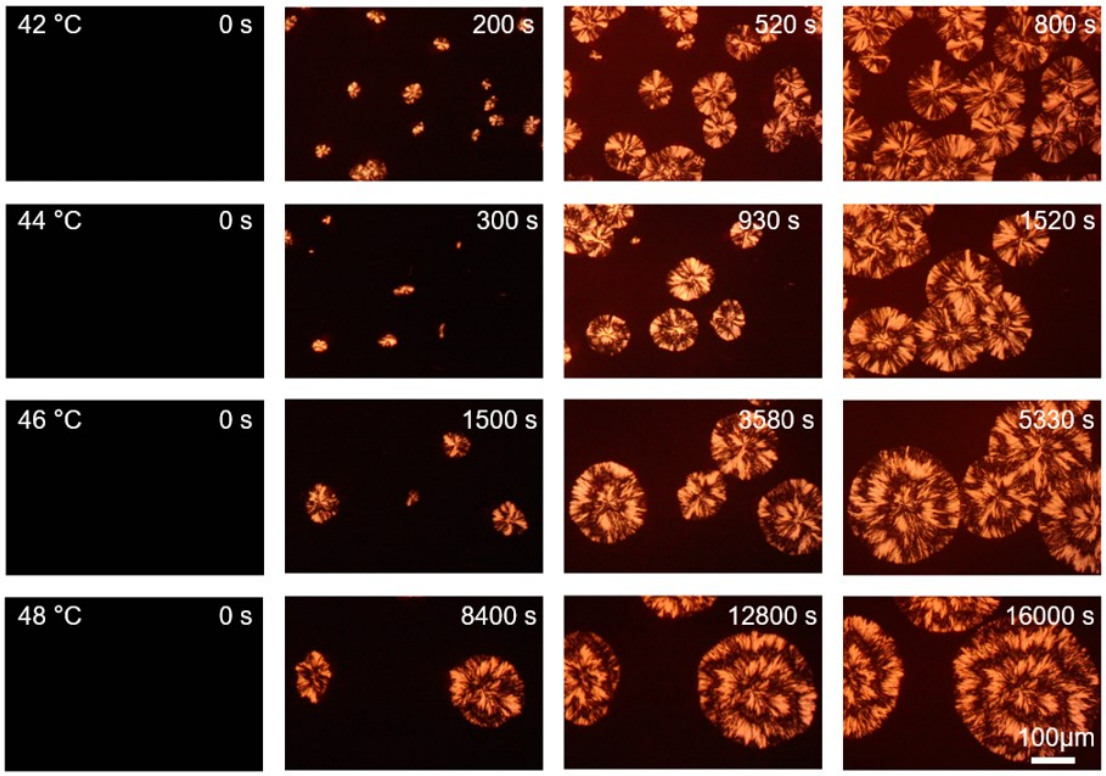


Fig. S10 Spherulite growth images of NBn-PCL-NBn-40 in isothermal crystallization at the indicated temperatures. The length of the scale bar is 100 μm.

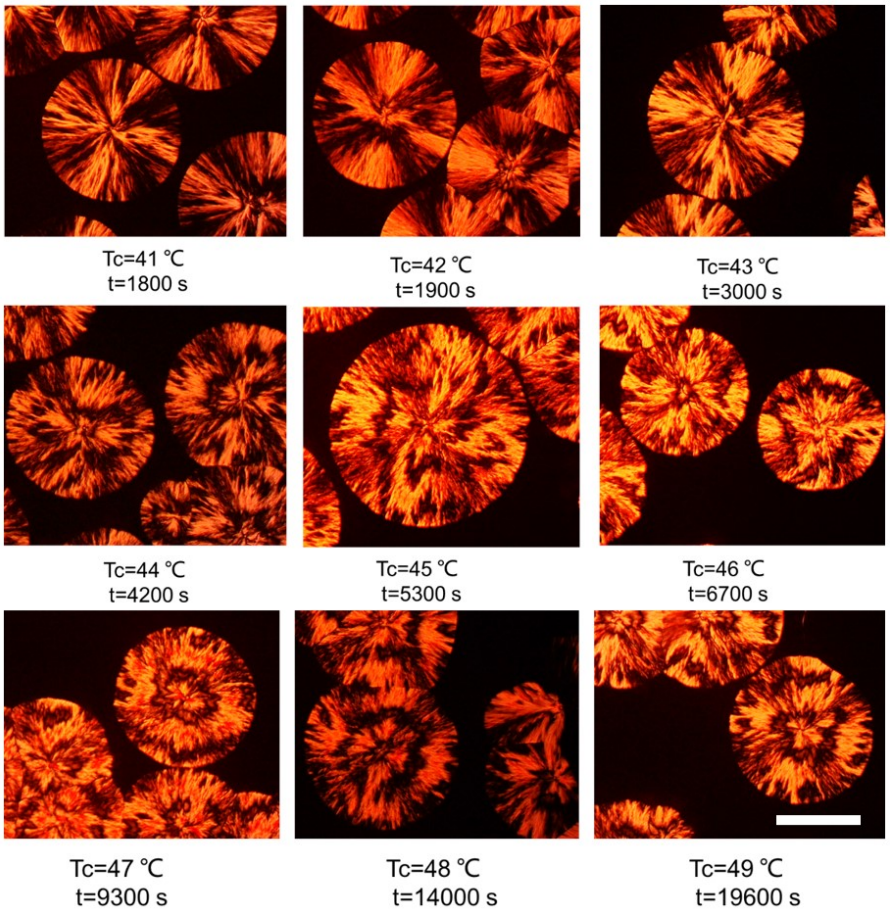


Fig. S11 Spherulite images of commercial PCL (M_n = 61 kg/mol) in isothermal crystallization at the indicated temperatures. The length of the scale bar is 100 μm.

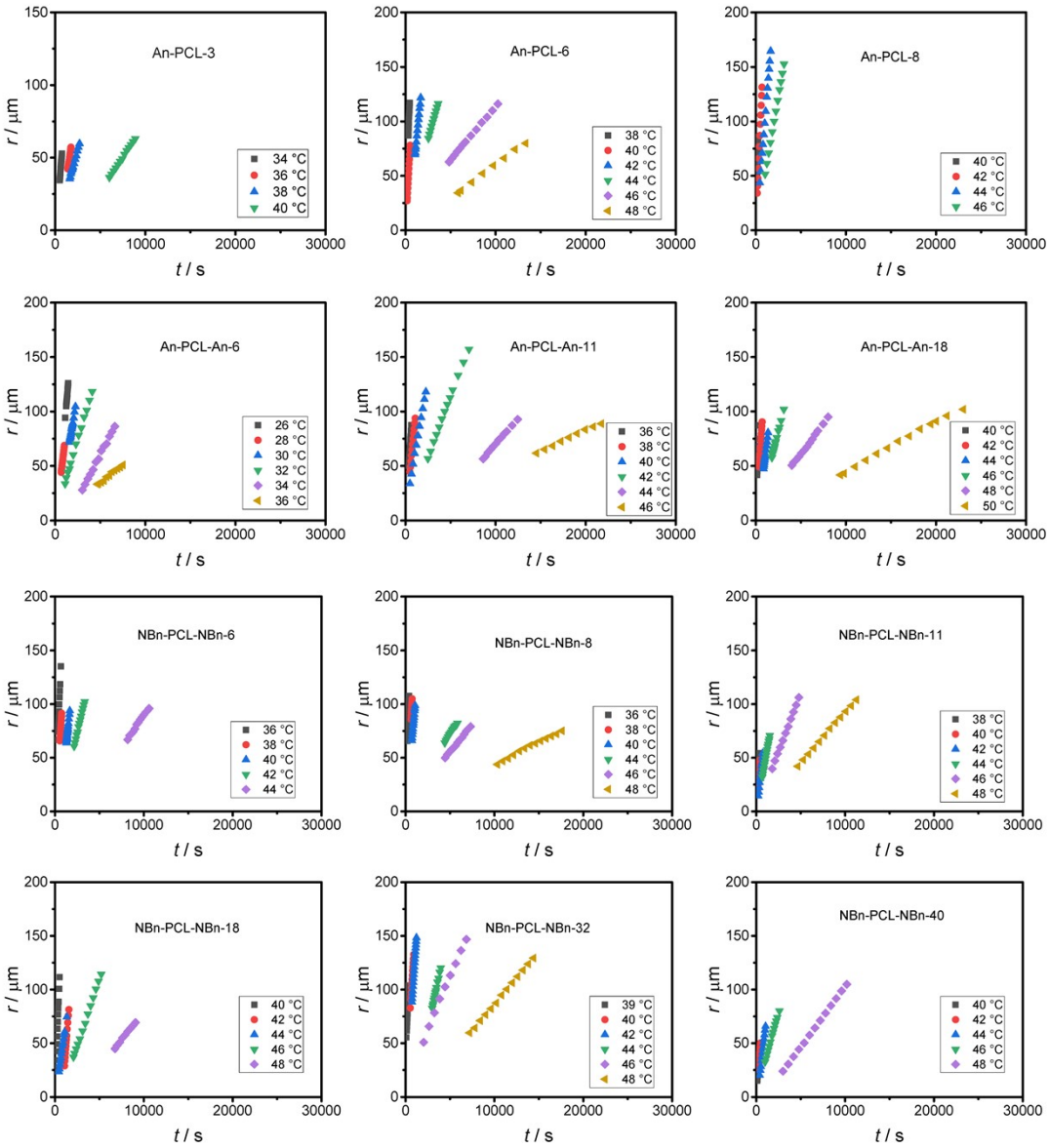


Fig. S12 Spherulite growth of the indicated samples in isothermal crystallization.

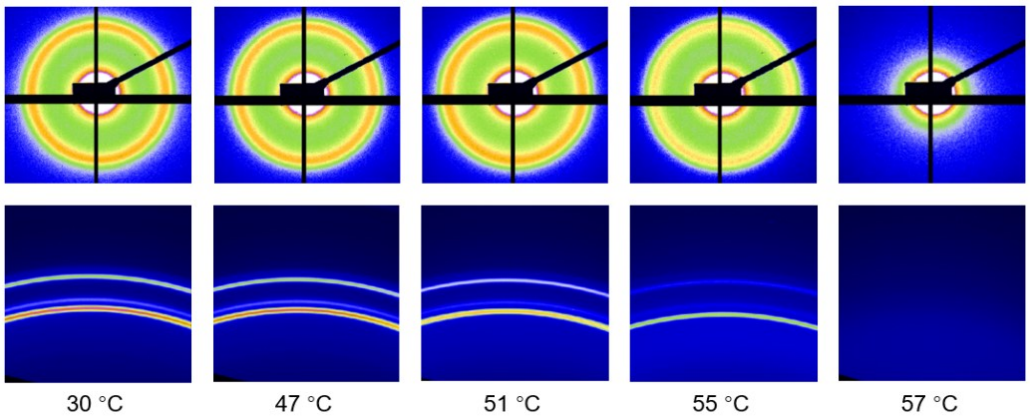


Fig. S13 2D profiles of An-PCL-6 detected by time-dependent simultaneous SAXS/WAXS after isothermal crystallization at 40 °C.

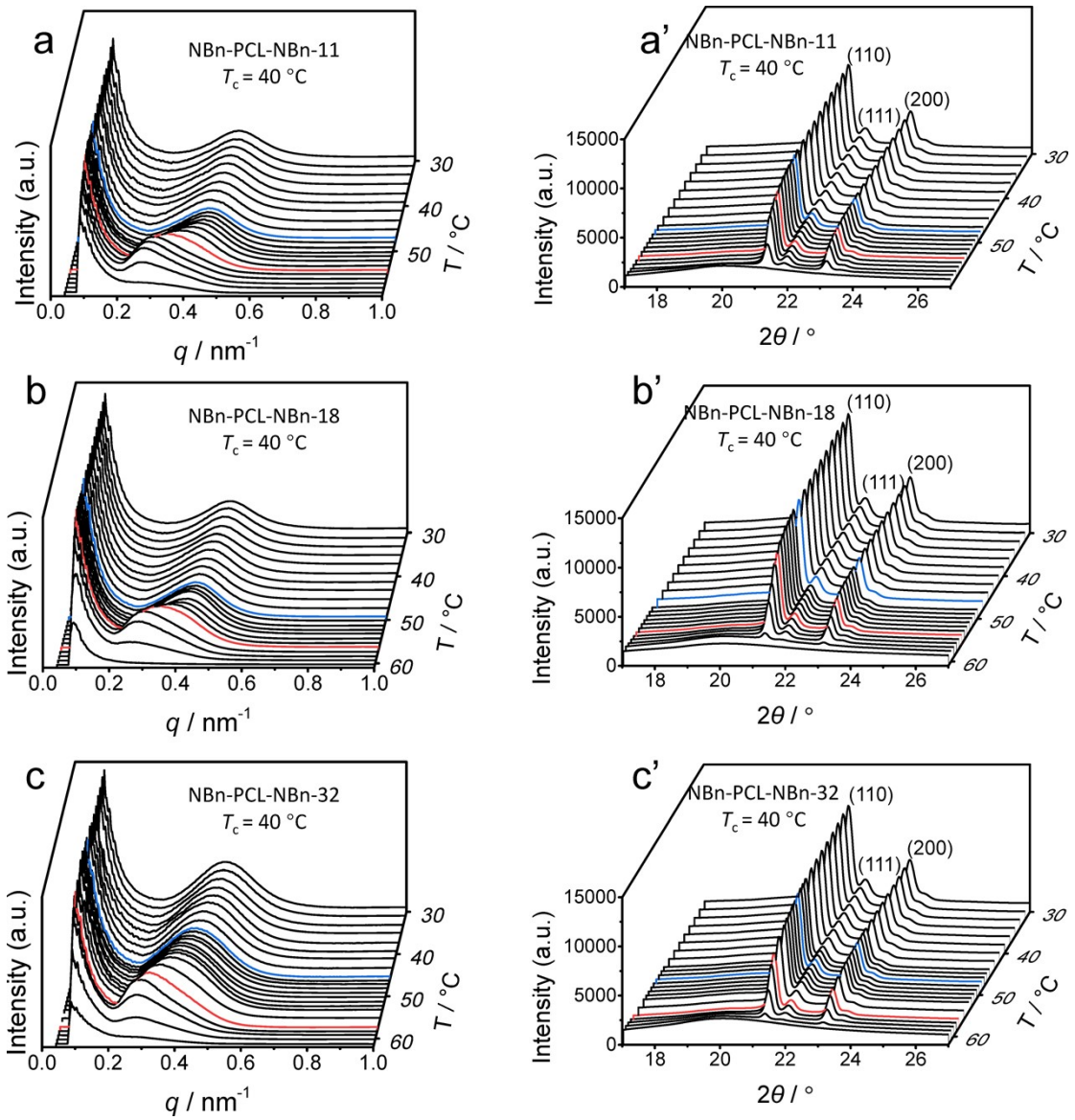


Fig. S14 SAXS and WAXS profiles were recorded simultaneously during heating (2 °C/min) of the indicated samples after isothermal crystallization at the indicated temperatures.

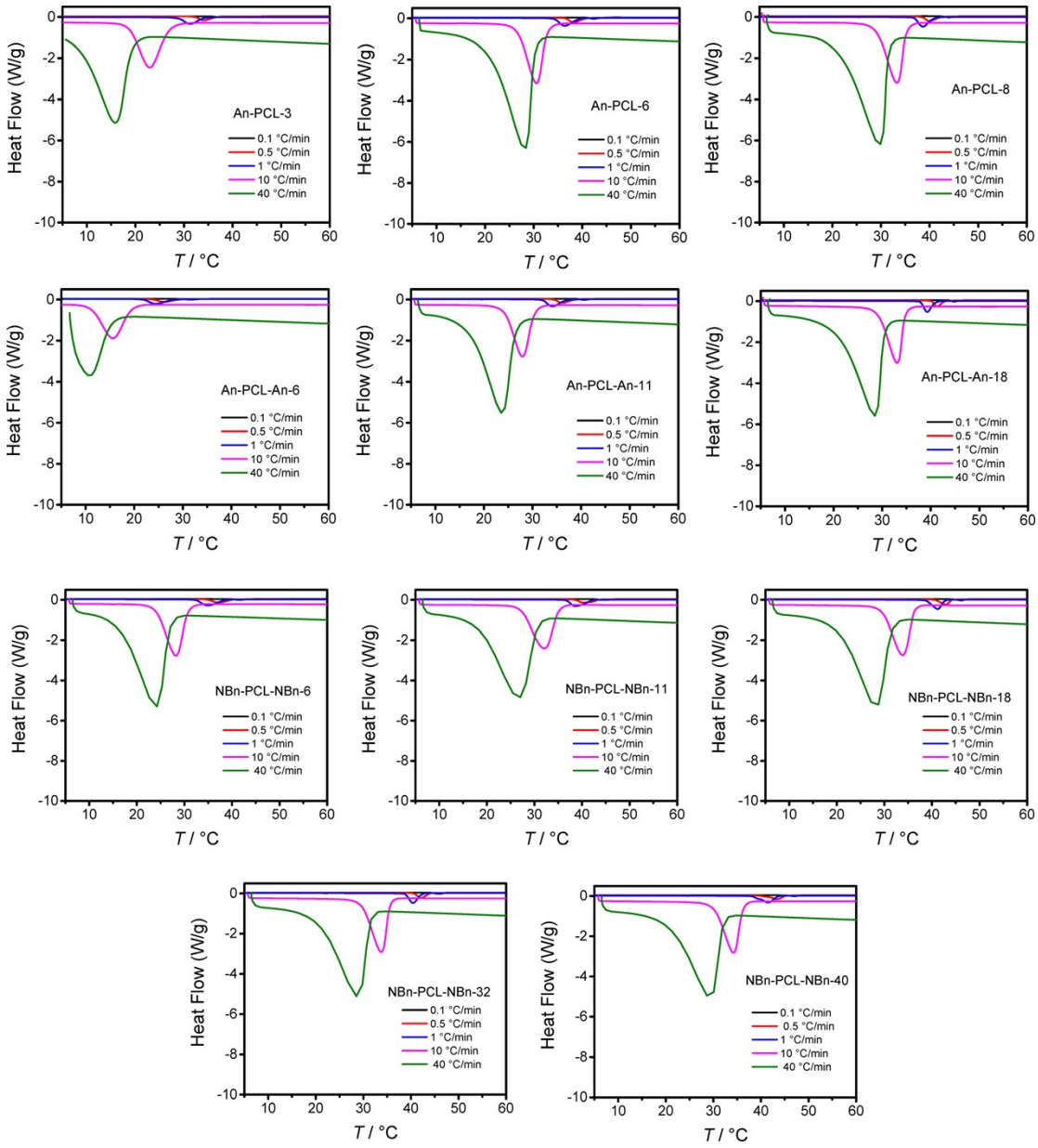


Fig. S15 DSC exothermic curves of the indicated samples at different cooling rates. Endothermic up.

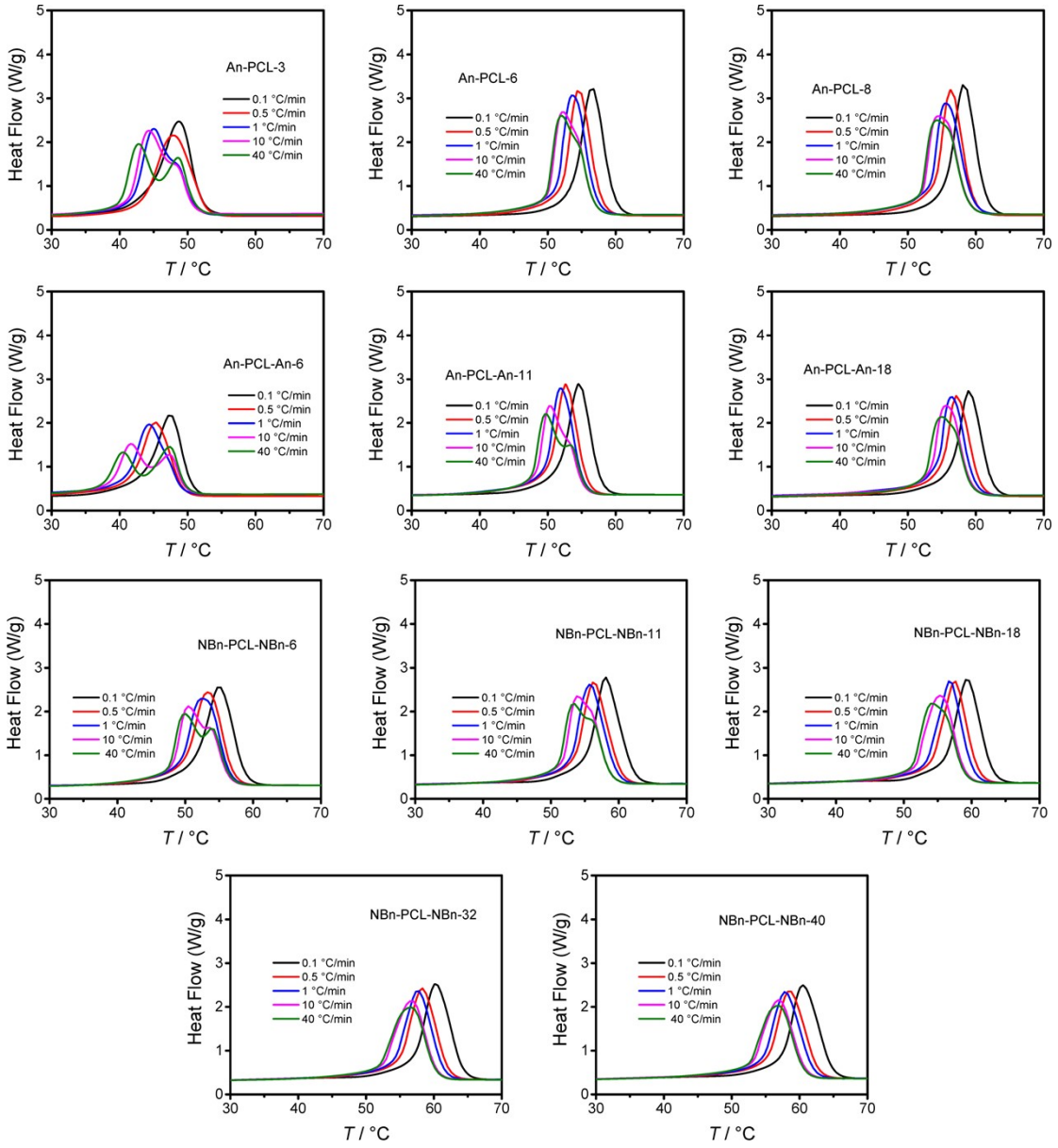


Fig. S16 DSC endothermic curves of the indicated samples during heating (10 °C/min) after cooling at different rates. Endothermic up.

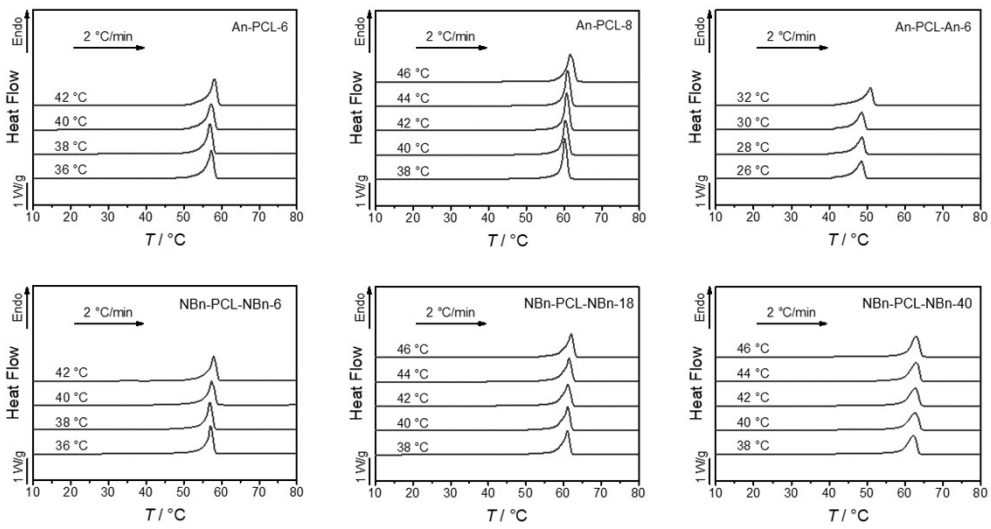


Fig. S17 DSC heating curves during heating (2 °C/min) of the indicated samples after isothermal crystallization at the indicated temperatures.

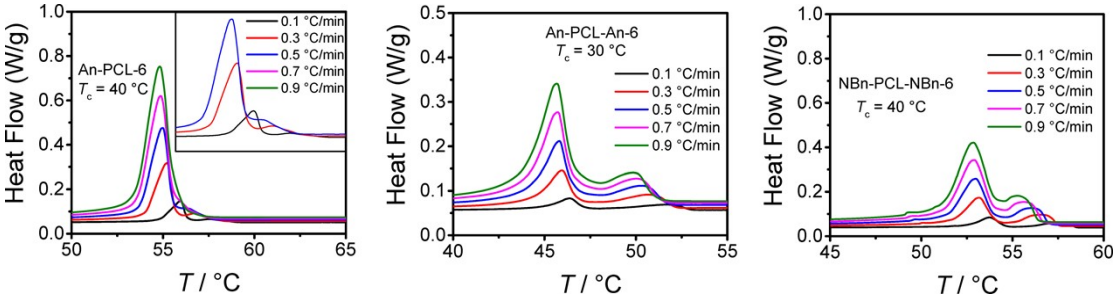


Fig. S18 DSC curves of the indicated samples in slow heating. An-PCL-6 including enlarged partial plots. Endothermic upward.

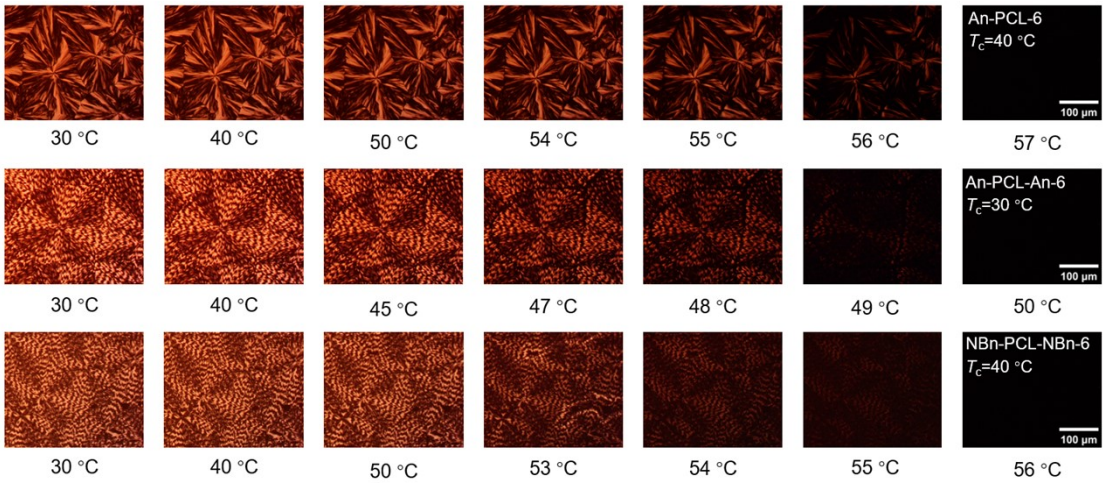


Fig. S19 POM images of the indicated samples in heating (2 °C/min) after isothermal crystallization at the indicated temperatures.

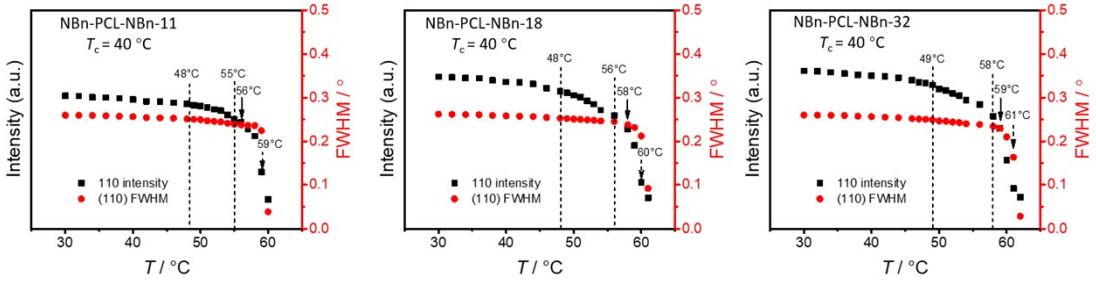


Fig. S20 110 intensity and (110) FWHM of the indicated samples in heating after isothermal crystallization at the T_cs.

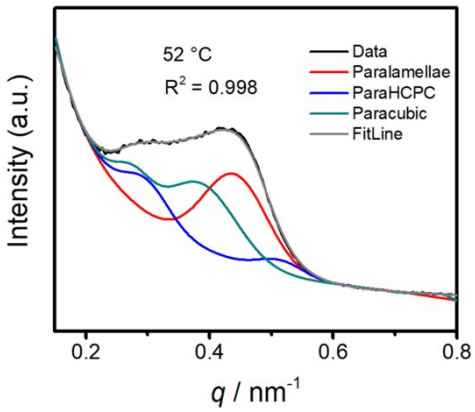


Fig. S21 Fitting results of SAXS data of An-PCL-6 at 52 °C.

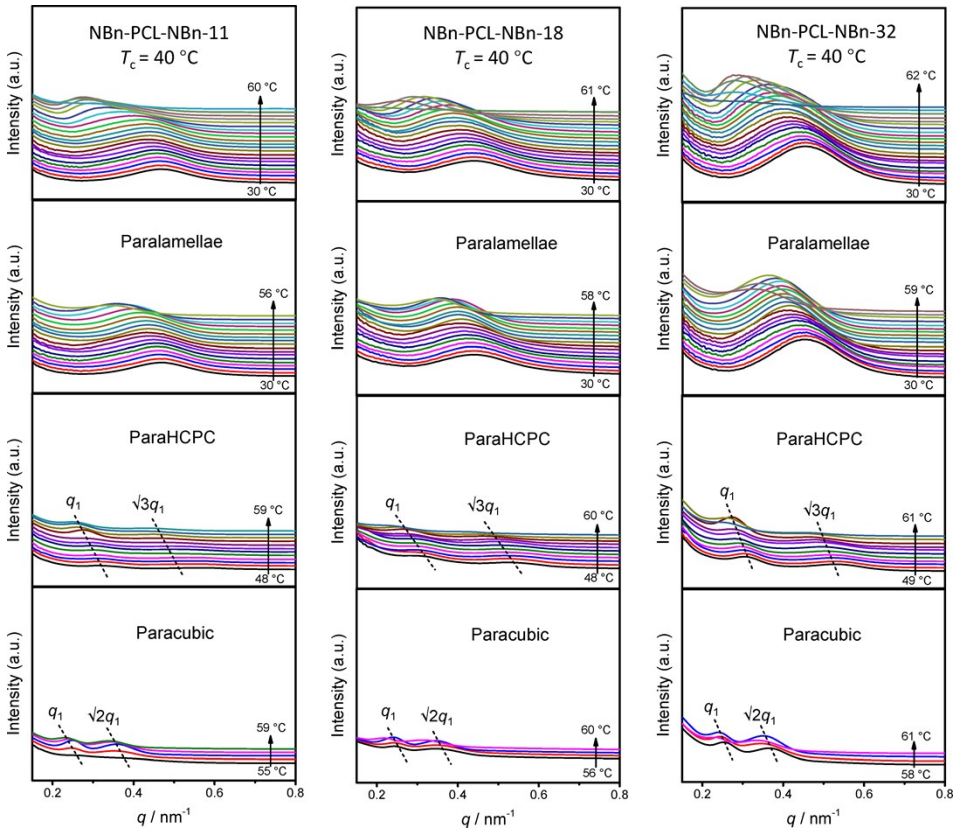


Fig. S22 Scattering profiles fitted from recorded SAXS data indicate structural evolution during heating: paralamellae, paraHCPC, and paracubic structures.

References

(1) Wang, H.; Zhang, L.; Liu, B.; Han, B.; Duan, Z.; Qi, C.; Park, D.-W.; Kim, I. Synthesis of High Molecular Weight Cyclic Poly(ε-Caprolactone)s of Variable Ring Size Based on a Light-Induced Ring-Closure Approach. *Macromol. Rapid Commun.* **2015**, *36* (18), 1646–1650. https://doi.org/10.1002/marc.201500171.

(2) Yamamoto, T.; Yagyu, S.; Tezuka, Y. Light- and Heat-Triggered Reversible Linear–Cyclic Topological Conversion of Telechelic Polymers with Anthryl End Groups. *J. Am. Chem. Soc.* **2016**, *138* (11), 3904–3911. https://doi.org/10.1021/jacs.6b00800.

(3) Kricheldorf, H. R.; Eggerstedt, S. Macrocycles 2. Living Macrocyclic Polymerization of ε-Caprolactone with 2,2-Dibutyl-2-Stanna-1,3-Dioxepane as Initiator. *Macromolecular Chemistry and Physics* **1998**, *199* (2), 283–290. https://doi.org/10.1002/(SICI)1521-3935(19980201)199:2<283::AID-MACP283>3.0.CO;2-9.

(4) Kricheldorf, H. R.; Hauser, K. Macrocycles. 3. Telechelic Polylactones via Macrocylic Polymerization. *Macromolecules* **1998**, *31* (3), 614–620. https://doi.org/10.1021/ma971055x.