

## Supporting information

### Crystallization and melting of unentangled poly( $\epsilon$ -caprolactone) cycles containing pendants

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## 1. Materials

### Materials-Synthesis of PCL

$\epsilon$ -Caprolactone ( $\epsilon$ -CL) (99%), purchased from ACROS. 9-anthracene methanol (98%), dibutyldimethoxytin (98%), 1,4-butanediol (99%), p-nitrobenzoyl chloride (98%), and stannous octoate Sn(Oct)<sub>2</sub> (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

### <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) Spectroscopy Measurement

After the sample was dissolved in CDCl<sub>3</sub> at room temperature, the <sup>1</sup>H NMR spectrum was tested on a Bruker AV400 NMR spectrometer (400 MHz for <sup>1</sup>H, 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

Based on the anthracene ring photocycloaddition approach, the difficulty lies in the precise control of the dosage of the coupling agent, which results in incomplete reaction. This will directly lead to the presence of linear molecules in the final cyclic sample. Therefore, we utilized esterification reaction to replace the coupling reaction. The advantage of esterification reaction is that an excess amount of 9-anthracene carboxylic acid can be added, ensuring complete reaction, and the excess 9-anthracene carboxylic acid can be easily removed after the reaction. Finally, UV irradiation was used to induce cycloaddition reaction between the two terminal anthracene rings. Refer to the methods of Wang<sup>1</sup> and Yamamoto<sup>2</sup> to synthesize PCLs with anthracenyl end groups, as shown in the synthetic route in the manuscript of Scheme 1. In a 25 mL reaction tube, add the initiator 9-anthracene methanol and caprolactone under argon protection, and finally add the catalyst Sn(Oct)<sub>2</sub> and solvent toluene. After reacting at 110 °C for 24 hours, hexamethylene diisocyanate(HMDI) was added to the system and stirred for 2 h at the identical conditions. After the reaction, Argon was passed into the reaction tube and cooled to room temperature to stop the experiment. 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 and named An-PCL-An.

### Synthesis of cyclic PCLs

Photodimerizations of An-PCL-An were carried out in a 150 mL flask fitted with a three-way stopcock under argon atmosphere free of moisture and oxygen. As a typical process, An-PCL-An and a Teflon-coated stirring bar were added into the dried flask. The flask was evacuated for 1 h at 40 °C and then THF was added to it with a syringe. It was irradiated upon 365 nm light at room temperature, keeping the distance between flask and light source about 30 cm. The reaction mixture was precipitated in methanol and filtered. The solids were washed with methanol several times, and dried in vacuum at 30 °C for 24 h.

## 4. Figures and tables

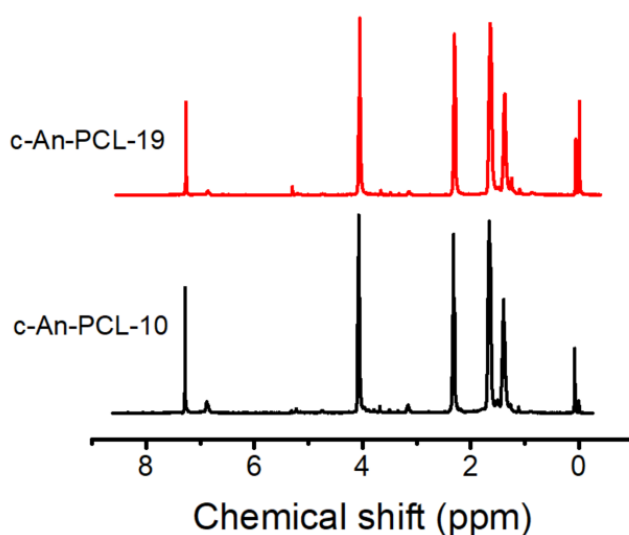


Fig. S1 <sup>1</sup>H NMR spectrum of c-An-PCLs. The structures corresponding to the chemical shifts are shown in Figure 1 of the article published by Wang et al.[1]

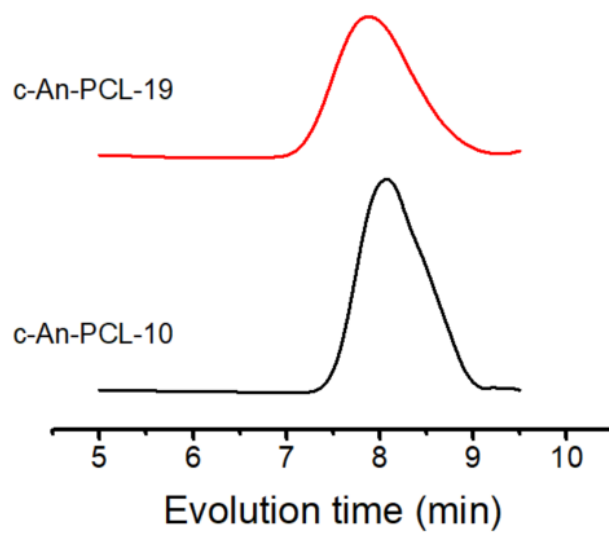


Fig. S2 GPC traces of c-An-PCLs.

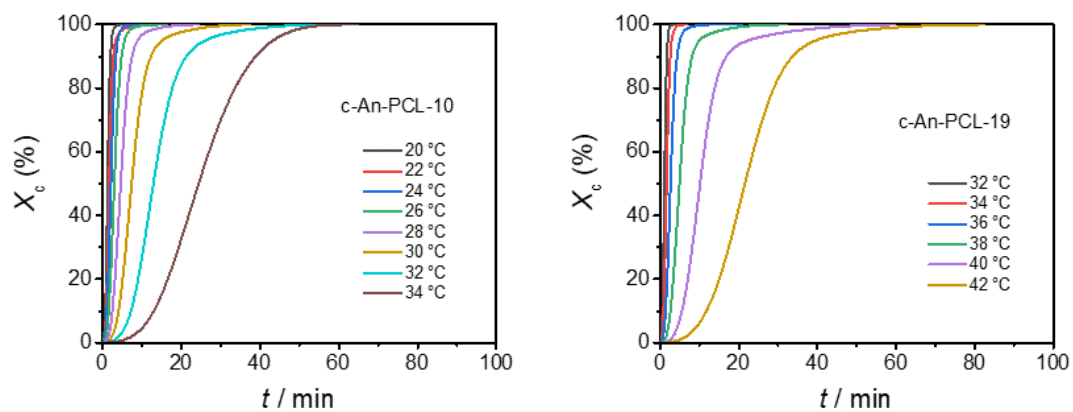


Fig. S3 Development of the crystallinity of the indicated samples over time.

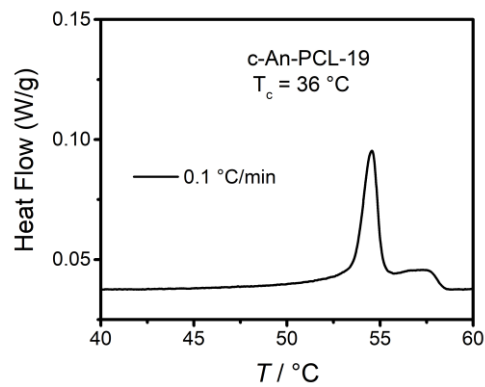


Fig. S4 Enlargement of the 0.1 °C/min curve in Figure 5b.

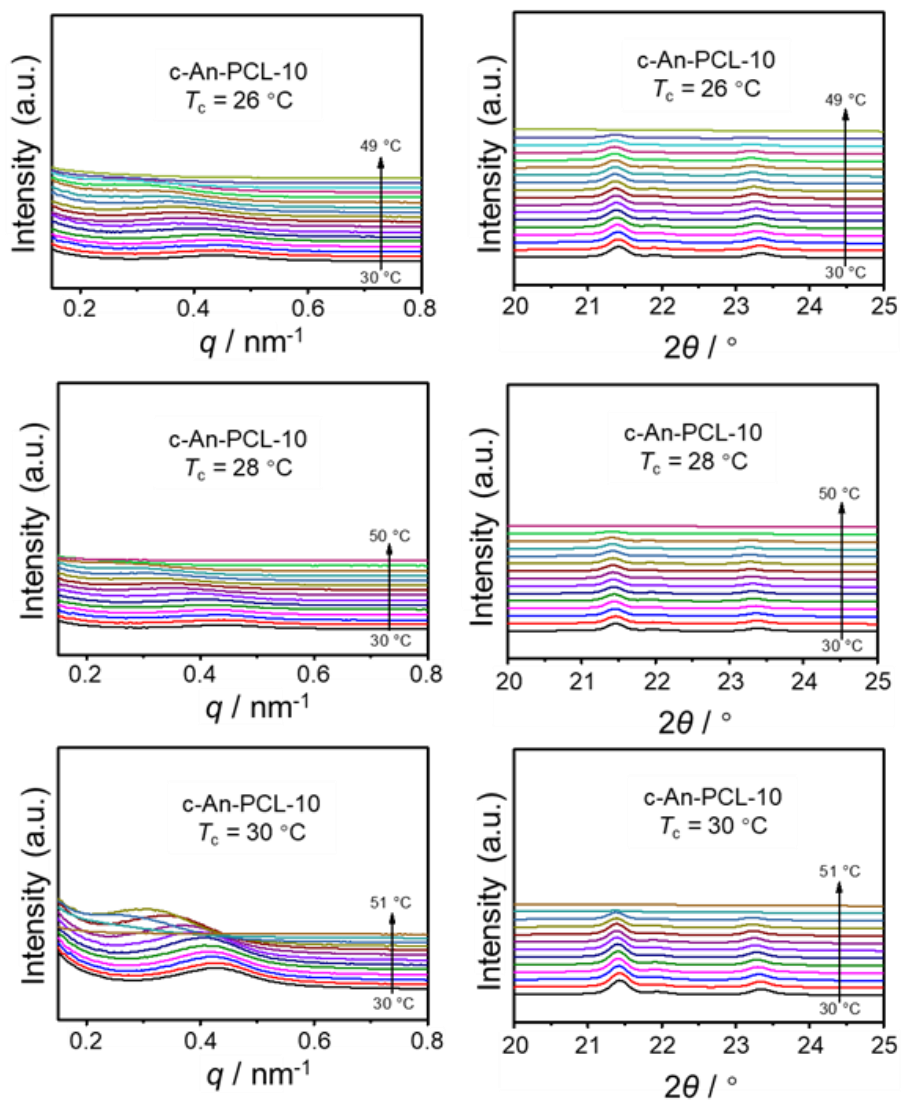


Fig. S5 Simultaneously obtained SAXS/WAXS profiles during heating (2 °C/min) of c-An-PCL-10 after isothermal crystallization at the indicated temperatures.

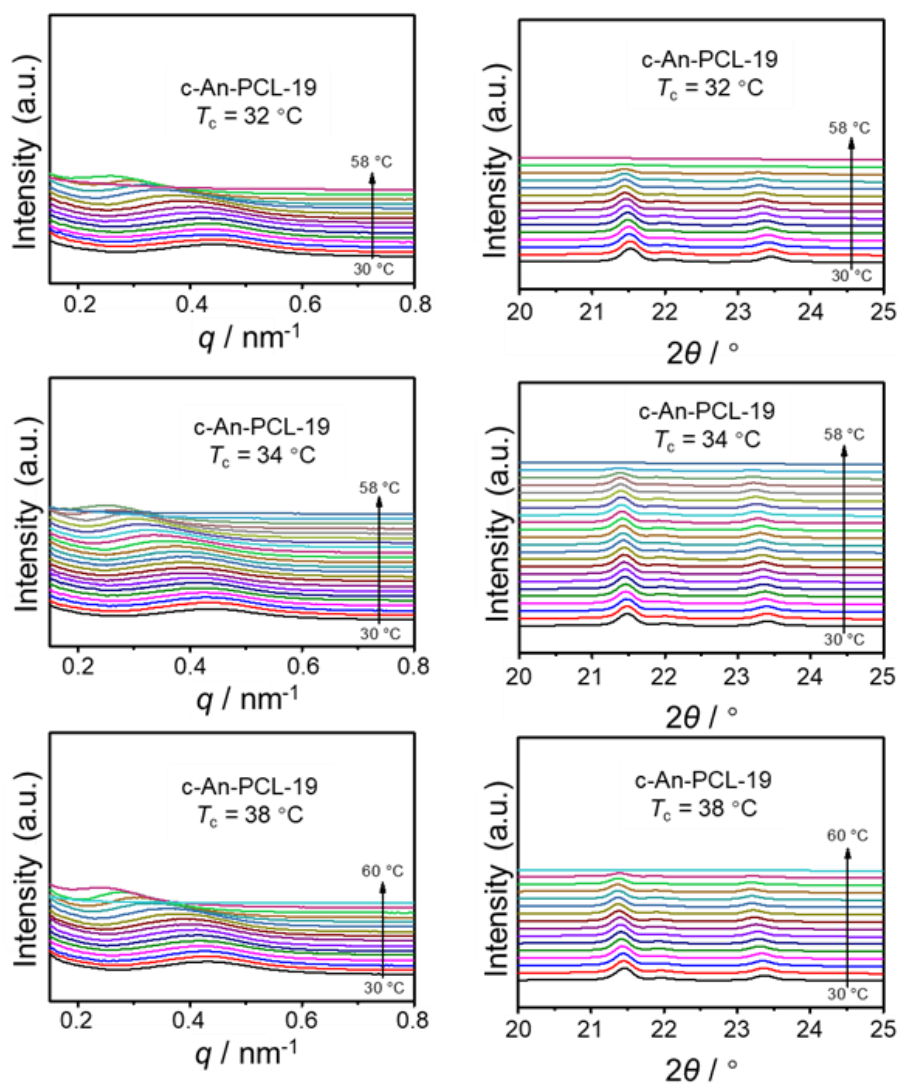


Fig. S6 Simultaneously obtained SAXS/WAXS profiles during heating (2 °C/min) of c-An-PCL-19 after isothermal crystallization at the indicated temperatures.

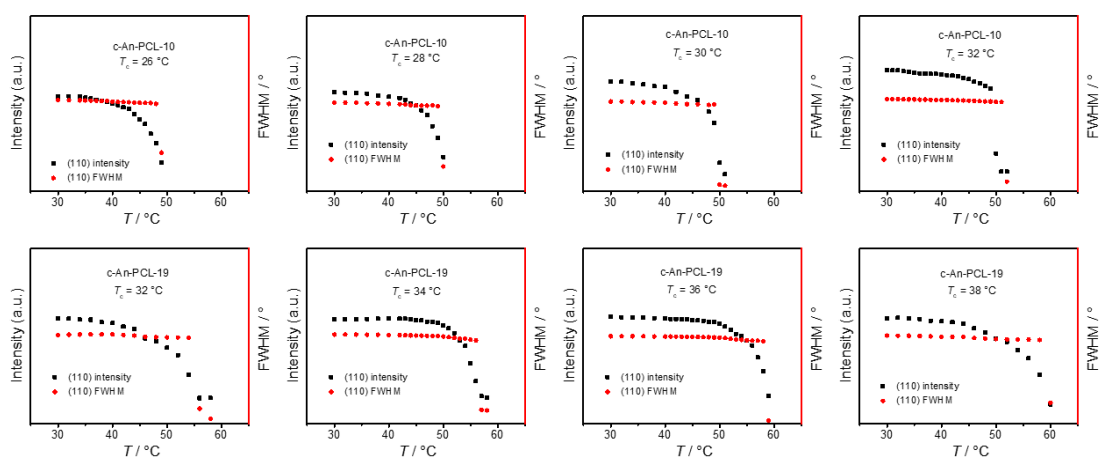


Fig. S7 (110) intensity and (110) FWHM of the indicated samples in heating after isothermal crystallization at  $T_c$ s.

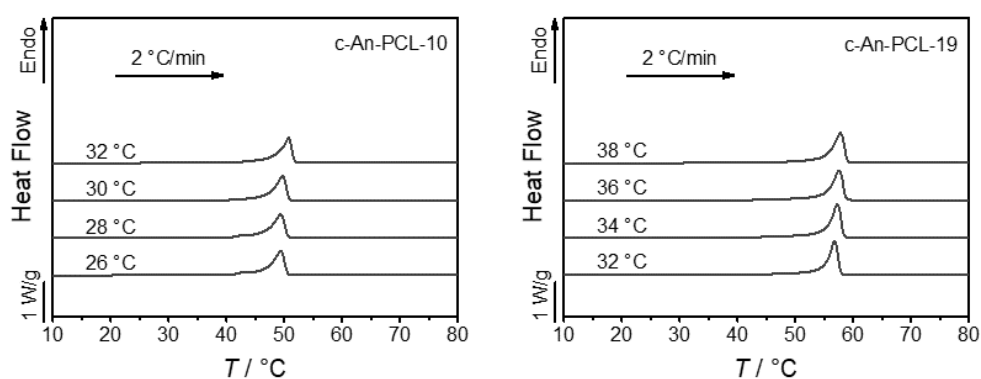


Fig. S8 DSC curves during heating (2 °C/min) of the indicated samples after isothermal crystallization at the indicated temperatures.

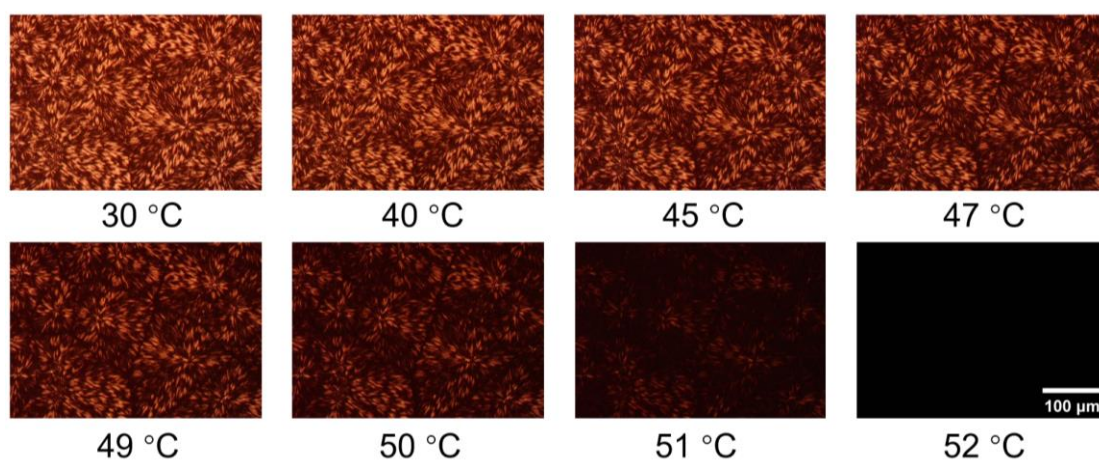


Fig. S9 POM images of c-An-PCL-10 under heating (2 °C/min) after isothermal crystallization at 32 °C. The length of the scale bar is 100 μm.

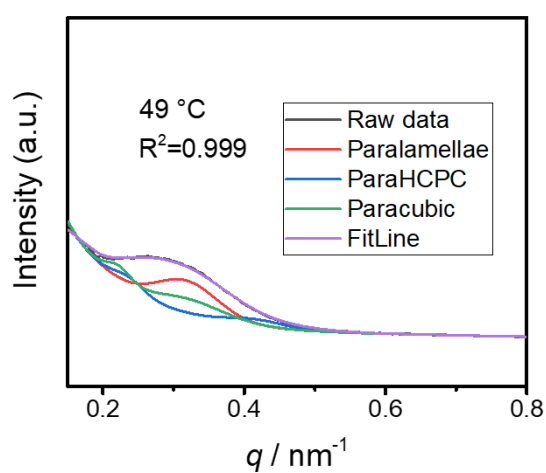


Fig. S10 Fitting results of SAXS data of c-An-PCL-10.

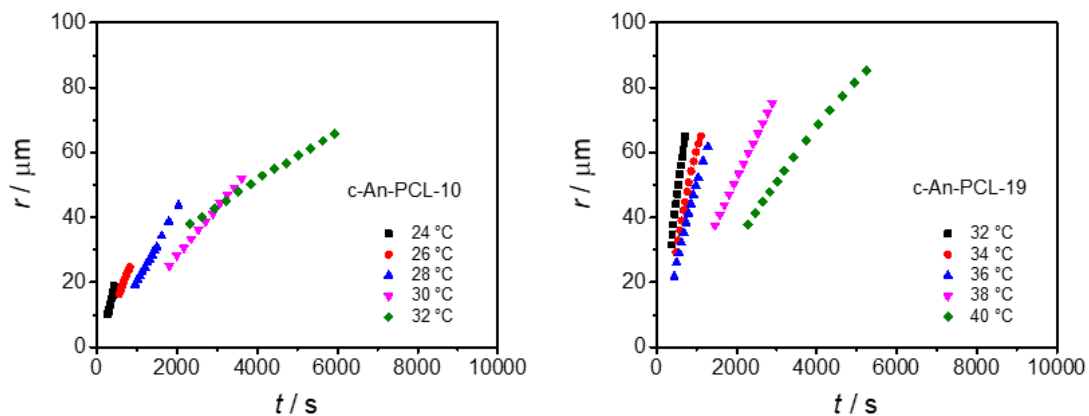


Fig. S11 Spherulite growth of cyclic PCLs in isothermal crystallization.

## 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( $\epsilon$ -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.; Yagyū, 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>.