

# Pendant affected crystallization behaviors of cyclic poly ( $\epsilon$ -caprolactone)

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## Experiments protocols

### Material, sample preparation and characterization

The cyclic poly( $\epsilon$ -caprolactone)s (PCLs), C-PCL-23600 and C-PCL-37800, were synthesized via light-induced ring closure of  $\alpha,\omega$ -anthracene-terminated PCL (An-PCL-An) by bimolecular cyclization of intermolecular coupling An-PCL-An as necklace with two pendants. The average molecular weights  $M_n$ s and the PDIs of the two cyclic PCLs are 23600 and 37800 g/mol, 2.06 and 2.03, respectively. Two linear PCLs used as reference samples are anthracene-terminated as asalato. The  $M_n$ s and PDIs of the linear PCLs are 25680 and 30700 g/mol, 1.59 and 1.52, respectively. The samples were synthesized and characterized according to previous work.<sup>[31]</sup> The schematic topology structures of the cyclic PCL as necklace with two pendants and linear PCL as asalato are given in Figure S1.

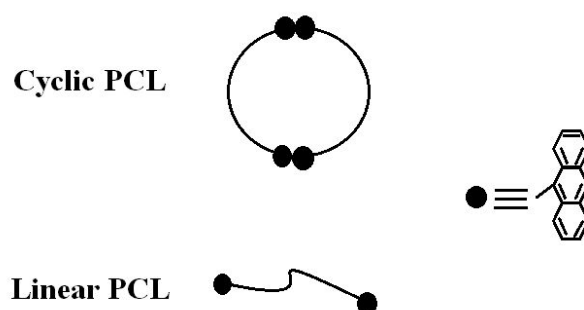


Figure S1 Illustration of the topology structures of cyclic and linear PCLs

The isothermal crystallization of all the PCLs was carried out by a Linkam hot stage and observed by an Olympus (BX51) Polarizing Optical Microscope (POM) installed with a digital camera. After heated to 90 °C and kept for 5 min to erase thermal history, the PCLs were cooled to various crystallization temperatures  $T_c$ s for further isothermal crystallization. The POM images were collected to obtain the spherulite growth rates. Both the heating and cooling rates were 30 °C/min.

Synchrotron radiation in-situ wide angle X-ray scattering (WAXS) experiments were performed at synchrotron beam line 1W2A ( $\lambda=0.154$  nm) of Beijing Synchrotron Radiation Facility (Beijing, China). A Mar165CCD was used to record experimental data. The distance between the sample and the detector is 134 mm.

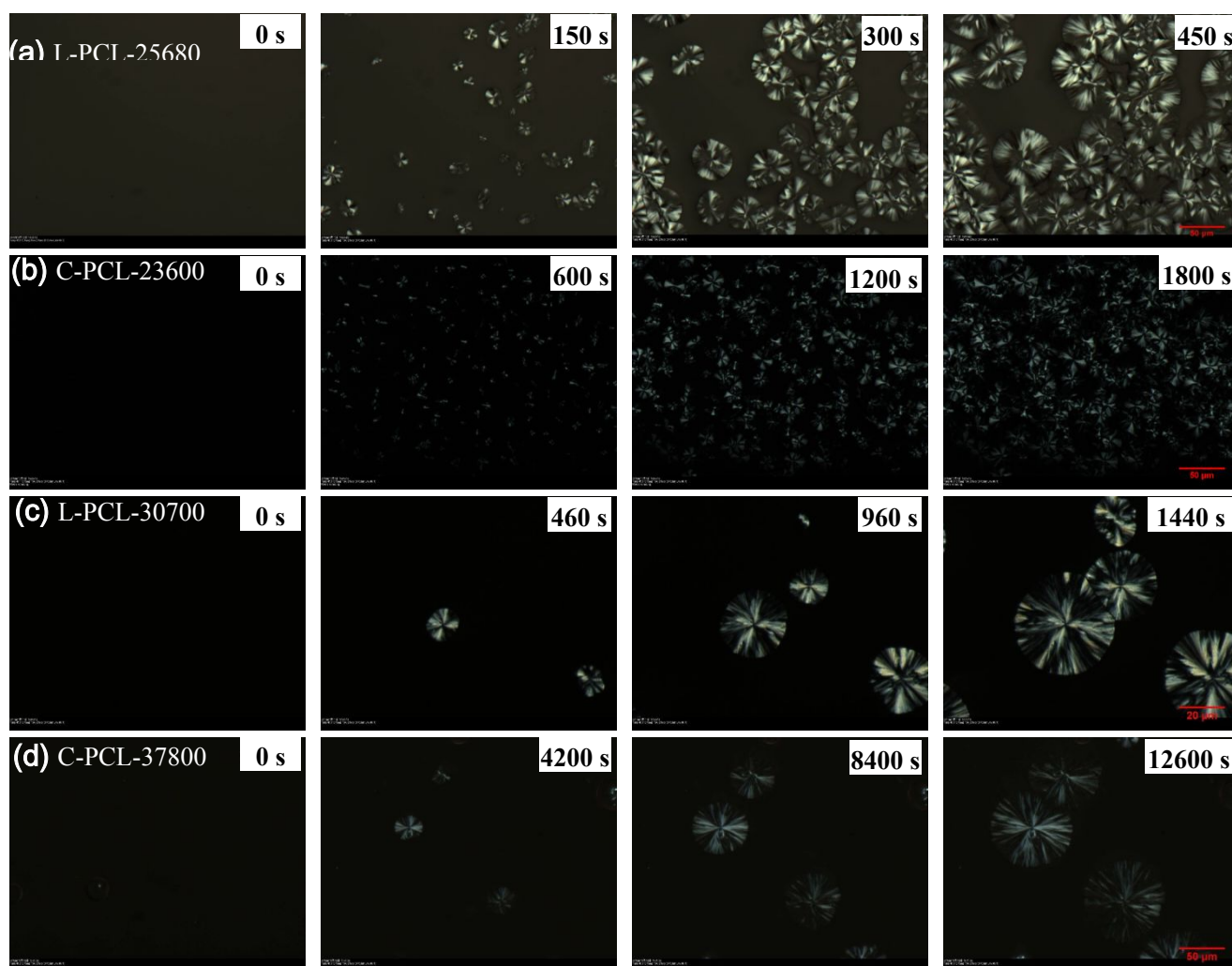


Figure S2. Spherulites of isothermal crystallization at 46 °C of L-PCL-25680 (a), C-PCL-23600 (b), L-PCL-30700 (c) and C-PCL-37800 (d)

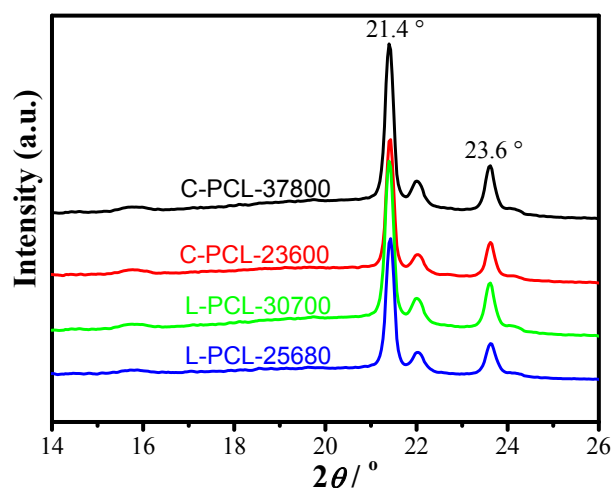


Figure S3. The 1D-WAXS profiles of linear PCL and cyclic PCLs with various average molecular weights.

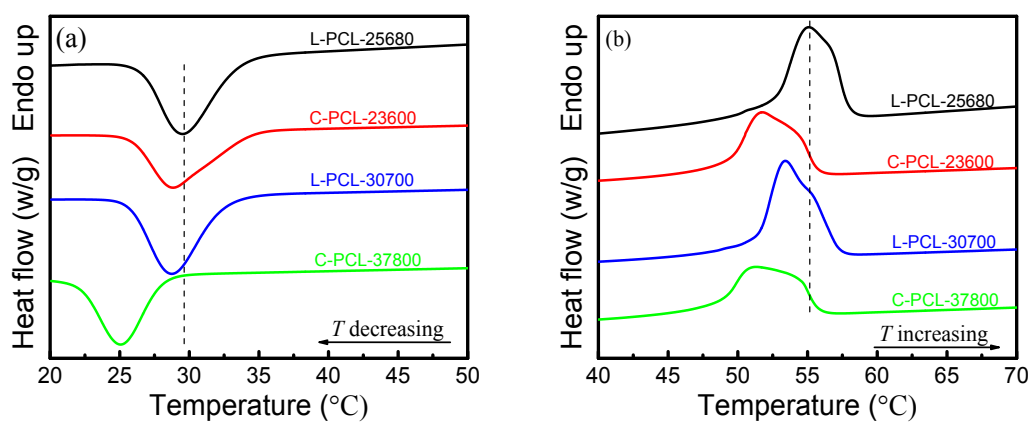


Figure S4. Heat flow curves of differential scanning calorimetry during cooling at 10 °C/min (a) and subsequently heating at 10 °C/min (b)

Table S1 The crystallization temperatures and melting points of the cyclic and linear PCLs

Sample	$T_c$ (°C)	$T_m$ (°C)
L-PCL-25680	29.6	55.1
L-PCL-30700	28.7	53.5
C-PCL-23600	28.8	51.8
C-PCL-37800	25.1	51.3

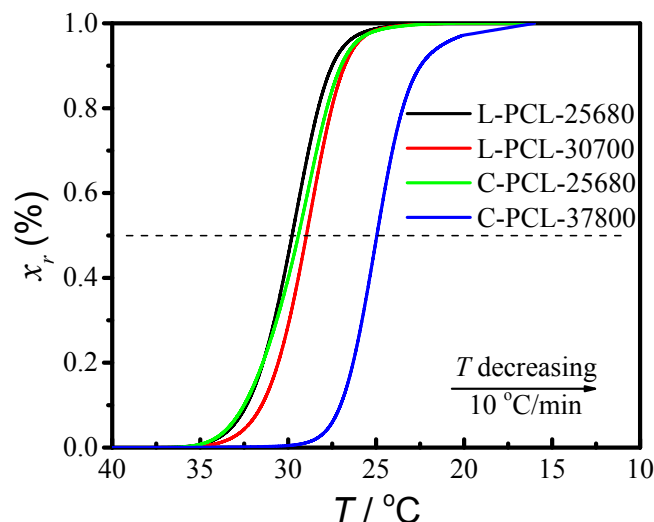
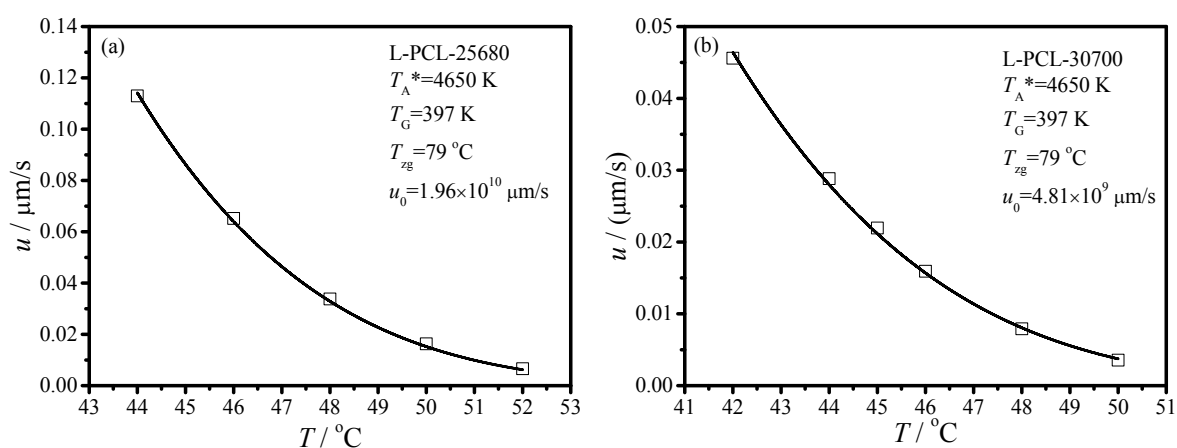


Figure S5. Temperature dependent relative crystallinity  $\chi_r$  of the cyclic and linear PCLs while cooling at 10 °C/min.

The differential scanning calorimetry analyses were carried out with a Perkin Elmer diamond DSC calibrated with pure indium. All the measurements were performed under ultra-high purity nitrogen atmosphere and all the samples used in experiments weight around 6 mg. After all the cyclic and linear PCLs were first heated at a rate of 30 °C/min to 90 °C for 5 min to have their thermal histories erased, they were cooled at a rate of 10 °C/min to 20 °C for 1 min to obtain the non-isothermal crystallization curves shown in Figure S4 a. Then the samples were heated again at a rate of 10 °C/min to 90 °C to obtain the melting curves shown in Figure S4 b.



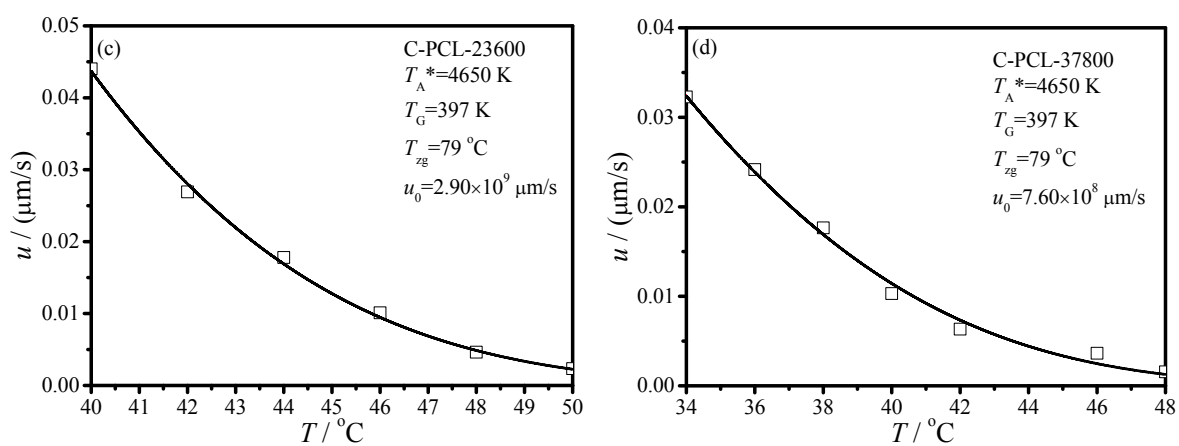


Figure S6. Detailed fitting of temperature dependent spherulite growth rates of L-PCL-25680 (a), L-30700 (b), C-PCL-23600 (c) and C-PCL-37800 (d)