

## **Supplementary Information**

### **Composition dependent phase transformation in side-chain liquid crystalline copolymers with mesogenic groups at different substituent positions**

Jiwei Pei, Wenjing Wei, Bian Li, Jundan Huang and Xiao-Fang Chen\*

Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China

E-mail: [xfchen75@suda.edu.cn](mailto:xfchen75@suda.edu.cn)

## Experimental section

### Materials

4-Hydroxy-4-biphenylcarboxylic acid (99%, Sdyano), 1-Bromododecane (99%, Adamas), Lithium aluminum hydride (97%, Aladdin), Potassium iodide (99%, Alfa Aesar), Methyl 2-hydroxybenzoate (99%, TCI), Methyl 3-hydroxybenzoate (99%, TCI), Methyl 2,3-dihydroxybenzoate (98%, TCI), 1-[3-(Dimethylamino) propyl]-propyl-3-ethylcarbodiimide hydrochloride (EDC·HCl) (99%, D&B), 4-(Dimethylamino) pyridine (DMAP) (99%, J&K), Grubbs catalyst (third generation) (98%, Energy). Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) (AR, Sinopharm) and Trichloromethane (CHCl<sub>3</sub>) (AR, Sinopharm) were distilled by refluxing over CaH<sub>2</sub> prior to use. Tetrahydrofuran (THF) (AR, Sinopharm) was heated under reflux over sodium for at least 8 h and distilled before use. All other reagents and solvents were obtained from commercial sources and used without further purification.

### Measurements

**NMR.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on an INOVA 400 MHz NMR spectrometer at ambient temperature with CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard.

**GPC.** Molecular weight ( $M_n$ ,  $M_w$ ) and polydispersity (PDI) of the copolymers were measured on an instrument comprised of a Waters 1515 isocratic HPLC pump, a Waters 717 plus autosampler, a Waters 2414 refractive-index detector with three 300 mm (length) × 7.5 mm (inner diameter) columns with a particle size of 5 μm (PL gel mixed-C, Polymer Laboratories). The measurements were performed using THF as the eluent with a flow rate of 1.0 mL·min<sup>-1</sup> at 35 °C. The calibration was carried out with a series of polystyrene standards.

**DSC.** Thermal behavior and phase transition temperature of all the copolymers were observed and obtained using a TA-Q100 DSC instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at a cooling and heating rate of 10 °C·min<sup>-1</sup>. Samples with a typical mass of about 4-6 mg were encapsulated in sealed aluminium pans. The DSC heating and cooling curves were recorded at a rate of 10 °C·min<sup>-1</sup>.

**TGA.** The thermal stability of all the copolymers was measured by Thermal Gravimetric Analysis (TGA) on a TGA Q500 (TA) instrument at a heating rate of 10 °C·min<sup>-1</sup> from ambient temperature to 800 °C under a nitrogen atmosphere.

**SAXS.** Small-angle X-ray scattering (SAXS) was measured at Shanghai Synchrotron Radiation Facility (SSRF, beamline BL16B1) with a Pilatus 2M detector. The energy of the X-ray radiation is 10 keV, resulting in a wavelength of 0.124 nm. The samples were performed with the completely identical conditions and specially the invariant sample-to-detector distance. The sample to detector distance is 1.92 m. The analyses of SAXS data were carried out by the Fit2d software.

**GISAXS.** Grazing-incidence small-angle X-ray scattering (GISAXS) was carried out to study the phase structures of thin films at SSRF, beamline BL16B1 with a Pilatus 2M detector. The energy of the X-ray radiation is 10 keV, resulting in a wavelength of 0.124 nm. The sample to detector distance is 1.92 m. The incident angle of the X-rays was fixed at 0.2-0.3°, which is above the critical angle of the mesostructured films but below the critical angle for Si.

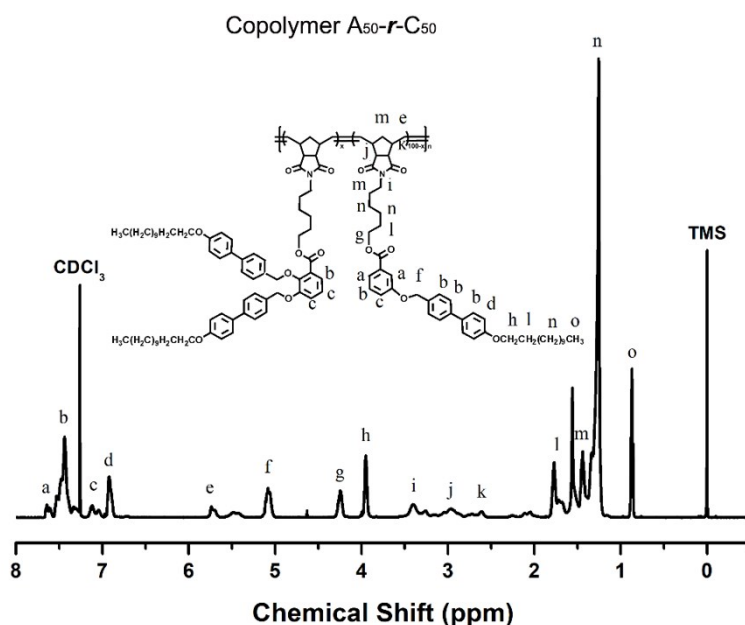
**S&WAXS.** Small & wide-angle X-ray scattering (S&WAXS) of copolymer samples was measured by a high-flux X-ray instrument (Anton Paar, SAXSess mc<sup>2</sup>) equipped with Kratky block-collimation system and a GE ID3003 sealed-tube X-ray generator (Cu Kα). The wavelength is 0.1542 nm. The X-ray scattering patterns were recorded in vacuum on an imaging-plate (IP) which extended to high-angle range (the  $q$  range covers from 0.06 to 29 nm<sup>-1</sup>).

**AFM.** Surface topographies of thin films were recorded by Bruker MultiMode8 Atomic Force Microscopy (AFM). Samples were deposited on piranha cleaned silicon substrates by spin casting 5 wt% complexed copolymer solution (2000 rpm/30 s) to obtain about 100 nm thickness (judged from a spectroscopic ellipsometer) thin film. The AFM images were recorded using ScanAsyst with a scan rate of 0.97 Hz, wherein the cantilever force was controlled to be large enough to explore the surface features, yet small enough to avoid the sample damage.

**POM.** Liquid crystalline (LC) textures and birefringence of samples were examined under Olympus BX51-P Polarized Optical Microscopy (POM) equipped with a Linkam THMS 600 hot stage. Samples were made by sandwiching the dried copolymer powder between a glass slide and a cover glass. Generally, several heating and cooling cycles with controlled rates were carried out to measure the phase transition by detecting the birefringence and texture change of the sample under POM. Typical LC textures could be formed when heating the sample to its isotropic temperature and then cooling to LC state at a rate of 1 °C·min<sup>-1</sup>.

#### Synthesis of monomers and copolymers.

Monomers (**A**, **B** and **C**) were synthesized and characterized via the procedure described in our previous work. Copolymers were synthesized via ROMP. A representative synthesis of random copolymer **A**<sub>52</sub>-*r*-**B**<sub>48</sub> is described as follows. Monomer **A** (100 mg, 0.091 mmol), **B** (67 mg, 0.091 mmol) and Grubbs third-generation catalyst (1.61 mg, 0.0018 mmol) were loaded in a dry Schlenk tube with a magnetic stirring bar. The tube was evacuated and filled with high purity nitrogen to degas. Anhydrous CHCl<sub>3</sub> (3 mL) was injected to the mixture. After three freeze-pump-thaw cycles, polymerization was carried out at room temperature under N<sub>2</sub> atmosphere. After the reaction mixture was stirred for 4 hours, vinyl ethyl ether (1 mL) was added to terminate the reaction. Then polymerization was stopped after an additional hour. The viscous liquid was diluted with 5 mL of CH<sub>2</sub>Cl<sub>2</sub> and passed through a short alumina column to separate the catalyst and then the copolymer was precipitated out in 300 mL of methanol. The product was collected by filtration and dried in a vacuum at 35 °C for 24 hours. The target copolymer **A**<sub>52</sub>-*r*-**B**<sub>48</sub> was obtained as a white solid (145 mg, 87%). All other copolymers are prepared with similar procedure.



**Fig. S1** <sup>1</sup>H NMR spectrum of copolymer **A**<sub>50</sub>-*r*-**C**<sub>50</sub> in CDCl<sub>3</sub>. The resonance peak of *a* at 7.55 ppm belongs to two protons in the phenyl group of monomer **C**. The molar content of **A** can be calculated as  $x_A = (n_f - 2)/4 \times 100\%$ . The copolymer composition can also be verified by calculating the integration of peaks *g* and *h*,  $x_A = (n_h - n_g)/n_g \times 100\%$ .

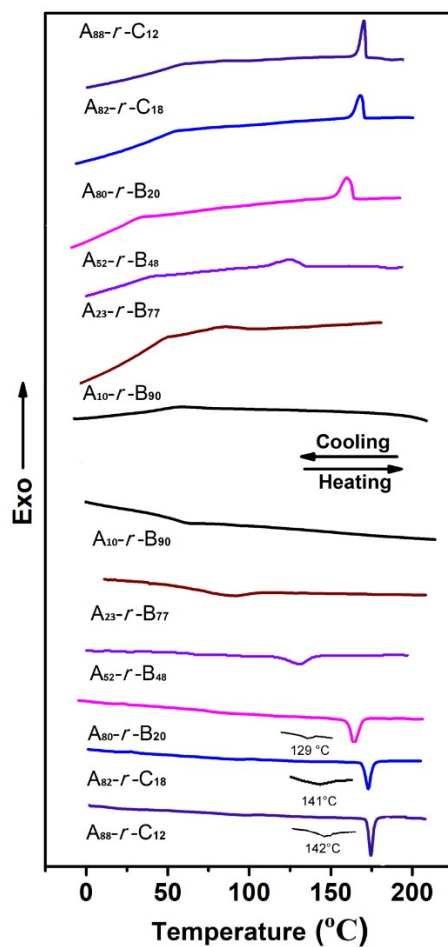


Fig. S2 DSC curves of A-r-B and A-r-C copolymers with different mole content during the first cooling and second heating cycle at a rate of 10°C·min<sup>-1</sup> under the nitrogen atmosphere.

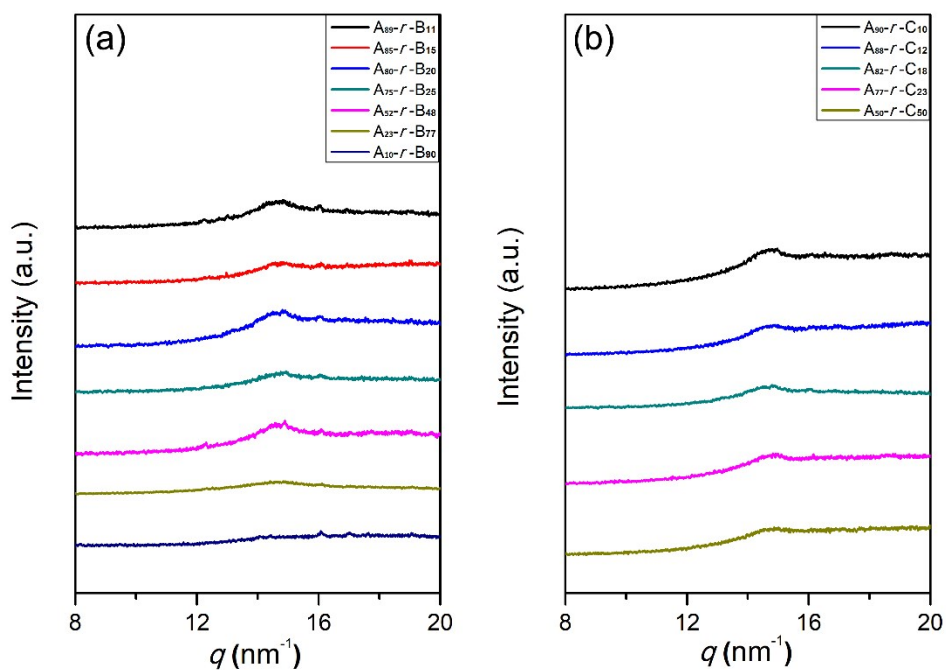


Fig. S3 WAXS profiles of (a) A-r-B and (b) A-r-C copolymers recorded at room temperature.

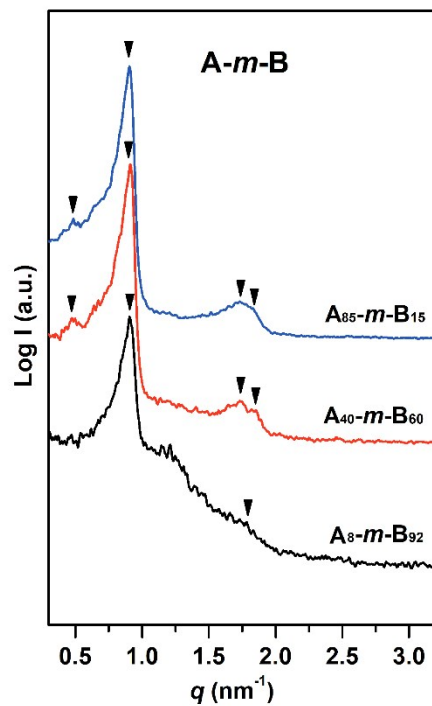


Fig. S4 SAXS profiles of polymer A and B mixture ( $A-m-B$ ) with different mole content. The samples  $A_8-m-B_{92}$ ,  $A_{40-m-B_{60}}$  and  $A_{85-m-B_{15}}$  were thermal annealed at 155 °C and recorded at room temperature.

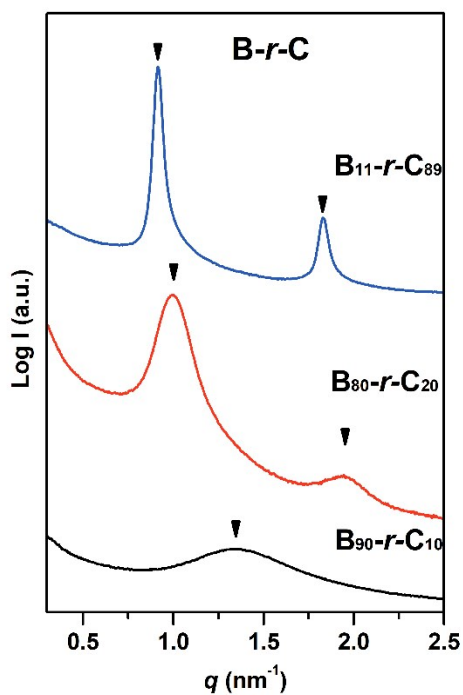
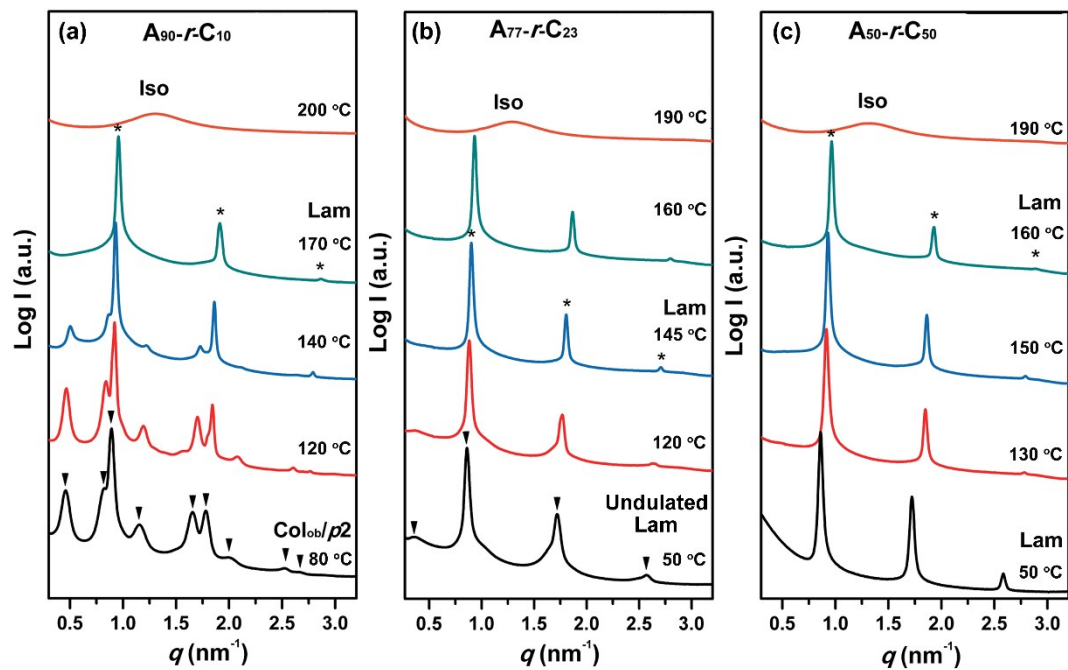


Fig. S5 SAXS profile of copolymers  $B-r-C$  with different mole content. The samples  $B_{11-r-C_{89}}$ ,  $B_{20-r-C_{80}}$  and  $B_{90-r-C_{10}}$  were thermally annealed at 90 °C and recorded at room temperature.



**Fig. S6** Temperature-dependent SAXS profiles of (a)  $A_{90}\text{-}r\text{-}C_{10}$ , (b)  $A_{77}\text{-}r\text{-}C_{23}$  and (c)  $A_{50}\text{-}r\text{-}C_{50}$  copolymers during the heating process.