

Electronic Supplementary Information for:

Gradient and Block Side-chain Liquid Crystalline Polyethers

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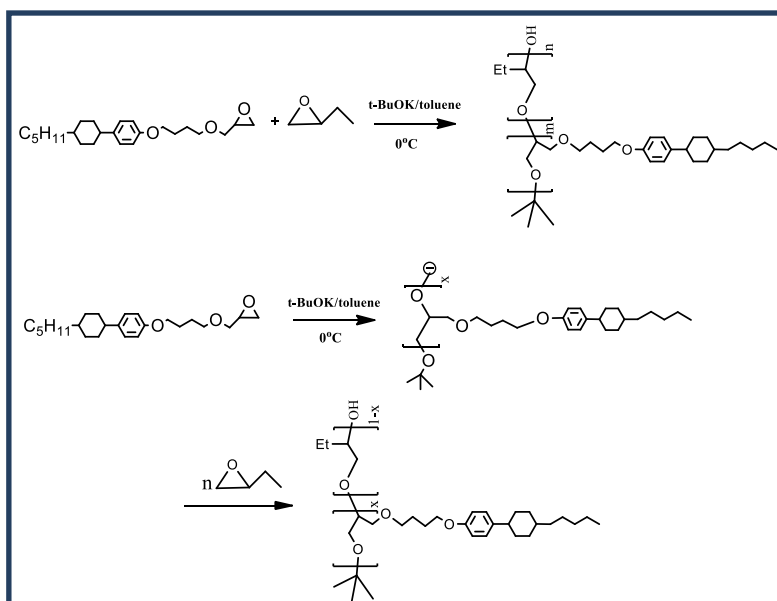


Figure S1. Synthetic routes of the gradient copolymer and the block copolymer.

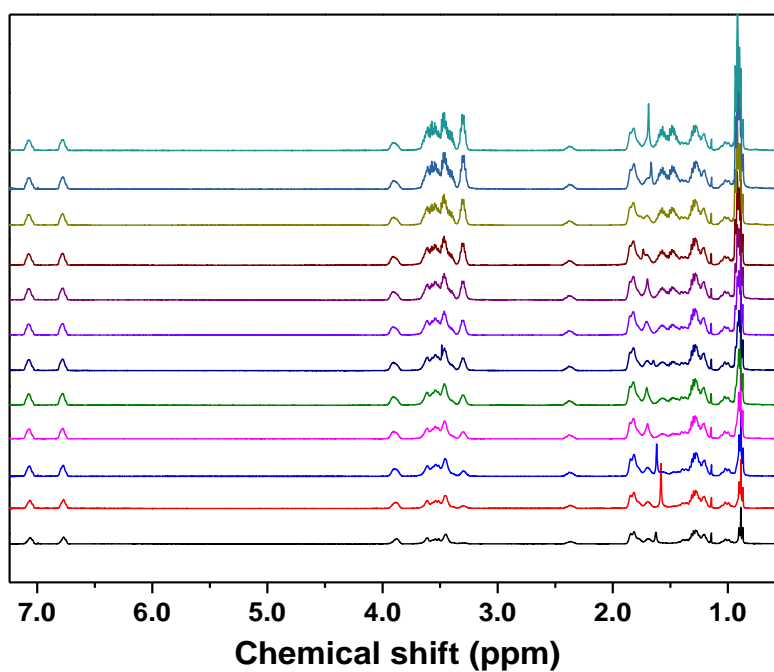


Figure S2. ¹H NMR spectra of the gradient copolymers with the growth of polymer chains.

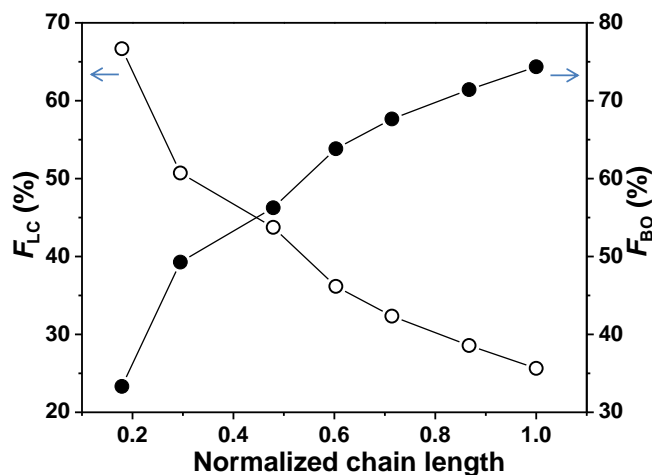


Figure S3. Cumulative molar fraction of liquid crystalline units (hollow dots) and BO units (solid dots) as a function of normalized chain length of the gradient copolymers up to E_{60-g}-B₁₇₄.

In situ ¹H NMR experiments

In order to obtain the insights into the copolymerization process, the consumption of monomers at each stage of the copolymerization has been followed directly by using real-time ¹H NMR spectroscopy technique.^{1, 2} The anionic ring-opening copolymerization of monomers E and B was carried out in deuterated toluene in an NMR tube at room temperature. The synthetic procedure in the NMR tube was carried out in analogy to the procedure described in the text. When the deuterated toluene was distilled into the NMR tube in the high vacuum line, the reaction mixture was frozen in liquid nitrogen immediately. The NMR tube was then flame-sealed. Immediately after melting and mixing of the reaction system, the first spectrum was recorded. In situ ¹H NMR spectra were recorded at 600 MHz on a Avance III nuclear magnetic resonance spectrometer, with a 5 mm CPTCI ¹H-¹³C/¹⁵N/D Z-GRD probe. All spectra were acquired with 8 scans. The polymerization time and the period of data collection lasted over 2 days. The NMR tube reactor is shown in Fig. S4.



Figure S4. The tube reactor for in situ NMR measurement.

Fig. S5. shows a typical series of ^1H NMR spectra for the copolymerization of monomer E and B. The reaction system has a starting molar fraction of $f_B = 0.70$ in the feed. The separated chemical shifts of protons on oxirane group of monomer E (2.73-2.78 ppm) and that of monomer B (2.42-2.5 ppm) can be identified, as illustrated in the zoom-in in Fig. S5, which were used to determine the consumption of the monomer E and the monomer B. The real-time ^1H NMR spectra demonstrate the consumption of these two monomers and the simultaneous formation of the polymer typically appearing in the spectral region of 3.4-4.0 ppm. Monomer incorporation was further determined as a function of total conversion as shown in Fig. S6, where M represents the residual monomer concentration, M_0 is the initial monomer concentration, determined from the real-time NMR spectra. This plot illustrates the evolution of monomer feed composition during the copolymerization and reveal the concurrent incorporation of E and B into the growing polymer chain. As seen in Fig. S6, concentration of monomer E decrease more rapidly than that of monomer B in the reaction mixture before $\sim 80\%$ E was consumed, indicating that E is incorporated considerably faster compared to B and a higher reactivity. These results are consistent with the compositional drift observed in the copolymers previously, where a gradient composition profile formed.

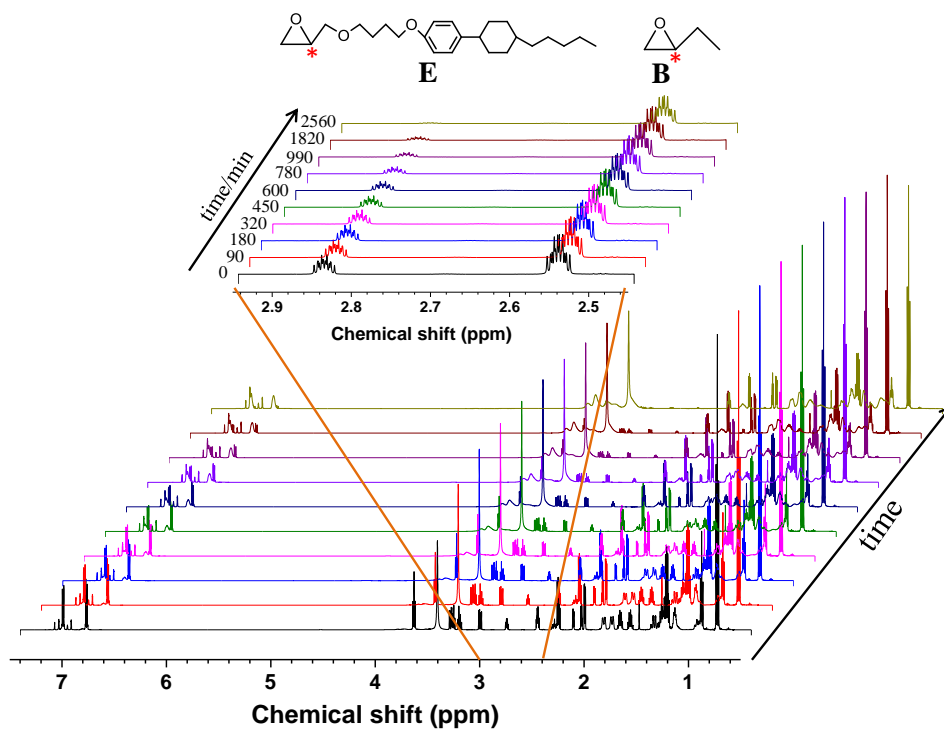


Figure S5. Real-time ^1H NMR spectra overlay (the bottom); the zoom-in of spectral region which are used to determine the consumption of the monomer E and the monomer B (the top).

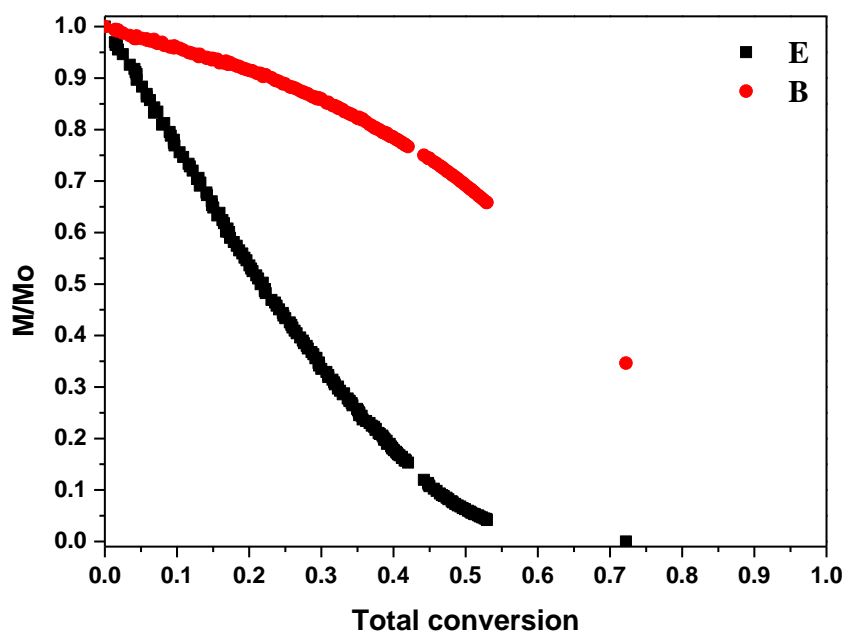


Figure S6. Percentage of monomer concentration in the reaction solution vs total conversion for copolymerization of E and B, determined from in situ ^1H NMR spectra.

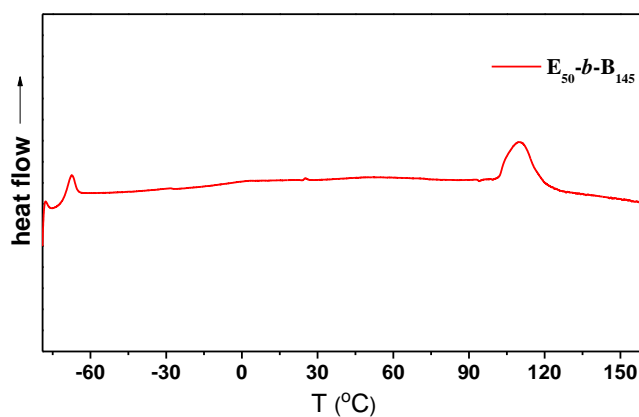


Figure S7. DSC heating curve of E_{50} - b - B_{145} at a scanning rate of 10 °C/min after a slow cooling.

In order to reveal the thermal glass transition of PBO block, additional DSC measurement has been carried out for E_{50} - b - B_{145} . The sample is first slowly cooled to -80 °C (~ 0.5 °C/min), then heated at a scanning rate of 10 °C/min. In such a way, the hysteresis of glass transition of PBO block can be developed. As shown in Fig. S7, the glass transition of PBO block due to its enthalpy relaxation can be clearly observed in comparison with the DSC reference baseline, which is consistent with the glass transition temperature of PBO homopolymer around -70 °C reported in literature.³

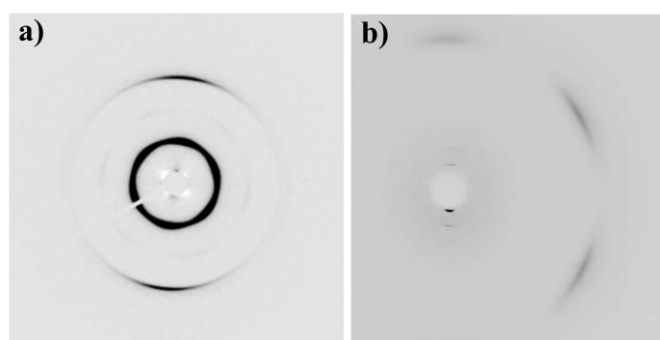


Figure S8. 2D SAXS pattern of E_{50} - b - B_{104} suggesting a HPC structure (a) and its WAXS pattern indicative of hexagonal mesogenic packing (b).

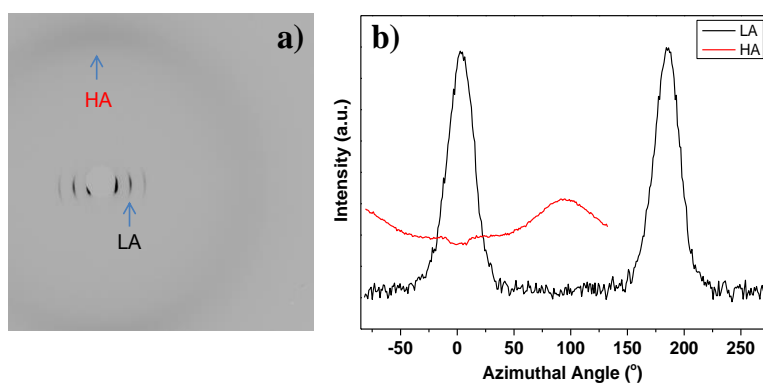


Figure S9. (a) 2D WAXS pattern of orientated $E_{54-g-B_{113}}$ sample and (b) Azimuthal scans of high-angle (HA) and low-angle (LA) regions of pattern a, which indicates the director of the mesogens is parallel to the normal of the liquid crystalline layer.

References

1. B. Obermeier, F. Wurm, H. Frey, *Macromolecules*, 2010, **43**, 2244.
2. W. Zhang, J. Allgaier, R. Zorn, *Macromolecules*, 2013, **46**, 3931.
3. J. Brandrup, E. H. Immergut, E. A. Grulke, *Polymer handbook, Fourth Edition*, John Wiley & Sons, 1998, Ch. 6, 214.