Electronic Supplementary Information (ESI) for

Self-Healing and Phase Behavior of the Self-Healing Liquid Crystalline Elastomer based on Block Copolymer Consisted of Side-Chain Liquid Crystalline Polymer and Hydrogen Bonding Block

Yan Miao[a], Jun Tang[a], He-lou Xie[a]*, Bin Ni[a],Hai-liang Zhang[a*], Er-qiang Chen[b]

[a]*Key Laboratory of Special Functional Polymer Materials of Hunan Province, Key Laboratory of Advanced Functional Polymer Materials of Colleges and Universities of Hunan Province and Key Lab of Environment-friendly Chemistry and Application in Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, Hunan Province, China*

[b]*Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*

** To whom the correspondence should be addressed.*

E-mail: xhl20040731@163.com (HLX)

Experimental section

In order to develop the diblock copolymer with the designed structure, a LC monomer (**MAzoC$_4$**) containing azobenzene and a 4C-length tail was prepared. After polymerization, the corresponding polymer (PMAzoC$_4$) exhibited the typical smectic phase as well as a low glass transition temperature (Tg). Especially, a certain amount of **Hexyl methacrylate** (**MHA**) was added during the polymerization process to lower the Tg of PM1. So precisely speaking, the polymer PM1 described in this paper was actually a copolymer of **MAzoC$_4$** and **MHA**. The block copolymers (BCPs) were synthesized using PM1 as the macro-chain transfer agent with the monomer **N-acetamidopentyl methacrylate** (**M(NCP)A**) containing hydrogen bond via RAFT.

Materials. Tetrahydrofuran (THF, 99%) was dried by $MgSO_4$, then refluxed with sodium and distilled. Triethylamine (TEA) (Aldrich, >99) was refluxed with *p*-toluenesulfonyl chloride (>99) and distilled. Chlorobenzene (Acros, 99%) was

purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with water, once with 5% sodium carbonate solution, and again with water before being dried with anhydrous calcium chloride and then distilled. And *N,N*-dimethylformamide (DMF, 99.8%) was dried with an hydrous magnesium sulfate and distilled under reduced pressure.

Synthesis of 4-((4-butylphenyl)diazenyl)phenol

4-((4-butylphenyl)diazenyl)phenol was synthesized through the following steps: In a typical experiment, 4-butylaniline (14.9 g, 100 mmol) and NaNO2 (7.2 g, 104 mmol) were first dissolved in a mixture of water (50 mL) and HCl (11.9 mol/L, 10 mL), then the resulting solution was added dropwise into an aqueous solution of phenol (10g, 110mmol) and NaOH (10g, 260 mmol) over a period of 2 h under magnetic stirring at 0 ^{o}C. After that, the reaction solution was filtered and the solvent was removed under reduced pressure. The crude product 4-((4-butylphenyl)diazenyl)phenol was purified and collected by flash chromatography.

Synthesis of 1-(4-((6-bromohexyl)oxy)phenyl)-2-(4-butylphenyl)diazene

4-((4-butylphenyl)diazenyl)phenol (12.7 g, 50 mmol), K2CO3 (13.4 g, 100 mmol), 1,6-dibromo-hexane (12.2 g, 50 mmol) and 200 mL refined acetone were added into a 500 mL flask with a magnetic stirring bar. The reaction mixture was heated to reflux and stirred for 24 h. After hot filtration, the crude product was precipitated into cold methanol and collected by vacuum filtration. The precipitation was separated through a silicon column using CH2Cl2 as the eluent. The first ingredient was collected. By removing the solvent with rotate vaporizing apparatus, the product, 1-(4-((6-bromohexyl)oxy)phenyl)-2-(4-butylphenyl)diazene (15 g, 36 mmol) was obtained.

Synthesis of MAzoC$_4$, 6-(4-((4-butylphenyl)diazenyl)phenoxy)hexyl methacrylate

In a 1000 mL flask with a magnetic stirrer, a mixture of 1-(4-((6-bromohexyl)oxy)phenyl)-2-(4-butylphenyl)diazene (15 g, 36 mmol), methacrylic acid (4.3 g, 50 mmol), K2CO3 (6.7 g, 50 mmol) and DMF (500mL) was added. The reaction mixture was heated to 100 oC and stirred for 24 h. The reaction mixture was allowed to cool and added to distilled water (2000 mL) and the resulting precipitate was collected. The crude product was separated through a silicon column using a

CH2Cl2 as the eluent. The second ingredient was collected. By removing the solvent with rotate vaporizing apparatus, the product 6-(4-((4-butylphenyl)diazenyl)phenoxy)hexyl methacrylate (11 g, 26 mmol) was obtained. 1H NMR (CDCl3)， δ (ppm): 7.88 -7.92 (s, 2H, Ar-H), 7.0(m, 1H, Ar-H), 5.58-6.1 (m, 2H, =CH2), 4.1-4.2 (m, 2H， -CH2-), 2.6 (m, 1H, -CH2-), 1.9 (m，1H， -CH3), 1.4-1.9(m, 5H, -CH2-), 1.0 (m 4H, -CH3).

Synthesis of M(NCP)A, N-acetamidopentyl methacrylate

5-Acetamido-1-pentanol (26.6 g, 183 mmol) was added to a solution of methacrylic acid (23.6 g, 275 mmol), EDC·HCl (57.9 g, 302 mmol) and DIPEA (39.0 g, 302 mmol) in DCM (500 mL). The mixture was stirred at room temperature for 24 h. Another 500 mL DCM was added and the mixture was washed sequentially with 1 M NaOH, 1M HCl, saturated NaHCO3 and brine. The organic phase was dried over Na2SO4, filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (100:1 DCM : Methanol), and the pure fractions combined and evaporated to give 35.0 g (90%). 1H NMR (500 MHz, DMSO-d 6, 298 K) δ 7.79 (s, 1H), 6.32 (dd, J = 17.3, 1.4, 1H), 6.17 (dd, J = 17.3, 10.3, 1H), 5.93 (dd, J = 10.3, 1.4, 1H), 4.09 (t, J = 6.6, 2H), 3.01 (dd, J = 12.8, 6.6, 2H), 1.77 (s, 3H), 1.57-1.63 (m, 2H), 1.37-1.41 (m, 2H), 1.28-1.33 (m, 2H);

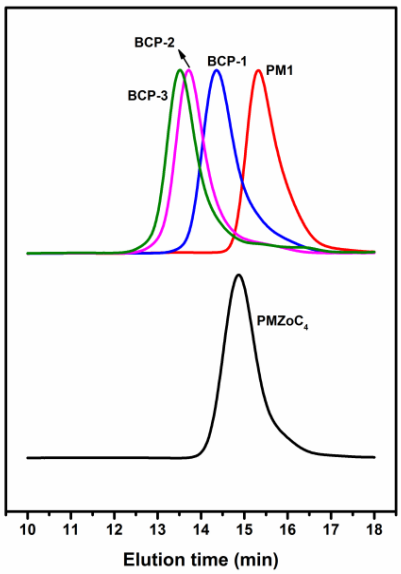
13C NMR (125 MHz, DMSO-d 6, 298 K) δ 168.9, 165.5, 131.4, 128.4, 64.0, 38.3, 28.8, 27.8, 22.9, 22.6

Synthesis of chain transfer agent 2-cyanopropan-2-yl benzodithioate (CPDB):

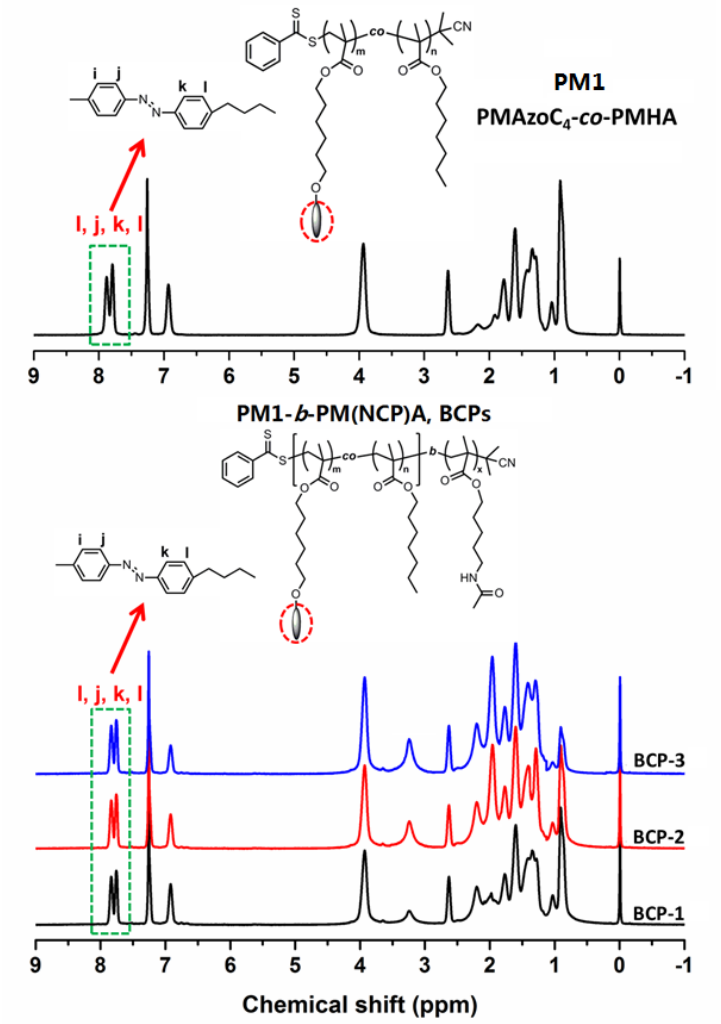
CPDB was synthesized using the procedure described by Lu et al.

Synthesis and Molecular Characterization of the Diblock Copolymers (BCPs). Reversible Addition-Fragmentation Chain Transfer Polymerization, also known as RAFT, is an efficient way to construct macromolecules with complex architectures (branched, dendritic, or ramified structures) and different types of topological copolymers (random or block) with controlled MWs. In this paper, the BCPs were prepared by RAFT using CPDB as the chain transfer agent. In the first step, we prepared macromolecular chain transfer agent PM1 with the Mn of 1.0×10^4. The BCPs with different macromolecular chain lengths of PM(NCP)A were

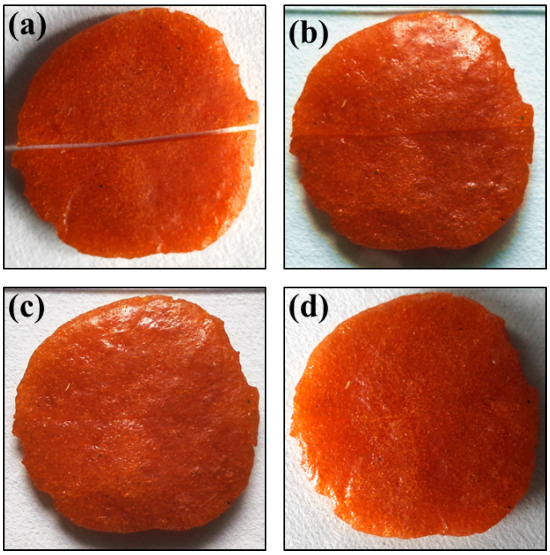
synthesized through RAFT chain extension reaction by the following step. The three BCP samples synthesized were denoted as BCP-x where x = 1, 2 and 3. S-Figure 1 describeed the GPC traces of macromolecular chain transfer agent PM1 as well as its corresponding BCPs, where the elution time of the samples obtained after RAFT chain extension reaction became shorter than that of before, indicating that the BCPs were successfully synthesized.



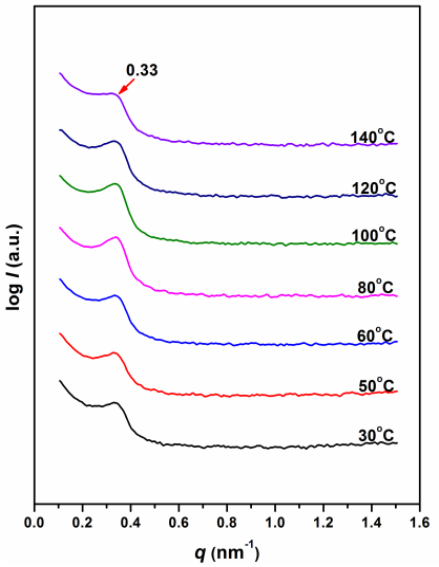
S-Figure 1. GPC traces of the PMAzoC_4, macro-chain transfer agent (PM1) and the BCPs



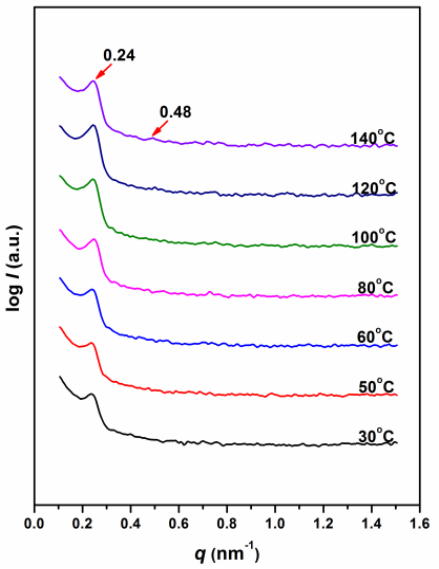
S-Figure 2. ^{1}H NMR spectra of PM1 and the BCPs.



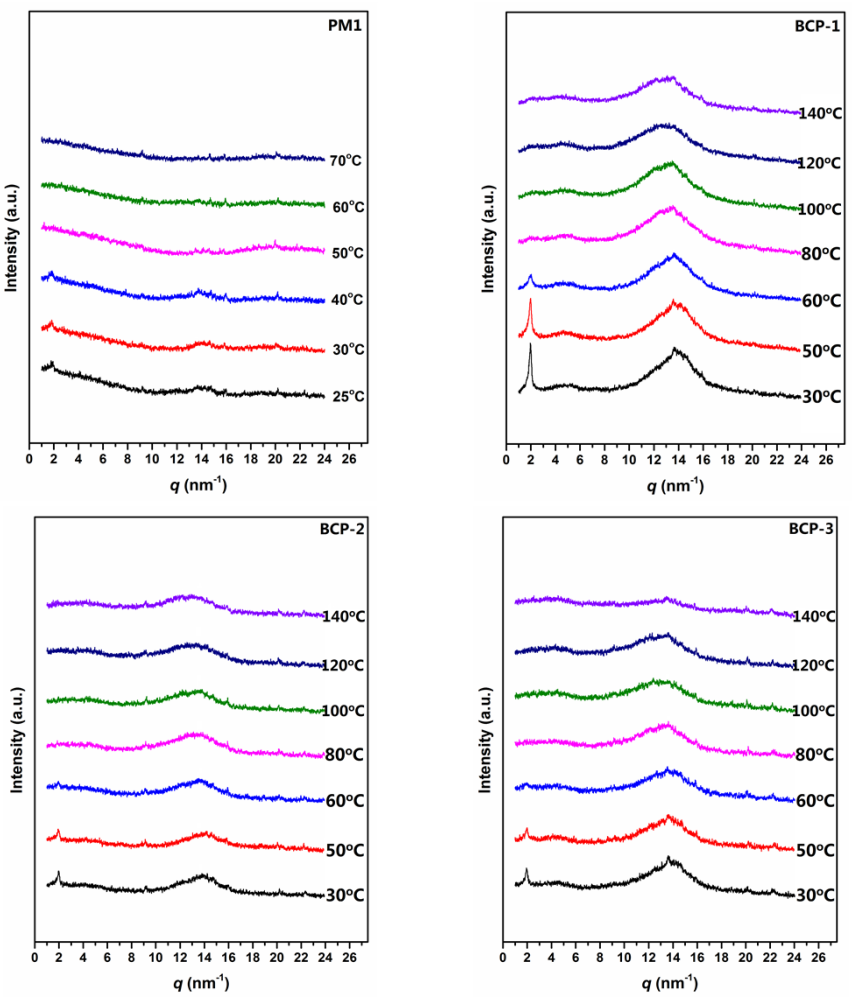
S-Figure 3. Self-healing test of BCP-3. (a) Cut Cut at room temperature, (b) warming at 50 °C for 5 min, (c) warming at 50 °C for 10 min; (d) warming at 50 °C for 20 min.



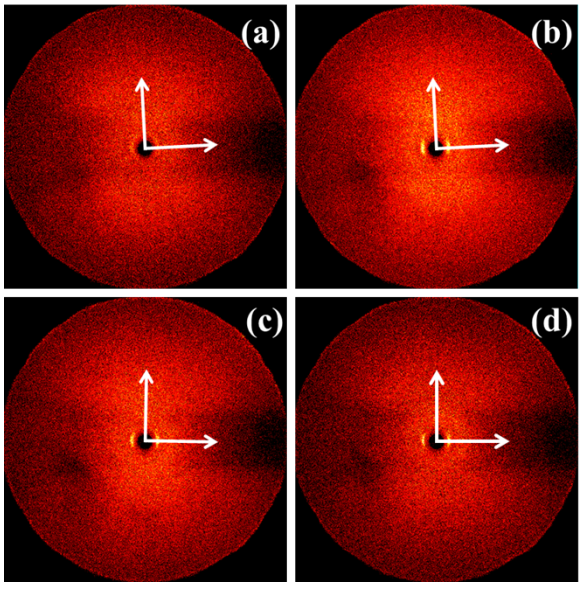
S-Figure 4. The scattering peaks for BCP-1



S-Figure 5. The scattering peaks for BCP-2



S-Figure 6. X-ray diffraction patterns of PM1 and BCPs at various temperatures.



S-Figure 7. Complete 2D-WAXD graphs of PM1 (a), BCP-1 (b), BCP-2 (c) and BCP-3 (d).