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### **Supporting Information**

## The first blue phase reactive monomers containing a bi-mesogenic core and their blue phase sidechain copolymers with different acrylate spacer lengths

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Reagents, measurements, and characterizations. All chemicals and solvents were reagent grades and purchased from ACROS, Aldrich, TCI, Fluka, and TEDIA. THF was distilled over sodium/benzophenone to keep anhydrous before use. After distillation over CaH<sub>2</sub>, DMF was purified by refluxing with calcium hydride and then distilled. The solvents were degassed by nitrogen 1 h prior to use before reaction. <sup>1</sup>H-NMR spectra were recorded on a Bruker DX-300 (300 MHz for <sup>1</sup>H) spectrometer using CDCl<sub>3</sub>, and DMSO-d<sub>6</sub> solvents. Elemental analyses were performed on HERAEUS CHN-OS RAPID elemental analyser. The phase transition properties of monomers and polymers were studied by polarizing optical microscopy (POM) using a Leica DMLP equipped with a temperature control hot stage (Mettler Toledo FP82HT) upon cooling process (cooling rate 0.5°Cmin<sup>-1</sup>). Temperatures and enthalpies of phase transitions were determined by differential scanning calorimetry (DSC, model: Perkin Elmer Pyris 7) under N<sub>2</sub> upon the first cooling and second heating cycles at a rate of 1°Cmin<sup>-1</sup>. The molecular weights of polymers were obtained via gel permeation chromatography (GPC) measurements, which were carried out at 40°C on a Waters 1515 instrument equipped with three Waters µ-Styragel columns (103, 104 and 105 Å) in series and a RI detector (ERMA Inc., ERC-7522). All GPC data were acquired by using tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min and polystyrene samples as the molecular weight standards. The AFM images were observed by an atomic-force microscope (AFM, Veeco diInnova, scanning rate 0.5 to 1 Hz).

Preparation of monomers and polymers

### Synthesis of 6-bromo-1-hexanol (n=6), 1a



A mixture of 1,6-hexanediol in aqueous 48% hydrogen bromide (1.2 e.q) and toluene was refluxed for 18 h and a side product H<sub>2</sub>O could be removed by Dean-Stark. The reaction mixture was washed with a saturated aqueous NaHCO<sub>3</sub> solution and water several times, and then the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 5:1 v/v) to afford compound **1a** as a pale yellow oil in a yield of 83%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 3.71 (t, J = 6.5 Hz, 2H), 3.53 (t, J = 6.8 Hz, 2H), 1.81-1.42 (m, 8H).

#### Synthesis of 12-bromododecan-1-ol (n=12), 1b

The similar manner was followed as that described above for the preparation of **1a**. Compound **1b** was obtained as a white solid in a yield of 80%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm) 3.65 (t, *J*= 6.52 Hz, 2H), 3.41 (t, *J*= 6.79 Hz, 2H), 1.92-1.83 (m, 2H), 1.63-1.54 (m, 2H), 1.52-1.34 (m, 18H), 1.30 ppm (s, 1H).

#### Synthesis of methyl 4-(heptyloxy)benzoate (n=6), 2a



A mixture of methyl 4-hydroxybenzoate (0.1 M), **1a** (1.2 e.q),  $K_2CO_3$  (2 e.q) and potassium iodide in dry acetone was stirred and refluxed under nitrogen for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was taken up in water and extracted with ethyl acetate. Then, the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 40:1 v/v) to afford compound **2a** as a white solid in a yield of 72%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.87 (d,*J*=9.0Hz, 2H), 6.97 (d, *J*=9.0Hz, 2H), 4.02 (t, *J*=6.3Hz, 2H), 3.88(s, 3H), 3.66 (t, *J*=6.1Hz, 2H), 1.86-1.46 (m, 8H), 4.32(s, 1H).

#### Synthesis of 4-((12-hydroxydodecyl)oxy)benzoate (n=12), 2b

The similar manner was followed as that described above for the preparation of **2a**. Compound **2b** was obtained as a white solid in a yield of 80%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 13.53 – 11.71 (m, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 4.32 (s, 1H), 4.02 (s, 2H), 1.71 (m, 2H), 1.39 (m, 4H), 1.24 (m, 14H).





To a stirred solution of **2a** in ethanol (0.1 M), an aqueous solution of potassium hydroxide (4 e.q) was added dropwise and heated to reflux overnight. After cooling to room temperature, the solvent was removed under reduced pressure, and acidified with 6 N HCl. The precipitated product was collected by filtration and recrystallization from ethanol/H<sub>2</sub>O (3:1 v/v) to afford compound **3a** as a white solid in a yield of 95%.

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 13.54–11.51 (m, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.32 (s, 1H), 4.01 (s, 2H), 1.70 (m, 2H), 1.38 (m, 4H), 1.25 (m, 4H).

#### Synthesis of 4-((12-hydroxydodecyl)oxy)benzoic acid (n=12), 3b

The similar manner was followed as that described above for the preparation of **3a**. Compound **3b** was obtained as a white solid in a yield of 86%.

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 13.53 – 11.71 (m, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 4.32 (s, 1H), 4.02 (s, 2H), 1.71 (m, 2H), 1.39 (m, 4H), 1.24 (m, 14H).

#### Synthesis of 4-((6-(acryloyloxy)hexyl)oxy)benzoic acid (n=6), 4a



To a solution of **3a** in 1,4-dioxane (0.7 M), acryloyl chloride in DMA (1.3 e.q) at 0°C under nitrogen was added dropwise to react for 15 min. After the mixture was warmed to room temperature and stirred at  $45^{\circ}$ C overnight. The resulting mixture was quenched by ice water, extracted with dichloromethane, and then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The precipitated product was collected by filtration and recrystallization from hexane to afford compound **4a** as a white solid in a yield of 92%.

<sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) 8.12 – 7.99 (d, 2H), 6.98 – 6.87 (d, 2H), 6.40 (m, J = 17.3, 1.5 Hz, 1H), 6.12 (m, J = 17.3, 10.4 Hz, 1H), 5.82 (m, J = 10.4, 1.6 Hz, 1H), 4.17 (t, J = 6.6 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 1.82 (m, J = 14.9, 7.0 Hz, 2H), 1.72 (m, J = 13.7, 6.8 Hz, 2H), 1.57 – 1.41 (m, 4H).

#### Synthesis of 4-((12-(acryloyloxy)dodecyl)oxy)benzoic acid (n=12), 4b

The similar manner was followed as that described above for the preparation of **4a**. Compound 4**b** was obtained as a white solid in a yield of 90%.

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 12.59 (s, 1H), 7.92 – 7.82 (d, 2H), 7.04 – 6.95 (d, 2H), 6.31 (m, 1H), 6.16 (m, 1H), 5.92 (m, 1H), 4.05 (m, 4H), 1.82 – 1.65 (m, 2H), 1.64 – 1.51 (m, 2H), 1.32 (m, 16H).

#### Synthesis of ethoxymethyl 4-hydroxybenzoate, 5



To a solution of 4-hydroxybenzoic acid in dry-DCM (1.3 M), triethylamine (1.2 e.q) and chloromethyl ethyl ether in dry-DCM (1 M) at 0°C under nitrogen were added dropwise to react for 90 min. After the mixture was warmed to room temperature and washed by HCl (0.25 M). The resulting mixture was extracted with ether, and then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 40:1 v/v) to afford compound **5** as a light yellow liquid in a yield of 70%.

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 10.40 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 6.86 (d, *J* = 7.5 Hz, 2H), 5.42 (s, 2H), 3.76 – 3.64 (m, 2H), 1.15 (m, *J* = 7.0, 5.8 Hz, 3H).

#### Synthesis of 4-((ethoxymethoxy)carbonyl)phenyl4-((6-(acryloyloxy)hexyl)oxy) benzoate (n=6), 6a



To a stirred solution of **4a** in dry-DCM (1 M), compound **5** in dry-DCM (1 M), 4-(*N*,*N*-dimethylamino)pyridine (DMAP) in dry dichloromethane and *N*,*N*-dicyclohexylcarbodiimide (DCC) (2.3 e.q) were added and the reaction mixture was stirred at room temperature overnight under nitrogen. The resulting precipitate of dicyclohexylurea (DCU) was filtered off and washed with an excess of dichloromethane. The solvent was evaporated and the crude product was purified by silica gel chromatography (*n*-hexane/dichloromethane = 1:1 v/v) to afford compound **6a** as a white solid in a yield of 82%.

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 8.09 (d, *J* = 8.8 Hz, 4H), 7.54 – 7.35 (m, 2H), 7.12 (d, *J* = 8.9 Hz, 2H), 6.32 (m, 1H), 6.17 (m, 1H), 5.93 (m, 1H), 5.51 (s, 2H), 4.11 (q, *J* = 6.5 Hz, 4H), 3.85 – 3.61 (m, 2H), 1.75 (m, 2H), 1.71 – 1.58 (m, 2H), 1.53 – 1.33 (m, 4H), 1.17 (t, *J* = 7.1 Hz, 3H).

## Synthesis of 4-((ethoxymethoxy)carbonyl)phenyl4-((12-(acryloyloxy)dodecyl)oxy) benzoate (n=12), 6b

The similar manner was followed as that described above for the preparation of **6a**. Compound **6b** was obtained as a white solid in a yield of 80%.

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 8.09 (d, *J* = 8.8 Hz, 4H), 7.54 – 7.35 (m, 2H), 7.12 (d, *J* = 8.9 Hz, 2H), 6.32 (m, 1H), 6.17 (m, 1H), 5.93 (m, 1H), 5.51 (s, 2H), 4.11 (q, *J* = 6.5 Hz, 4H), 3.85 – 3.61 (m, 2H), 1.75 (m, 2H), 1.71 – 1.58 (m, 2H), 1.53 – 1.33 (m, 4H), 1.17 (t, *J* = 7.1 Hz, 3H).

Synthesis of 4-((4-((6-(acryloyloxy)hexyl)oxy)benzoyl)oxy)benzoic acid (n=6), 7a



To a solution of **6a** in dry-EtOH (0.5 M), PPST (1 e.q) at 50°C under nitrogen was added to react for 16 hrs. After the mixture was warmed to room temperature, the resulting mixture was extracted with dichloromethane, and then dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The precipitated product was collected by filtration and recrystallization from hexane to afford compound **7a** as a white solid in a yield of 80%. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 13.05 (s, 1H), 8.05 (m, *J*=15.2, 4H), 7.40 (d, *J*=8.7 Hz, 2H), 7.12 (d, *J*=8.9 Hz, 2H), 6.32 (m, 3H), 6.17 (m, 1H), 5.93 (m, 1H), 4.11 (q, *J*=6.6 Hz, 4H), 1.75 (m, 2H), 1.71 – 1.58 (m, 2H), 1.53 – 1.33 (m, 4H), 1.17 (t, *J*=7.1 Hz, 3H).

#### Synthesis of 4-((4-((12-(acryloyloxy)dodecyl)oxy)benzoyl)oxy)benzoic acid (n=12), 7b

The similar manner was followed as that described above for the preparation of 7a. Compound 7b was obtained as a white solid in a yield of 82%.

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) 8.05 (m, *J* = 15.1, 8.8 Hz, 4H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.36 – 6.26 (m, 1H), 6.21 – 6.10 (m, 1H), 5.93 (d, *J* = 10.2 Hz, 1H), 4.09 (t, *J* = 6.5 Hz, 1H), 1.74 (s, 1H), 1.59 (s, 1H), 1.26 (s, 4H).

#### Synthesis of (S)-8-bromo-2,6-dimethyl-2-octene, 8



To a stirred solution of (S)-3,7-dimethyloct-6-en-1-ol (0.25 M) and carbon tetrabromide (CBr<sub>4</sub>) (1.1 e.q) in minimal dichloromethane, a solution of triphenylphosphine (PPh<sub>3</sub>) (1.2 e.q) in DCM was added to react at 0 °C under nitrogen. After the mixture was warmed to room temperature and stirred for 2 h. The

resulting mixture was poured into water and extracted with dichloromethane. The organic layer was dried over  $Na_2SO_4$  and evaporated. The crude product was purified by silica gel chromatography (*n*-hexane) to afford compound **8** as a colorless oil in a yield of 90%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 5.22 (t, *J* = 6.8 Hz, 1H), 3.41 (m, 2H), 2.02-1.51 (m, 13H), 1.12 (d, *J* = 6.2 Hz, 3H).

#### Synthesis of (S)-6-bromo-4-methylhexan-1-ol, 9



A solution of **8** in methanol (0.2 M) at -78 °C was ozonized under a stream of ozone purge for 2 h. The solution color changed from transparent to light yellow. After termination of the ozonolysis, compound **9** was monitored until disappearance by TLC. Subsequently, sodium borohydride in methanol (1.1 M) was added in portions to the solution and the mixture was brought to -65 °C, and the solution color changed from light yellow to transparent. A further portion of sodium borohydride (1 e.q) was added within 15 min, and the mixture was warmed to room temperature and stirred overnight. Water was added to the resulting mixture, and the solution was acidified with sulphuric acid and saturated with ammonium chloride and extracted with diethyl ether. The organic layer was sequentially washed with water, 10% aqueous sodium bicarbonate solution, and water, and then dried with sodium sulfate. The solvent was evaporated and the crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate = 5:1 v/v) to afford compound **9** as a colorless oil in a yield of 55%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 3.81 (t, *J* = 6.3 Hz, 2H), 3.42 (t, *J* = 6.3 Hz, 2H), 1.81-1.21 (m, 7H), 1.13 (d, *J* = 6.2 Hz, 3H).

#### Synthesis of (S)-6-[(4-cyano-4'-biphenylyl)oxy]-4-methylhexanol, 10



The similar manner was followed as that described above for the preparation of **2a**. Compound **10** was obtained as a light yellow solid in a yield of 74%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.83 (t, J = 8.9 Hz, 4H), 7.61 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.9 Hz, 2H), 4.23 (t, J = 6.4 Hz, 2H), 4.12 (t, J = 6.3 Hz, 2H), 1.82-1.24 (m, 7H), 1.11 (d, J = 6.2 Hz, 3H).

# Synthesisof(S)-6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)-4-methylhexyl4-((4-((6-(acryloyloxy)hexyl)oxy)benzoyl)oxy)benzoate, M1



The similar manner was followed as that described above for the preparation of **6a**. Compound **M1** was obtained as a light yellow solid in a yield of 78%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.02 (t, J = 8.5 Hz, 4H), 7.81 (s, 4H), 7.68 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.32 (m, 1H), 6.17 (m, 1H), 5.93 (m, 1H), 4.30 (t, J = 6.3 Hz, 2H), 4.11 (m, 6H), 1.75 (m, 6H), 1.66 (m, 4H), 1.43 (m, 7H), 0.97 (d, J = 6.3 Hz, 3H). Anal. calcd for C<sub>43</sub>H<sub>45</sub>NO<sub>8</sub>: C, 72.69, H, 6.22, N, 1,82; found: C, 73.38, H, 6.44, N, 1.99%.

# Synthesisof(S)-6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)-4-methylhexyl4-((4-((12-<br/>(acryloyloxy)benzoyl)oxy)benzoyl)oxy)benzoate, M2

The similar manner was followed as that described above for the preparation of **6b**. Compound **M2** was obtained as a light yellow solid in a yield of 76%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.02 (t, J = 8.1 Hz, 4H), 7.81 (s, 4H), 7.68 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 9.0 Hz, 4H), 7.05 (d, J = 8.8 Hz, 2H), 6.31 (m, 1H), 6.16 (m, 1H), 5.92 (m, 1H), 4.29 (t, J = 6.3 Hz, 2H), 4.08 (m, 6H), 1.75 (m, 6H), 1.59 (m, 5H), 1.42 (m, 2H), 1.26 (m, 15H), 0.97 (d, J = 6.0 Hz, 3H). Anal. calcd for C<sub>49</sub>H<sub>57</sub>NO<sub>8</sub>: C, 74.38, H, 7.39, N, 1,69; found: C, 74.69, H, 7.29, N, 1.78%.



#### General synthetic procedures of homopolymers and copolymers.

All of the polymerizations were carried out by the free radical polymerization described as follows: To a Schlenk tube, monomers **M1** and **M2** were mixed with appropriate molar ratios (0:10, 9:1, 3:7, 5:5, 7:3, 1:9 and 10:0) dissolved in dry chlorobenzen (0.146 M) and AIBN (0.03 e.q) as an initiator. The solution was degassed by three freeze-pump-thaw cycles and then sealed off. The reaction mixture was stirred and

heated at 60°C for 24 h. After polymerization, the polymer was precipitated into diethyl ether for homoand co-polymers. The precipitated polymers were collected, washed with diethyl ether, and dried under high vacuum.

**P1(soln) (m/n = 10/0)** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm): 8.01 (br, 4H), 7.67-7.45 (m, 6H), 7.14 (br, 2H), 6.94-6.87 (m, 4H), 4.29-3.96 (m, 8H), 1.77-1.55 (br, 10H), 1.43-0.96 (br, 11H). Mn: 331,559 g mol<sup>-1</sup>, PDI: 1.25 Mw/Mn.

**P12(soln:9/1) (m/n = 8.4/1.6)** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm): 7.98 (br, 4H), 7.58-7.43 (m, 6H), 6.97 (br, 2H), 6.92 (m, 4H), 4.27-3.97 (m, 8H), 2.09-1.55 (br, 12H), 1.25-0.97 (br, 11H). Mn: 323,381 g mol<sup>-1</sup>, PDI: 1.25 Mw/Mn.

**P12(soln:3/7) (m/n = 7/3)** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm): 8.00 (br, 4H), 7.56-7.45 (m, 6H), 7.15 (br, 2H), 6.99-6.89 (m, 4H), 4.34-3.96 (m, 8H), 1.78-1.56 (br, 11H), 1.37-0.94 (br, 14H). Mn: 326,051 g mol<sup>-1</sup>, PDI: 1.22 Mw/Mn.

**P12(soln:5/5) (m/n = 5/5)** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm): 8.00 (br, 4H), 7.57-7.45 (m, 6H), 7.14 (br, 2H), 6.91 (m, 4H), 4.29-4.00 (m, 8H), 1.78-1.54 (br, 10H), 1.26-1.03 (br, 17H). Mn: 303,541 g mol<sup>-1</sup>, PDI: 1.27 Mw/Mn.

**P12(soln:7/3) (m/n = 3/7)** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm): 8.07 (br, 4H), 7.55-7.44 (m, 6H), 6.99 (br, 2H), 6.99-6.89 (m, 4H), 4.34-3.99 (m, 8H), 1.78-1.56 (br, 13H), 1.37-0.94 (br, 16H). Mn: 323,145 g mol<sup>-1</sup>, PDI: 1.20 Mw/Mn.

**P12(soln:9/1) (m/n = 1.3/8.7)** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm): 8.04 (br, 4H), 7.60-7.48 (m, 6H), 6.93 (br, 2H), 6.93 (m, 4H), 4.30-4.00 (m, 8H), 1.79-1.54 (br, 10H), 1.29-0.98 (br, 21H). Mn: 330,047 g mol<sup>-1</sup>, PDI: 1.28 Mw/Mn.

**P2(soln) (m/n = 0/10)** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm): 8.04 (br, 4H), 7.60-7.48 (m, 6H), 6.93 (br, 2H), 6.93-6.84 (m, 4H), 4.30-4.00 (m, 8H), 1.79-1.54 (br, 15H), 1.43-1.01 (br, 18H). Mn: 334,718 g mol<sup>-1</sup>, PDI: 1.21 Mw/Mn.



**Fig. S1** <sup>1</sup>HNMR spectra of (a) **M1/M2(5/5)** and (b) **P12(soln:5/5)** in CDCl<sub>3</sub>. The copolymer composition of **P12(soln:5/5)** was estimated by comparing with **M1/M2(5/5)** after solution polymerization with the relative integration areas of the peaks at 0.5-2.0 ppm as 3 protons (i.e., the vinyl acrylate group). This result indicated that the feed-in and output molar ratios were almost consistent. The compositions of all copolymers were all evaluated by this method.



Fig. S2 GPC curves of (a) P1(soln) (b) P12(soln:5/5) (c) P2(soln) (d) P1(photo) (e) P12(photo:5/5) and (f) P2(photo).



**Fig. S3** DSC curves of (a) **P1(soln)** (b) **P12(soln:5/5)** (c) **P2(soln)** (d) **P1(photo)** (e) **P12(photo:5/5)** and (f) **P2(photo)**.



Fig. S4 Phase diagrams (upon cooling) of binary mixtures, photo- and solution-polymerizations with different molar ratios of M1.



Fig. S5 An expanded AFM image of P12(soln:5/5) in BPIII (at 146.1°C) was quenched by liquid  $N_2$ . (White scale bar: 1µm.)

Common da	Solution-Polymerization		Compounds	Photo-Polymerization	
Compounds	Mn (g/mol)	PDI (Mw/Mn)	Compounds	Mn (g/mol)	PDI (Mw/Mn)
P1(soln)	331,559	1.25	P1(photo)	260,766	1.42
P12(soln:9/1)	323,381	1.25	P12(photo:9/1)	264,462	1.39
P12(soln:7/3)	326,051	1.22	P12(photo:7/3)	244,592	1.40
P12(soln:5/5)	303,541	1.27	P12(photo:5/5)	241,019	1.42
P12(soln:3/7)	323,145	1.20	P12(photo:3/7)	245,902	1.40
P12(soln:1/9)	330,047	1.28	P12(photo:1/9)	266,011	1.39
P2(soln)	334,718	1.21	P2(photo)	267,871	1.41

 

 Table S1
 Molecular weights (Mn and Mw) and polydispersity indexes (PDI) of solution- and photopolymers <sup>a</sup>

<sup>a</sup> These datas were determined by gel permeation chromatography (GPC).