

# Supplementary Materials: SRG Inscription in Supramolecular Liquid Crystalline Polymer Film: Replacement of Mesogens

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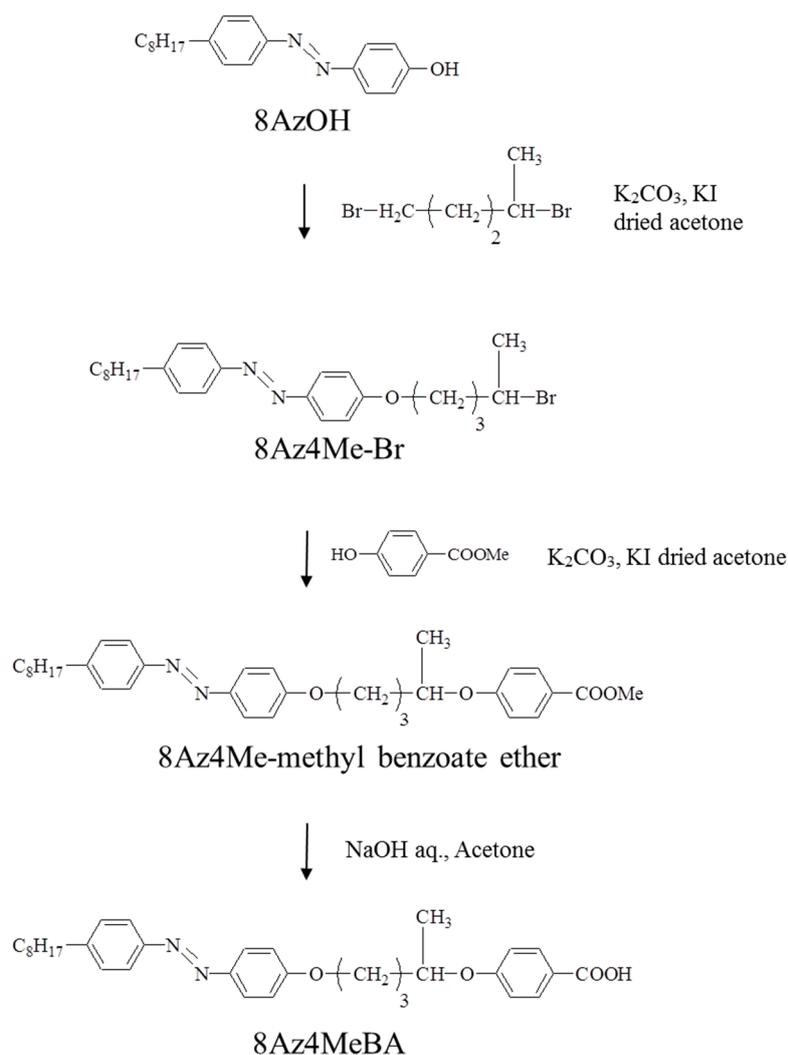
## S1. Synthesis

### Materials

Sodium hydroxide, potassium carbonate, triethylamine, 2,2'-azobisisobutyronitril (AIBN) were purchased from Kanto Chemicals Co. 6-bromo-1-hexanol and methacryloyl chloride were obtained from TCI, and potassium iodide was purchased from Koso Chemicals. A methacrylate monomer containing oligo(ethylene oxide) ((PE200, EO unit:  $n = 4.5$  on average) was kindly provided from NOF Corp.

### Synthesis of azobenzene derivative

The synthetic route for the azobenzene-containing benzoic acid 8Az4MeBA was shown in the scheme below.



*4-(4'-octylazo)phenol (8AzOH)*

8AzOH was synthesized according to the method previously described [1].

*4-[(4'-octylazophenyl)-4-bromo-4-methylbutoxy]benzene (8Az4Me-Br)*

Potassium carbonate (3.57 g, 25.8 mmol) and a trace of potassium iodide, 8AzOH (2.0 g, 6.45 mmol) in acetone (30 mL) was placed in a three-necked flask, and mixed for 15 min. Into this mixture, 1-methyl-1,4-bromopentane (2.79 g, 12.9 mmol) dissolved in acetone was added dropwise. The mixture was stirred at 70 °C for 2 h. After the reaction the undissolved materials were filtered off, and the solvent was evaporated. The reactant was dissolved in chloroform and washed with water twice and dried over anhydrous sodium sulfate. The product was purified by column chromatography. Yield: 71 %. <sup>1</sup>H-NMR (δ [ppm], 270 MHz, CDCl<sub>3</sub>): 0.879 (3H, *t*, CH<sub>3</sub>-), 1.15-1.80 (15H, *m*, -CH<sub>2</sub>-), 1.82-2.15 (4H, *m*, -CH<sub>2</sub>-), 2.67 (2H, *t*, -CH<sub>2</sub>-Ph), 4.00 (2H, *t*, -CH<sub>2</sub>-O-Ph), 4.15 (1H, *m*, Br-CHCH<sub>3</sub>-), 6.99 (2H, *d*, Ph-H), 7.28 (2H, *d*, Ph-H), 7.80 (2H, *d*, Ph-H), 7.89 (2H, *d*, Ph-H) (Figure S1a)

*8Az4Me-methyl benzoate ether*

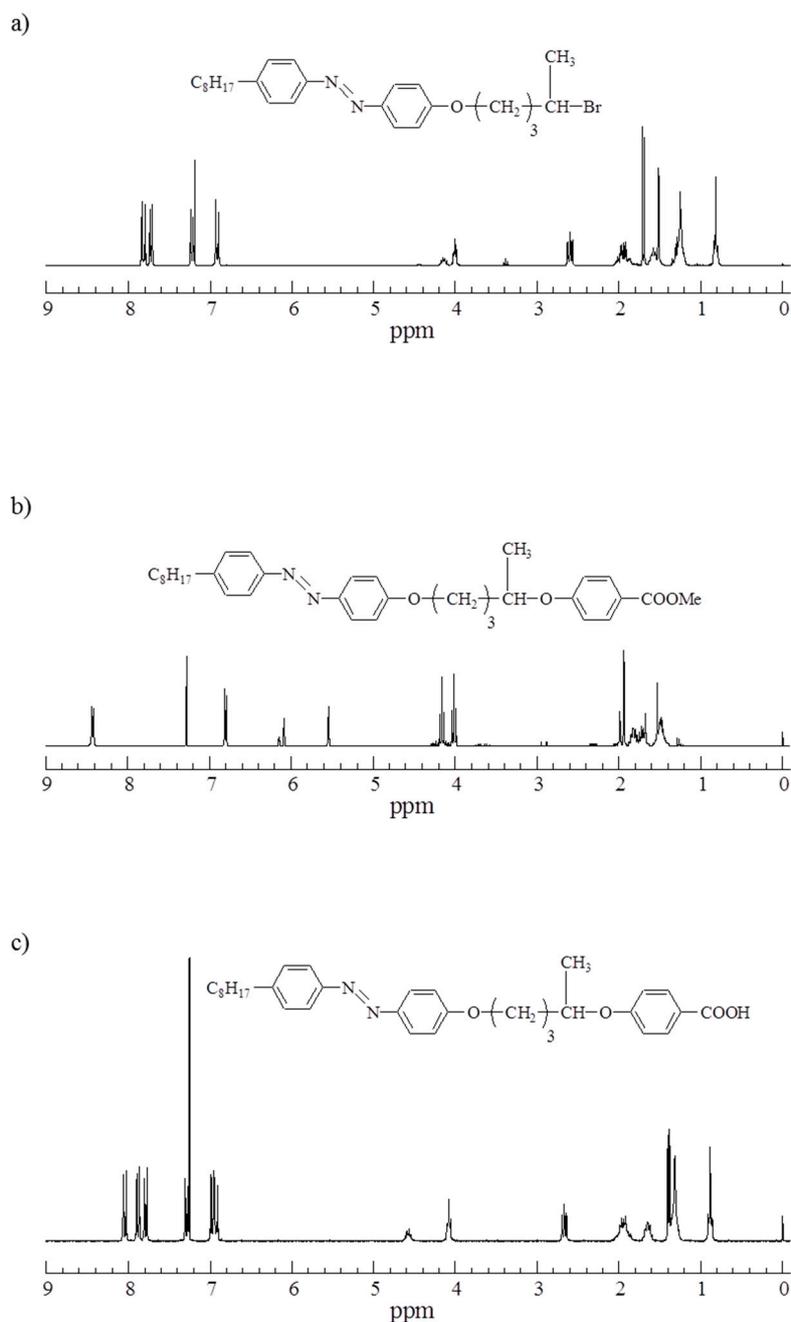
Potassium carbonate (6.47 g, 48.78 mmol) and a trace of potassium iodide, and 4-hydroxyl benzoic acid methyl ether (1.48 g, 9.76 mmol) in 50 mL dried N,N-dimethylformamide (DMF) was placed in a three-necked flask and stirred for 15 min. Into this solution, p-8Az4MeBr in 50 mL dried DMF was added dropwise, and stirred at 130 °C for 54 h. After the reaction, the solvent (DMF) was evaporated, and dissolved in chloroform. This solution was washed with water twice and dried over anhydrous sodium sulfate. After the solvent was evaporated, the product was purified by column chromatography. Yield: 32 %.

<sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>, TMS) δ [ppm]: 0.879 (3H, *t*, CH<sub>3</sub>-), 1.10-1.80 (12H, *m*, -CH<sub>2</sub>-), 1.82-2.20 (4H, *m*, -CH<sub>2</sub>-), 2.67 (2H, *t*, -CH<sub>2</sub>-), 4.08 (2H, *t*, -CH<sub>2</sub>-O-Ph), 6.99 (2H, *d*, Ph-H), 7.28 (2H, *d*, Ph-H), 7.80 (2H, *d*, Ph-H), 7.89 (2H, *d*, Ph-H) (Figure S1b)

## Hydrolysis of 8Az4Me-methyl benzoate ether

8Az4Me-(4-methyl benzoate) ether (1.2 g, 2.4 mmol) was dissolved in acetone (20 mL) and placed in a 200 mL three-necked flask. A small amount of sodium hydroxide (0.48 g, 12 mmol) was added to this solution and refluxed for 70 °C for 1 h. The reacted solution was neutralized with a 10 % hydrochloric acid aqueous solution, and the resulting precipitate was collected by filtration and recrystallized from a mixture of chloroform and hexane. Orange powdered crystal was obtained. Yield: 83 %.

<sup>1</sup>H-NMR (δ [ppm], 270 MHz, CDCl<sub>3</sub>): 0.879 (3H, *t*, CH<sub>3</sub>-), 1.15-1.80 (15H, *m*, -CH<sub>2</sub>-), 1.82-2.15 (4H, *m*, -CH<sub>2</sub>-), 2.67 (2H, *t*, -CH<sub>2</sub>-Ph), 4.10 (2H, *t*, -CH<sub>2</sub>-O-Ph), 6.99 (2H, *d*, Ph-H), 7.15 (1H, *m*, Ph-H), 7.28 (2H, *d*, Ph-H), 7.37 (1H, *m*, Ph-H), 7.61 (2H, *d*, Ph-H), 7.70 (1H, *m*, Ph-H), 7.80 (2H, *d*, Ph-H), 7.89 (2H, *d*, Ph-H) (Figure S1c)



**Figure S1** 270 MHz  $^1\text{H-NMR}$  spectra of Az derivatives in  $\text{CDCl}_3$ , 8Az4Me-Br (a), 8Az4Me-methyl benzoate ether (b), and 8Az4Me-Bz.

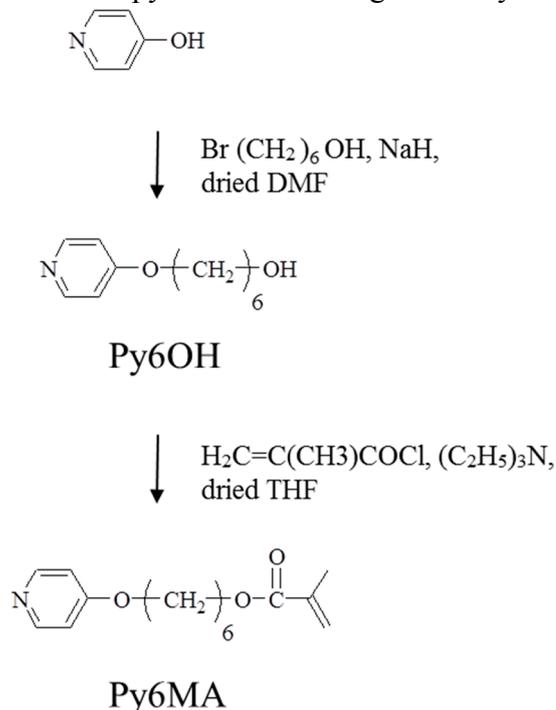
#### Synthesis of 4'-cyano-4-(4-bromobutyl)biphenyl (CB-Br)

In a three-necked flask, potassium carbonate (3.6 g, 25 mmol), a trace of potassium iodide, and 4'-cyano-4-hydroxyl biphenyl (1.3 g, 6.5 mmol) dissolved in acetone (30 mL) was placed and stirred for 15 min at room temperature. Into this solution, 1,4-dibromobutane (2.8 g, 13 mmol) in 10 mL acetone was added dropwise. The mixture was stirred at 70 °C for 4 h. After the reaction, solid substances were filtered off, and chloroform was added to the reacted solution, washed with water twice and dried over anhydrous sodium sulfate. After solvent evaporation, the resultant product (oil) was purified by column chromatography. Yield: 68 %.

$^1\text{H-NMR}$  ( $\delta$  [ppm], 270MHz,  $\text{CDCl}_3$ ): 1.10-1.80 (4H, *m*,  $-\text{CH}_2-$ ), 3.51 (2H, *t*,  $\text{Br-CH}_2-$ ), 4.08 (2H, *t*,  $-\text{CH}_2-\text{O-Ph}$ ), 6.99 (2H, *d*, Ph-H), 7.28 (2H, *d*, Ph-H), 7.60-7.80 (4H, *d+d*, Ph-H).

Synthesis of polymer, *P(Py-EO)*

The synthetic route to the pyridine-containing methacrylate is shown below.



#### 4-(hydroxyhexyloxy) pyridine (Py6OH)

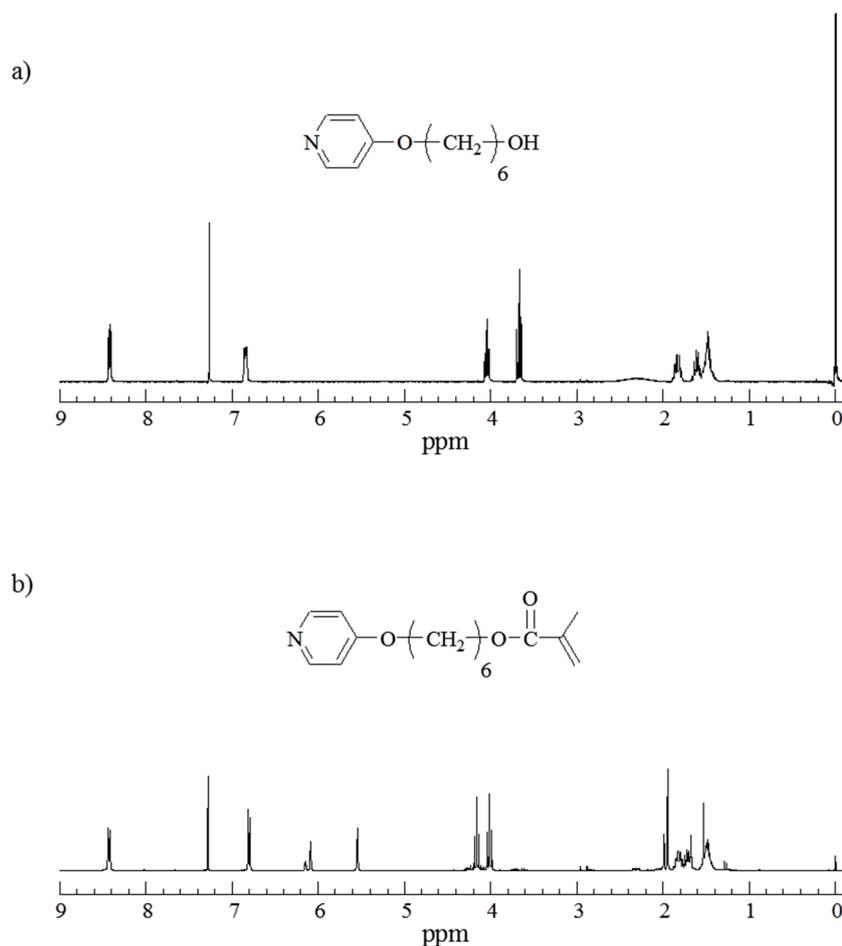
Dried DMF was placed in a 500 mL three-necked flask, and sodium hydride (3.8 g, 160 mmol) was added. Into this mixture, 4-hydroxypyridine (8.6 g, 80 mmol) dissolved in dry DMF was added using a syringe, and stirred at 60 °C for 1 h. Then, 6-bromo-1-hexanol (16 g, 88 mmol) dissolved in dry DMF was added dropwise and stirred at 60 °C for 12 h. After the reaction, chloroform was added and washed with water twice. The organic phase was dried over anhydrous sodium sulfate and concentrated. The resulting oily product was purified by column chromatography, and a white powder was obtained. Yield: 22 %.

$^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  [ppm]: 1.40-1.90 (8H, *m*,  $-\text{CH}_2-$ ), 1.6-2.6 (1H, broad,  $-\text{OH}$ ), 3.61-3.70 (2H, *t*,  $\text{HO-CH}_2-$ ), 4.08 (2H, *t*,  $-\text{CH}_2-\text{O-Ph}$ ), 6.82 (2H, *d*, Ph-H), 8.4 (2H, *d*, Ph-H). (Figure S2a)

#### 4-(methacryloyloxy hexylhexyloxy) pyridine (Py6MA)

Py6OH (5.0 g, 26 mmol) and trimethylamine (4.4 g, 44 mmol) dissolved in dry THF (100 mL) was placed in 300 mL three-necked flask and stirred at room temperature for 10 min. Then, methacryl chloride (4.0 g, 38 mmol) in dry THF was added into the above solution in ice bath. The mixture was stirred for 15 min in ice bath and then 30 min at room temperature. After the solvent and trimethylamine was evaporated, the resultant oil was dissolved in chloroform, washed with water twice and the organic phase was dried over anhydrous sodium sulfate. After the chloroform was evaporated the resultant brown oil was purified by column chromatography. The product was obtained as yellowish oil. Yield: 68 %.

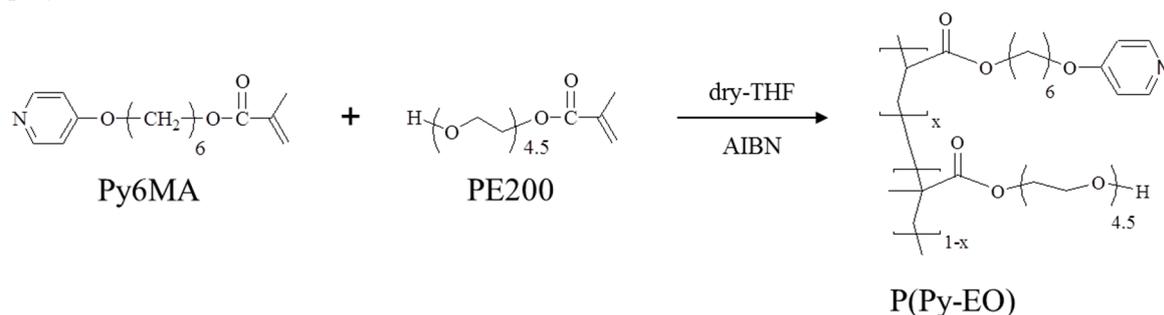
$^1\text{H-NMR}$  (270 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  [ppm]: 1.40-1.90 (8H, *m*,  $-\text{CH}_2-$ ), 1.6-2.6 (1H, broad,  $-\text{OH}$ ), 1.95 (3H, *s*,  $-\text{CH}_3$  (methacryl)), 4.00 (2H, *t*,  $-\text{CH}_2-\text{O-Ph}$ ), 4.17 (2H, *t*,  $\text{CH}_2-\text{O-C-O}$ ), 5.56 and 6.1 (2H, *d*,  $\text{C}=\text{CH}_2$ ), 6.82 (2H, *d*, Ph-H), 8.4 (2H, *d*, Ph-H). (Figure S2b)



**Figure S2** 270 MHz <sup>1</sup>H-NMR spectra of pyridine derivatives in CDCl<sub>3</sub>, Py6OH (a) and Py6MA (b).

#### Polymerization to P(Py-EO)

The random copolymer containing Py6MA and PE200 was synthesized by radical polymerization with AIBN as the initiator.



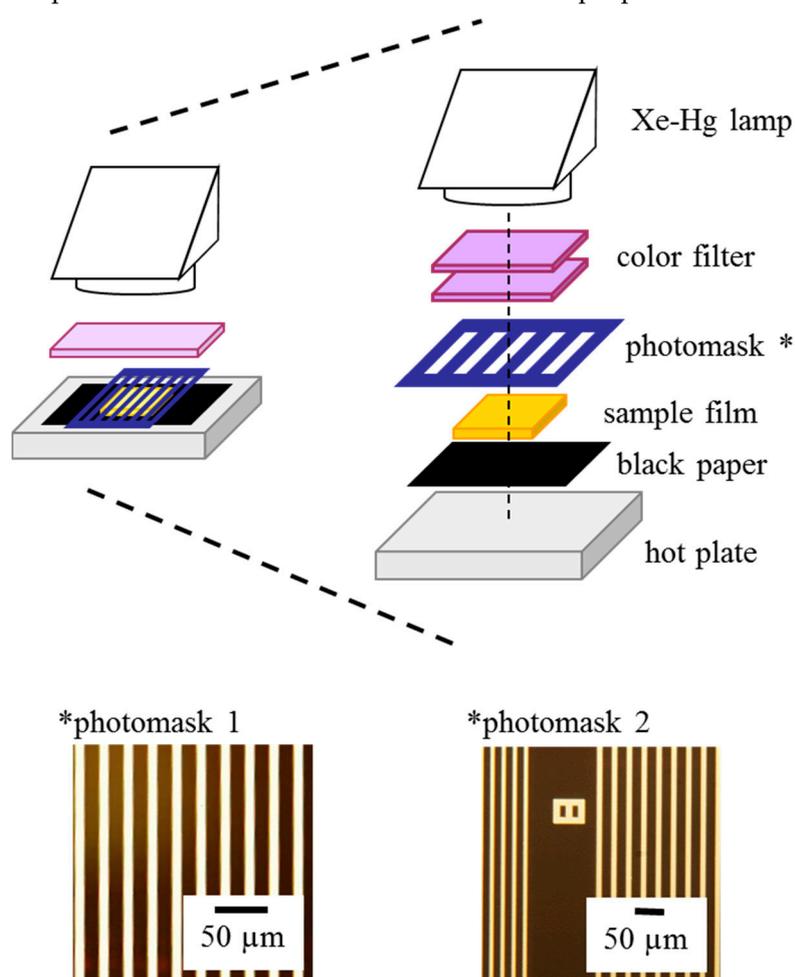
Py6MA and the oligo(ethylene oxide)-containing methacrylate monomer (PE-200) at 7:3 molar ratio and AIBN (1 % by weight) were dissolved in distilled THF and degassed by freeze-pump-thaw method three times using an ampule. The sealed ampule was heated to 70 °C for 4 h with stirring. After the ampule was open, some amount of THF was evaporated, and precipitated by pouring into hexane. Reprecipitation was repeated twice. Yield: 52 %. The number-averaged molecular weight ( $M_n$ ) and polydispersity index ( $M_w/M_n$ ) were determined by gel permeation chromatography (GPC) using Shodex DS-4 (UV detector) with columns of KF 803F and KF 805L (eluent solvent: THF). The  $M_n$  and  $M_w/M_n$  P(Py-EO) used in this work were found to be  $8.9 \times 10^3$  and 1.24, respectively. The content of

pyridine unit in the resulting copolymer was determined by  $^1\text{H-NMR}$  using a JNM-GSX270 (JEOL). The content of pyridine was 0.48.

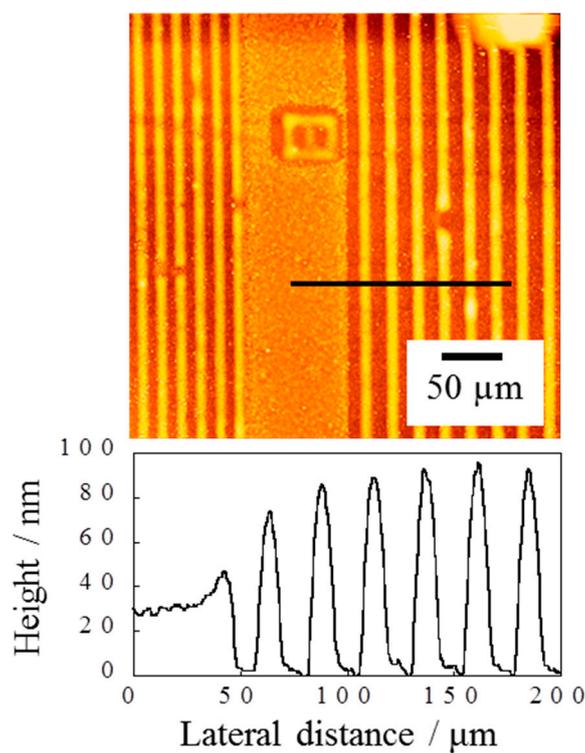
## S2. Photo-triggered Mass transfer with a photomask

The setup for the irradiation with a photomask is indicated in Figure S3. Two types of photomask were used. Temperature was controlled with a hot plate. Photomask 1 ( $10 \times 10 \mu\text{m}$  line and space) was routinely used to observe the photo-triggered mass transfer as shown in the main text. Photomask 2 was employed to evaluate the direction of mass transfer. Figure S4 indicates the resulting surface profile after irradiation with UV (365 nm light) using Photomask 2. The irradiated areas became higher than the surrounding areas, indicating that the mass migration occurred from masked regions to irradiated ones [2].

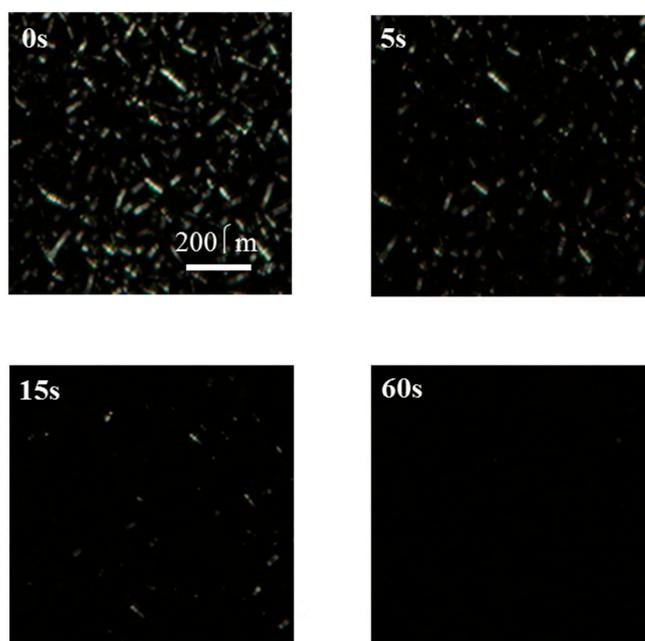
Figure S4 shows the change in the birefringence nature of P(Py-EO)/8Az4MeBA film during irradiation with UV light ( $2 \text{ mW cm}^{-2}$ ) at  $120 \text{ }^\circ\text{C}$ . Disappearance of birefringent character indicates the occurrence of a photoinduced isothermal smectic A to isotropic phase transition [3,4].



**Figure S3** Illustration of irradiation setup for the observation of photo-triggered mass migration in a P(Py-EO)/8Az4MeBA film.



**Figure S4** AFM image and surface profile after irradiation with UV light on a P(Py-EO)/8Az4MeBA film through Photomask 2.



**Figure S5** POM images of a P(Py-EO)/8Az4MeBA film after irradiation with UV light ( $2 \text{ mW cm}^{-2}$ ) at  $120 \text{ }^{\circ}\text{C}$ .

## References

1. Li, W.; Nagano, S.; Seki, T. Photo-crosslinkable liquid-crystalline azo-polymer for surface relief gratings and persistent fixation. *New J. Chem.* **2009**, *33*, 1343-1348.
2. Isayama, J.; Nagano, S.; Seki, T. Phototriggered Mass Migrating Motions in Liquid Crystalline Azobenzene Polymer Films with Systematically Varied Thermal Properties. *Macromolecules* **2010**, *43*, 4105-4112.

3. Zettsu, N.; Ogasawara, T.; Arakawa, R.; Nagano, S.; Ubukata, T.; Seki, T. Highly Photosensitive Surface Relief Gratings Formation in a Liquid Crystalline Azobenzene Polymer: New Implications for the Migration Process. *Macromolecules* **2007**, *40*, 4607-4613.
4. Zettsu, N.; Ogasawara, T.; Mizoshita, N.; Nagano, S.; Seki, T. Photo-Triggered Surface Relief Grating Formation in Supramolecular Liquid Crystalline Polymer Systems with Detachable Azobenzene Unit. *Adv. Mater.* **2008**, *20*, 516-521.



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