

Supplementary Information

ON/OFF switching of structural color by using multi-bilayered films containing copolymers having azobenzene and biphenyl side groups

Ryohei Yagi,^a Hiroyuki Iwamoto,^a Yutaka Kuwahara,^{a,d} Sun-Nam Kim,^a Tomonari Ogata,^b and Seiji Kurihara^{a,c,d,*}

^aGraduate School of Science and Technology, and ^bInnovative Collaboration Organization, Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan

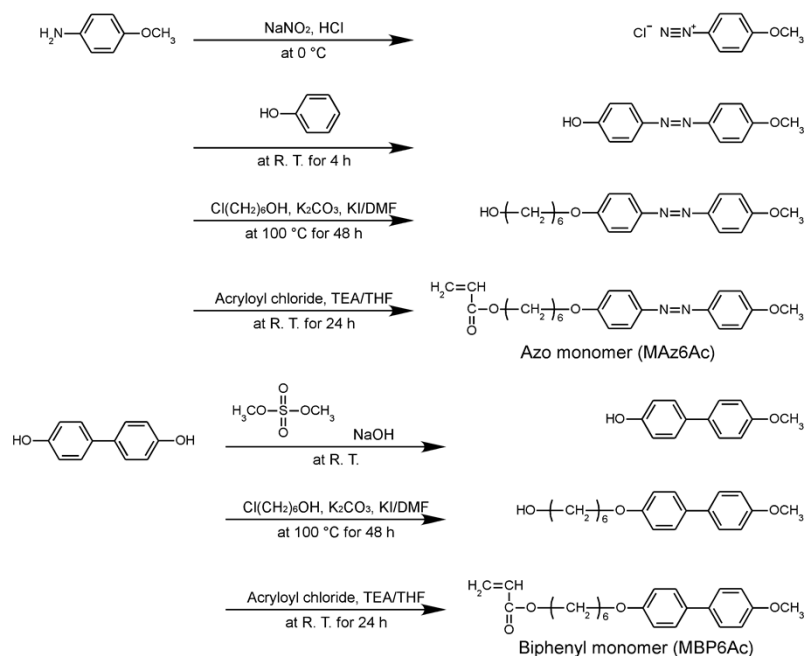
^cJST, CREST, 7 Gobancho, Chiyoda-ku, Tokyo 102-0076, Japan

^dKumamoto Institute for Photo-Electro Organics (PHOENICS), 3-11-38 Higashimachi, Higashi-ku, Kumamoto, 862-0901, Japan.

*Correspondence to: Seiji Kurihara (E-mail: kurihara@gpo.kumamoto-u.ac.jp)

Synthesis of monomers, MAz6Ac and MBP6Ac

The azobenzene monomer and the biphenyl monomer, MAz6Ac and MBP6Ac were synthesized by the synthetic route shown in scheme S1. [1, 2]



Scheme S1 Synthetic route of azo monomer and biphenyl monomer

Ref[1] Ikeda T, Horiuchi S, Karanjit DB, Kurihara S, Tazuke S. *Macromolecules* 1990, **23**, 36-42

Ref[2] Li Chen, Tian-hui Hu, He-lou Xie, Hai-liang Zhang *Journal of Polymer Science: Part A: Polymer Chemistry* 2010, **48**, 2838-45

4-Methoxy-4-hydroxyazobenzene

p-Anisidine (9 g, 73 mmol) was dissolved in 300 mL of 2 mol L⁻¹ HCl and the resulting solution was cooled to 0 °C in an ice bath. An amount of 5 g (72.5 mmol) of NaNO₂ dissolved in 150 mL of water was added dropwise to the solution of anisidine to form a diazonium salt. This solution was added to 6.9 g (73 mmol) of phenol dissolved in 200 mL of 2 mol L⁻¹ NaOH at 0 °C. A yellow precipitate was formed. The reaction mixture was then stirred at room temperature for 2 h. The precipitate was filtered out and recrystallized from a solution of hexane and benzene (7 : 2) and was dried under vacuum.

Yield: 70% as solid. M.p. 138-141 °C. Analysis. Calcd for C₁₃H₁₂N₂O₂ (%): C, 68.41; H, 5.30; N, 12.27. Found: C, 68.53; H, 5.39; N, 12.10.

4-Methoxy-4-(6-hydroxyhexyloxy)azobenzene

To a mixture of 5 g (22.3 mmol) of 4-methoxy-4-hydroxyazobenzene, 2.8 g (20mmol) of K₂CO₃ and about 50 mg of KI dissolved in 100 mL of DMF, 3.1 g (22.3 mmol) of 6-chlorohexanol was added. After refluxing for 24 h at 100 °C the reaction mixture was poured into water, extracted with CHCl₃, washed with water and dried over anhydrous magnesium sulfate. After removal of CHCl₃ by evaporation the liquid obtained was poured into water. The precipitate was collected by filtration and was purified by recrystallization from methanol.

Yield: 60% as solid. M.p. 124-125 °C.

¹H NMR (400 MHz, CDCl₃; δ, ppm): 1.23-1.86 (m, 8H, methylene), 3.67 (m, 2H, CH₂OH), 3.89 (s, 3H), 4.0-4.1(m, 2H), 4.4 (t, 1H, OH), 6.9-7.9 (m, 8H, aromatic). Elemental analysis calcd for C₁₉H₂₄N₂O₃ (%): C, 69.49; H, 7.36; N, 8.52. Found: C, 69.36; H, 7.34; N, 8.51.

MAz6Ac

To a solution of 3 g (9.14 mmol) of 4-methoxy-4-(6-hydroxyhexyloxy)azobenzene and a minute amount of hydroquinone 1 mg dissolved in 50 mL of tetrahydrofuran, 1.85 g (18.30 mmol) of triethylamine and 1.91 g (18.30 mmol) of acryloyl chloride were slowly added at 0 °C with stirring. After stirring at room temperature for 24 h the reaction mixture was poured into water. The precipitated product was collected and recrystallized from methanol.

Yield: 53% as solid. M.p. 96-97 °C.

¹H NMR (400 MHz, CDCl₃; δ, ppm): 1.42-2.19 (m, 8H), 3.67 (t, *J*=6.0 Hz, 2H), 3.89 (s, 3H), 4.04 (t, *J*=6.0 Hz, 2H), 4.18 (t, *J*=6.0 Hz, 2H), 5.81 (d, *J*=10.8 Hz, 1H), 6.08-6.18 (m, 1H), 6.42 (d, *J*=17.6 Hz, 1H), 6.95-7.90 (m, 8H). Elemental analysis calcd for C₂₂H₂₆N₂O₄ (%): C, 69.09; H, 6.85; N, 7.32. Found: C, 69.05; H, 6.91; N, 7.30.

Biphenyl monomer was synthesized by a similar manner with azobenzene monomer.

4-Methoxy-4-hydroxybiphenyl

4,4'-Dihydroxybiphenyl (25 g, 0.13 mol) was dissolved in 400 mL of 10wt% NaOH water solution, and dimethyl sulfate (17 g, 0.13 mol) was added and the solution was stirred. The reaction mixture gradually solidified. The precipitate was collected and washed with 10% NaOH water solution. Then, the product was dissolved in boiling water and insoluble by-products were separated by hot filtration. Upon addition of dilute hydrochloric acid the product precipitated. The precipitate was filtered, washed with water, and recrystallized from ethanol.

Yield: 53 % as solid. M.p. 96-97 °C.

^1H NMR (400 MHz, CDCl_3 ; δ , ppm): 4.0 (s, 2H), 4.7 (s, 1H), 6.9-7.5 (m, 8H). Elemental analysis calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2$ (%): C, 75.97; H, 8.05. Found: C, 75.20; H, 7.86.

4-Methoxy-4-(6-hydroxyhexyloxy)biphenyl

Yield: 41 % as solid. M.p. 145-15 °C.

^1H NMR (400 MHz, CDCl_3 ; δ , ppm): 1.4-2.0 (m, 8H), 3.6-3.7 (s, 3H), 3.7-3.8 (t, 1H), 4.0 (t, 2H), 6.9-7.5 (m, 8H). Elemental analysis calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3$ (%): C, 75.97; H, 8.05. Found: C, 75.93; H, 8.21.

4-[6-(acryloyloxy)hexyloxy]-4-methoxybiphenyl (MBP6Ac)

Yield: 47 % as solid. M.p. 89-91 °C.

^1H NMR (400 MHz, CDCl_3 ; δ , ppm): 1.43-1.85 (m, 8H), 3.84 (s, 3H), 3.97-4.00 (t, 12.7 Hz, 2H), 4.16-4.19 (t, 13.7 Hz, 2H), 5.80-5.82 (d, 10.8 Hz, 1H), 6.09-6.15 (m, 17.6 Hz, 1H), 6.37-6.42 (d, 15.6 Hz, 1H), 6.93-6.99 (m, 4H), 7.44-7.48 (m, 4H). Elemental analysis calcd for $\text{C}_{22}\text{H}_{26}\text{O}_4$ (%): C, 74.55; H, 7.39. Found: C, 74.43; H, 7.43.

The structure characterization of PMAz-PMBP(m:n)

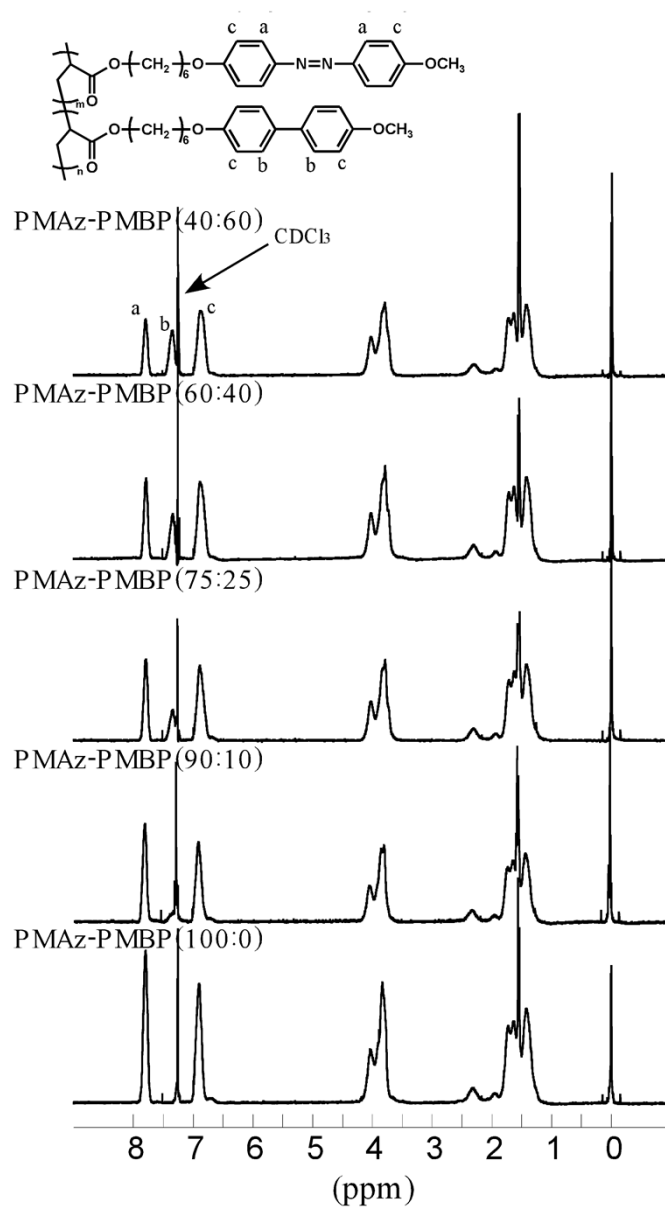


Figure S1 ¹H NMR spectra of PMAz-PMBP(m:n).

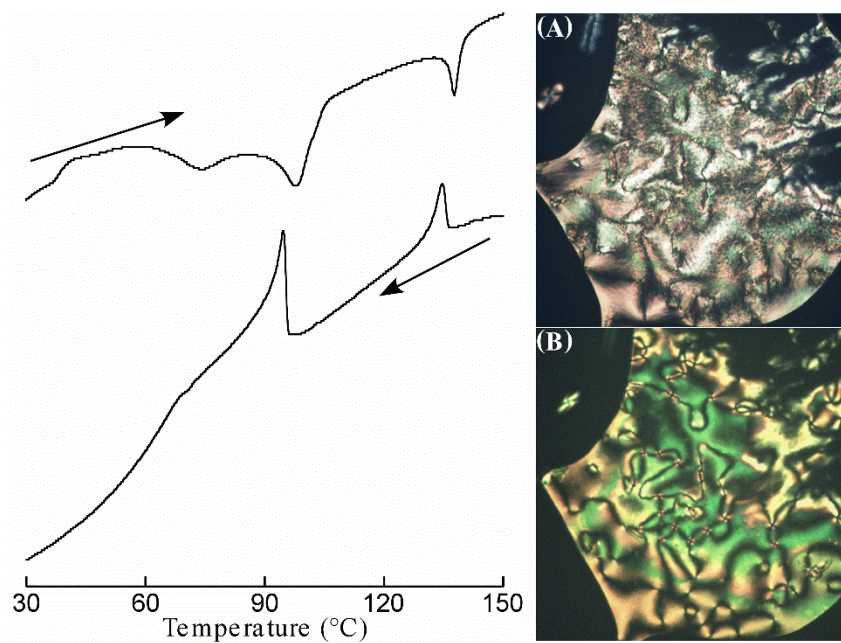


Figure S2 DSC curve on second cooling and heating cycle and polarized optical microscope (POM) image of PMAz-PMBP(100:0) at 80 °C (A) and 120 °C (B).

Photoisomerization of PMAz-PMBP(m:n) in chloroform by irradiation with UV and Vis light.

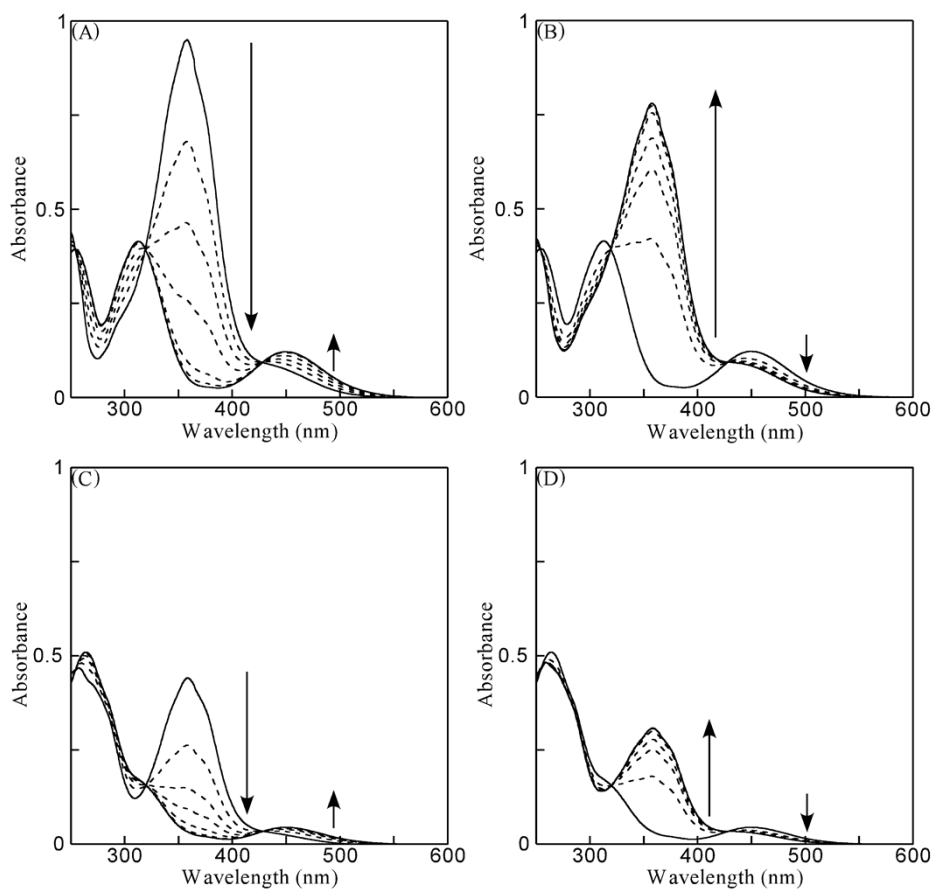


Figure S3 Changes in absorption spectra of PMAz-PMBP(100:0) (A, B) and PMAz-PMBP(40:60) (C, D) in chloroform by irradiation with UV light (365 nm, 5 mW/cm²) and following Vis light (436 nm, 80 mW/cm²).

Molecular orientation of PMAz-PMBP(m:n) solid film

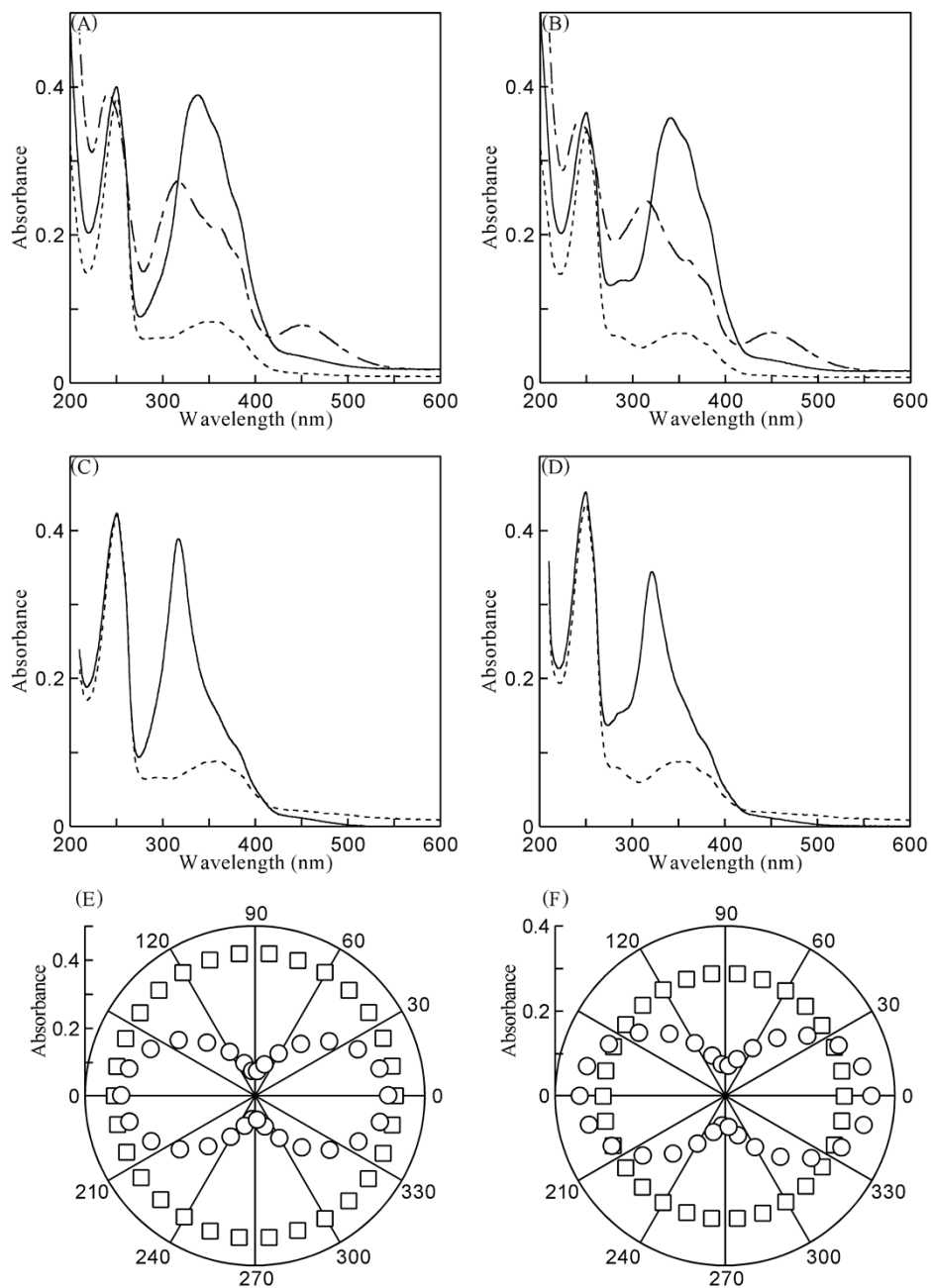


Figure S4-1 Changes in absorption spectra of PMAz-PMBP(m:n) fresh film (solid line) by irradiation of Vis light (436 nm, 150 mW/cm², dotted line) and following UV light (365nm, 28 mW/cm², dot-and-dash line) (A, B). Polarized absorption spectra at an incident angle of 40° to the normal of the film by rotating the polarization plane of the monitored light (A₀ and A₉₀) (C, D) and change in polar plots of the poly (m:n) film at an incident angle of 40° by irradiation of non-polarized Vis light and following UV light (circle: after non-polarized Vis light irradiation, square: after UV light irradiation) (E, F). PMAz-PMBP(100:0) (A, C, E), PMAz-PMBP (90:10) (B, D, F).

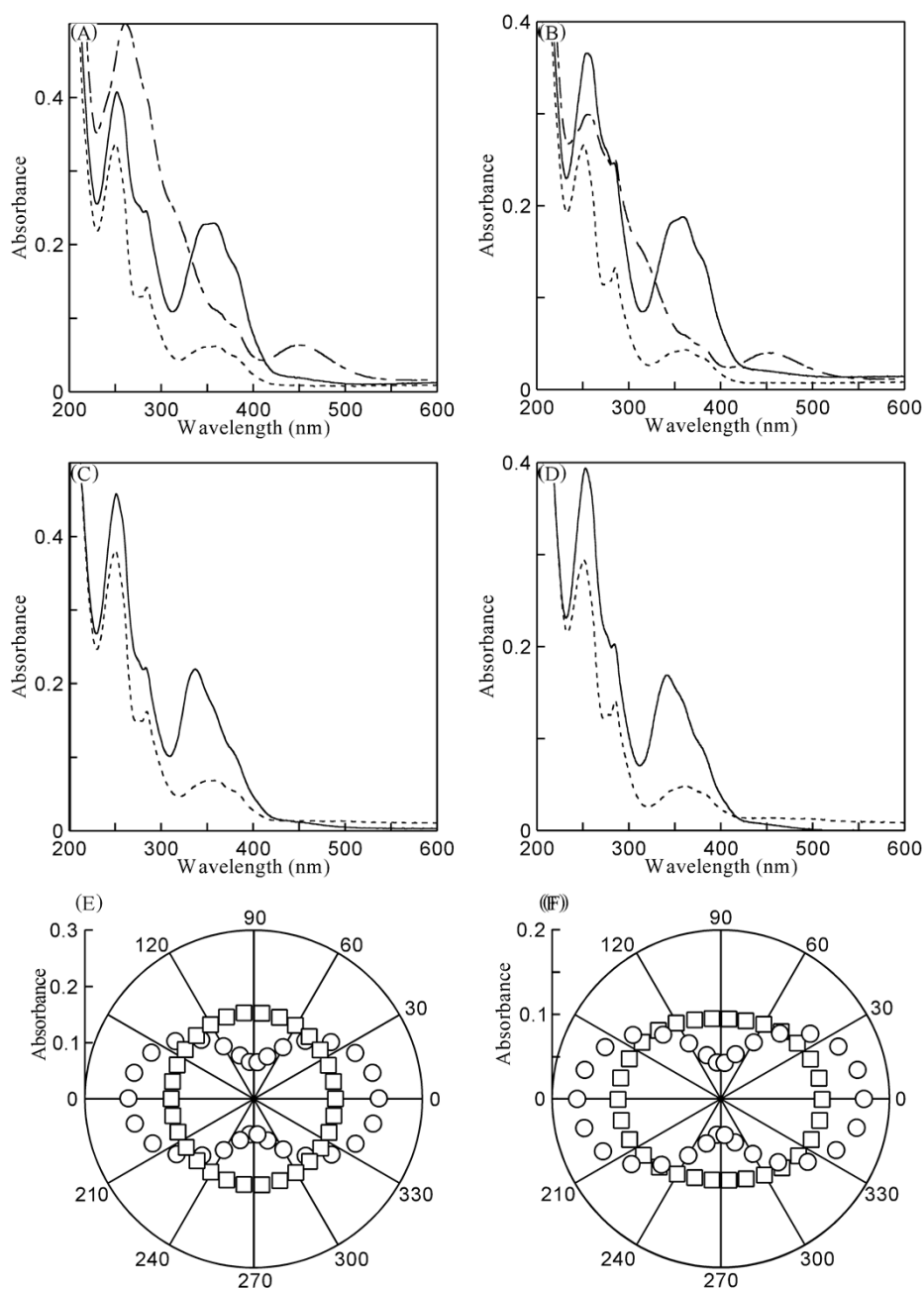


Figure S4-2 Changes in absorption spectra of PMAz-PMBP(m:n) fresh film (solid line) by irradiation of Vis light (436 nm, 150 mW/cm², dotted line) and following UV light (365nm, 28 mW/cm², dot-and-dash line) (A, B). Polarized absorption spectra at an incident angle of 40° to the normal of the film by rotating the polarization plane of the monitored light (A₀ and A₉₀) (C, D) and change in polar plots of the poly (m:n) film at an incident angle of 40° by irradiation of non-polarized Vis light and following UV light (circle: after non-polarized Vis light irradiation, square: after UV light irradiation) (E, F). PMAz-PMBP(60:40) (A, C, E), PMAz-PMBP (40:60) (B, D, F).

Change in reflection spectra of PMAz-PMBP(m:n)/PVA 20-multilayered films.

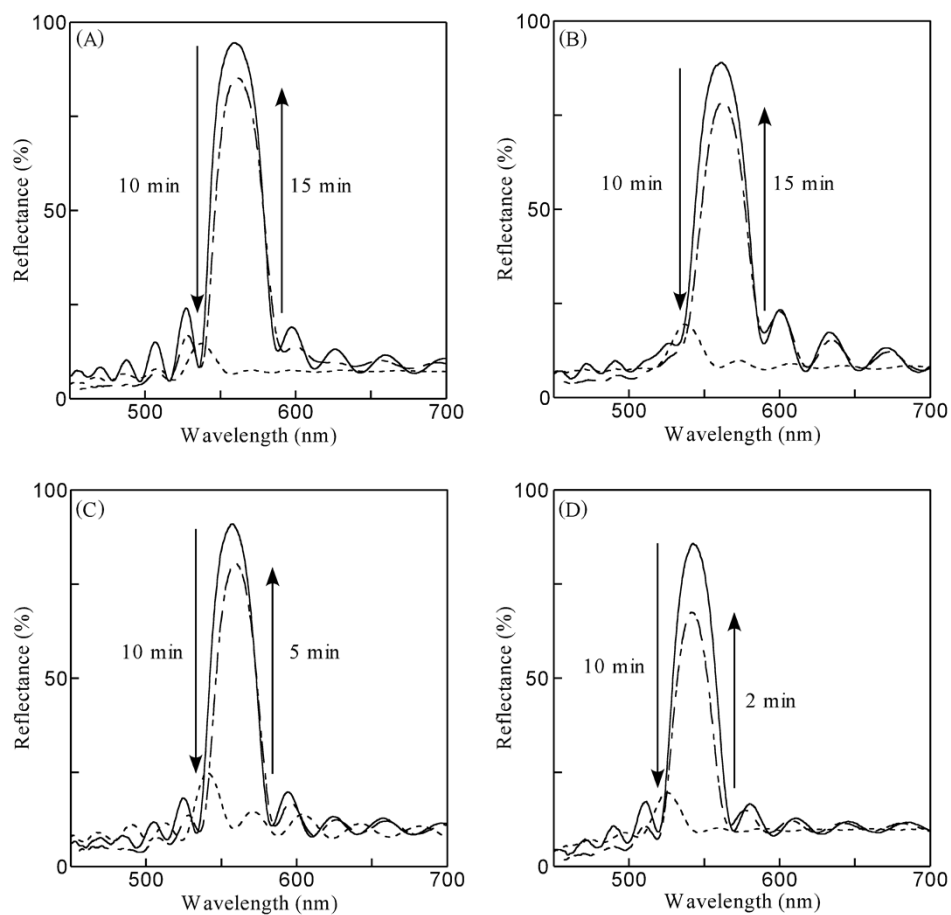


Figure S5 Change in reflection spectra of the PMAz-PMBP(100:0) (A), PMAz-PMBP(90:10) (B), PMAz-PMBP(60:40) (C) and PMAz-PMBP(40:60) (D)/PVA 20-multilayered film by irradiation with non-polarized Vis light ($\lambda=436\text{nm}$, 150 mW/cm^2) and following UV light ($\lambda=365\text{nm}$, 28 mW/cm^2). (solid line) before irradiation, (dotted line) after visible light and (dot-and-dash line) UV light irradiation.