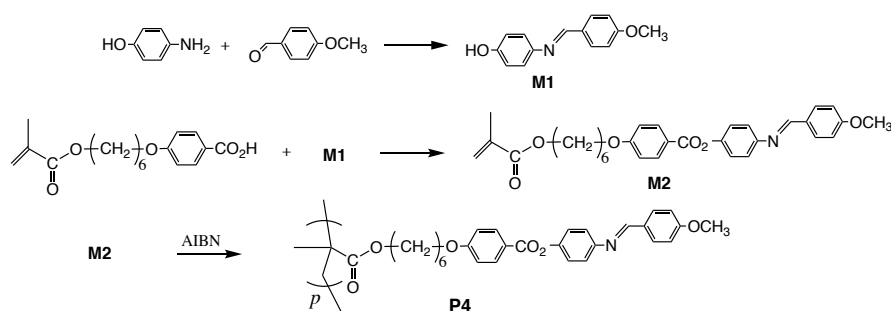


Supporting Information

Photoinduced reorientation and polarized fluorescence of photoalignable liquid crystalline polymer

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Scheme S1. Synthetic route of **P4**.

Synthetic procedures:

Synthesis of M1. A solution of 2.2 g (20.0 mmol) of 4-aminophenol and 3.3 g (24 mmol) of *p*-anisaldehyde in 24 ml of methanol was stirred at room temperature for 3 h. Then the solution was filtered and the residue was recrystallized from THF. Yield 3.4 g, 75 mol%, M.p. 187–189 °C. ¹H-NMR (DMSO-*d*₆), δ (ppm): 3.82 (s, 3H), 6.78(d, *J*=8.4 Hz, 2H), 7.05 (d, *J*=8.8 Hz, 2H), 7.15 (d, *J*=8.8 Hz, 2H), 7.84 (d, *J*=8.9 Hz, 2H), 8.52 (s, 1H), 9.45 (brs, 1H).

Synthesis of M2. A solution of 3.34g (14.7 mmol) of **M1**, 5.40 g (17.6 mmol) of 6-(4'-carboxyphenyl)oxyhexyl methacrylate, 2.82 g (14.7 mmol) of EDCI-HCl and trace amount of DMAP in 40 ml of THF was stirred at r. t. for 26 h. The solution was filtered and evaporated. The residue was dissolved in chloroform and washed by water for 3 times. The organic layer was dried over sodium sulfate and evaporated. The crude product was recrystallized from THF. Yield: 4.85 g (64 %). M.p.=210 °C. ¹H-nmr (DMSO-*d*₆), δ (ppm): 1.41-1.51 (m, 4H), 1.62-1.69 (m, 2H), 1.74-1.80 (m, 2H), 3.85 (s, 3H), 4.08-4.13 (m, 4H), 5.67 (t, *J* = 1.6 Hz, 1H), 6.02 (s, 1H), 7.10 (dd, *J* = 13.0 Hz, 4H), 7.27-7.33 (m, 4H), 7.90 (d, *J* = 8.7 Hz, 2H), 8.08 (d, *J* = 9.1 Hz, 2H), 8.59 (s, 1H). FT-IR (KBr) ν (cm⁻¹): 2942, 2870, 1731, 1718, 1702, 1622, 1605, 1572, 1510, 1472, 1422, 1324, 1251, 1204, 1187, 1164, 1075, 1011.

Synthesis of P4. A solution of 0.84 g (1.6 mmol) of **M2** and 135. mg (0.08 mmol) of AIBN

in 13 ml of THF was degassed followed by heating at 55°C for 24 h. Then, the solution was poured into diethyl ether. The precipitated polymer was purified by reprecipitation from THF to diethyl ether for 3 times. Yield: 0.62 g (74 wt %). $M_n=41000$, $M_w/M_n=3.5$. $^1\text{H-nmr}$ (CDCl_3), δ (ppm): 0.91–1.77 (m, 13H), 3.78 (brs, 3H), 3.94 (brs, 4H), 6.88 (brs, 4H), 7.12 (brs, 4H), 7.75 (brs, 2H), 8.05 (brs, 2H), 8.28 (s, 1H). FTIR (KBr), ν (cm^{-1}): 2937, 2855, 1729, 1718, 1626, 1604, 1575, 1511, 1310, 1254.

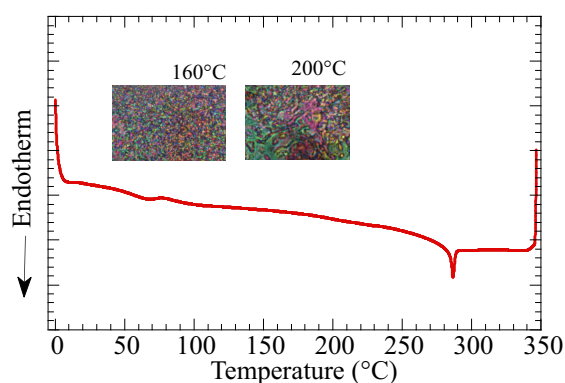


Figure S1. DSC second heating curve of **P4**. Inset shows POM texture photographs.

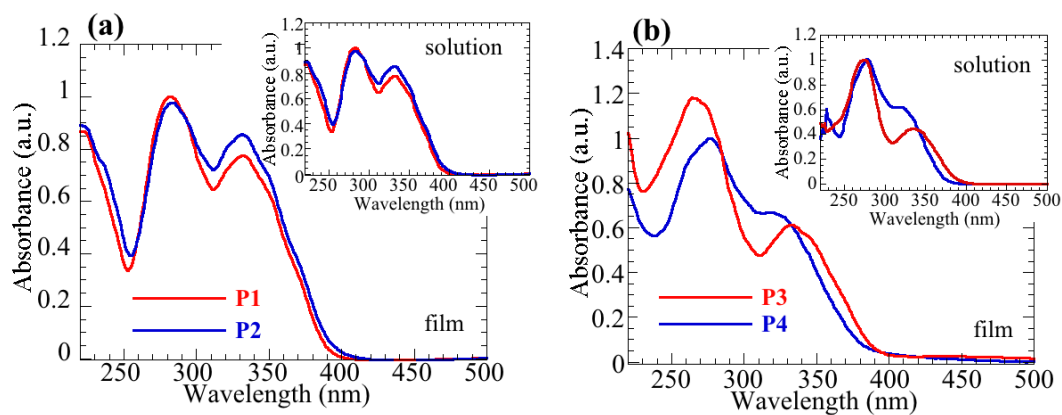


Figure S2. UV-Vis absorption spectra of **P1–P4** films on quartz substrate. (a) **P1**, **P2**, (b) **P3**, **P4**. Insets show absorption spectra in THF solution.

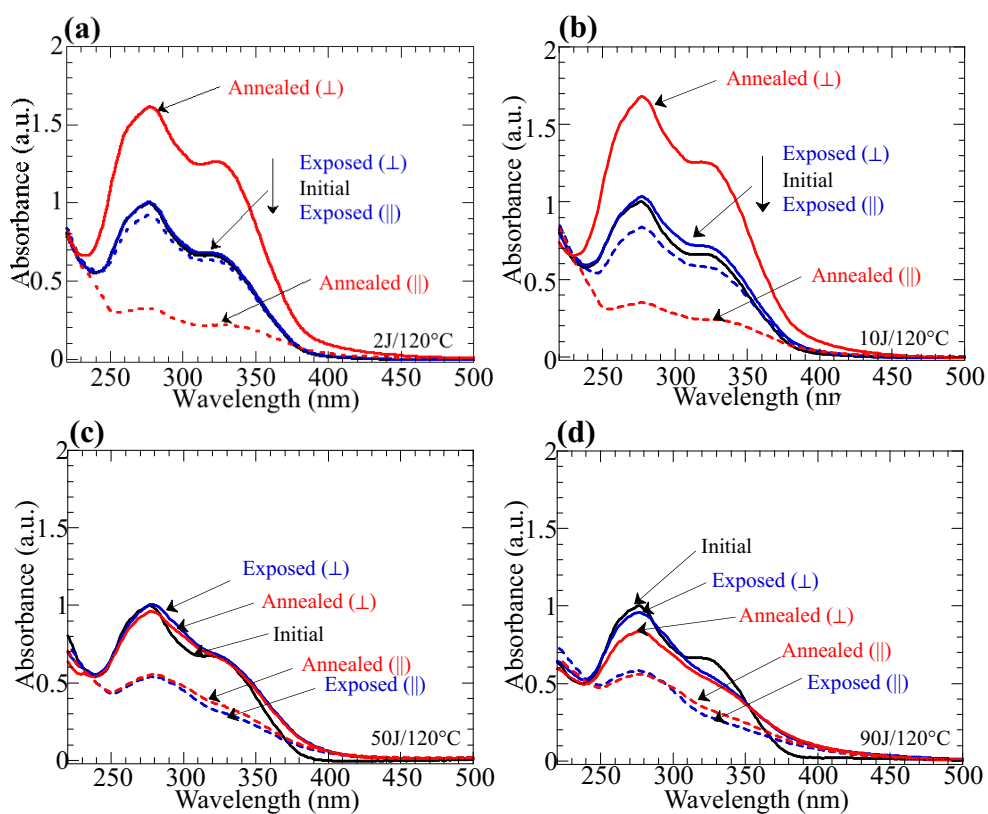


Figure S3. Change in the polarized absorption spectra of **P4** films before and after exposure to linearly polarized 313-nm light, and subsequent annealing at 120°C for 10 min. Exposure energy is (a) 2 J/cm², (b) 10 J/cm², (c) 50 J/cm², and (d) 90 J/cm².

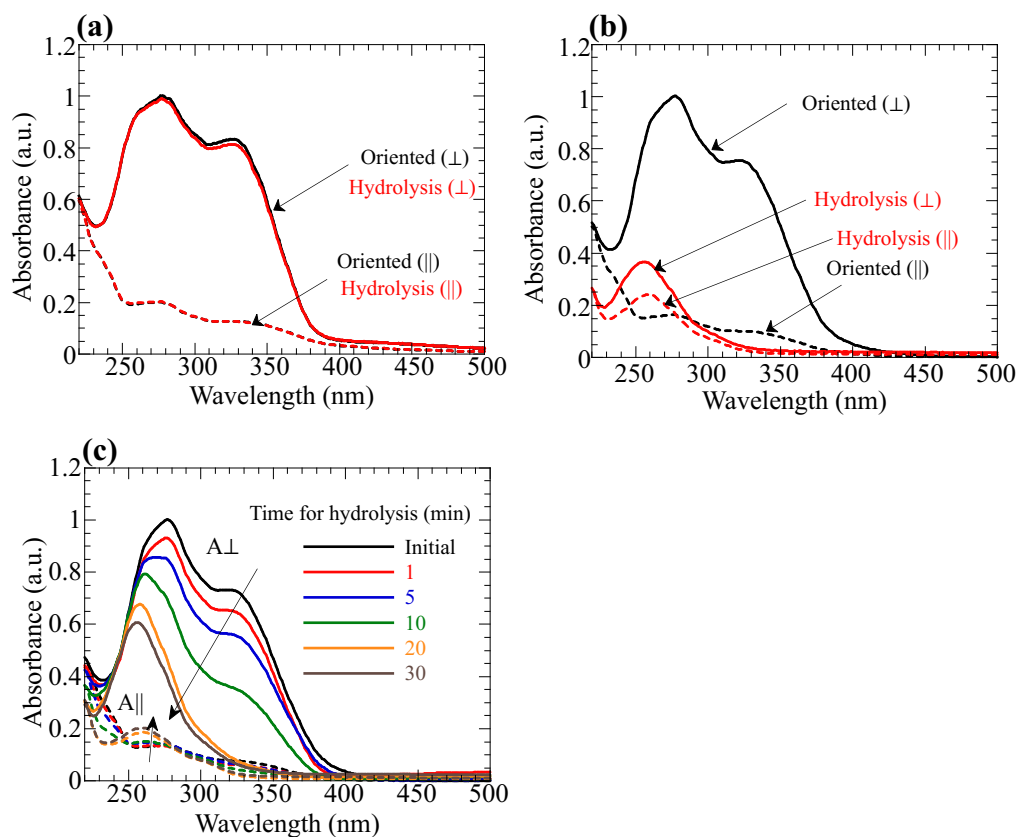


Figure S4. Changes in the polarized absorption spectra of oriented **P4** films before and after hydrolysis. (a) Immersed in water for 10 min at 50 °C, (b) Immersed in acetic acid/water (1/1 vol/vol) for 10 min at 50 °C. (c) Immersed in acetic acid/water (1/5 vol/vol) at 50 °C when changing the immersing time. Initial oriented films are prepared by exposing to linearly polarized 313-nm light for 3 J/cm² and subsequent annealing at 180 °C for 10 min.