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Supplementary Information

Interpenetrating polymer network of liquid-crystalline azobenzene polymer and poly(dimethylsiloxane) as photomobile materials

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Experimental setup

Optical anisotropy of films was observed using polarizing optical microscope (Nikon, Optiphot) equipped with a CMOS camera (Wraymer, WRAYCAM-NF130). The photoinduced bending and unbending of films were observed on a hot stage at 30 ˚C by CCD camera (Artray, ARTCAM-130SN) equipped with CCTV lens (EMVL-MP3020, Misumi) upon irradiation with UV light (365 nm) from UV-LED (NS lighting, ULEDN-102CT), and visible light (>540 nm) from a halogen lamp (Tokina, KTX-100E) through glass filters (Tokina, Y52 and HA50). Stress–strain curves of films were obtained using a digital force gauge (Imada, ZTA5N) and a motorized test stand (Imada, MX2-500N) at a constant elongation speed of 10 mm min^{-1}. Strain was calculated as l/l_0, where l_0 and l are lengths of the film along the stretching direction before and after the elongation, respectively. Stress was evaluated as F/A_0, where F denotes force applied to the sample, and A_0 denotes cross-sectional area of the sample before elongation.

Sample preparation

Materials: A6AB6 and DA6AB were synthesized according to the previously reported procedures.[1] 1BZ6 was synthesized through the esterification of *p*-anisic acid and 4-hexyloxyphenol in dichloromethane catalyzed by *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). D_4V was purchased and used as received.

Synthesis of HT-PDMS: A mixture of octamethylcyclotetrasiloxane (14 g, 47 mmol, 70 mol%), 1,1,3,3-tetramethyldisiloxane (2.7 g, 20 mmol, 30 mol%) and trifluoromethanesulfonic acid (65 μL) was stirred at 60 ˚C for 24 h. After cooling to room temperature, diethyl ether was added and the solution was washed with water until pH of aqueous layer became 7. The organic layer was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by evaporation under reduced pressure. The reactants were removed by heating at 120 ˚C under reduced pressure, giving HT-PDMS as colorless liquid (14 g). The degree of polymerization was evaluated from ^{1}H NMR spectrum.
^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.70 (m, 2H), 0.18 (d, 12H), 0.07 (s, 84H).

Preparation of PAzoTP: A mixture of A6AB6 (35 mol%), DA6AB (15 mol%), a photoinitiator (Irgacure 784, 2 mol% of the polymerizable molecules) and 1BZ6 (50 mol%) was injected into a glass cell coated with rubbed polyimides in an isotropic phase (90 ˚C). After the mixture was cooled down (0.5 ˚C min^{-1}) to LC

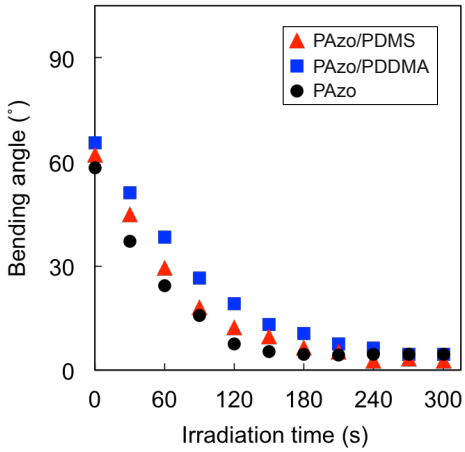
temperature (72 ˚C), photopolymerization was carried out with light (>540 nm, 2 mW cm^{-2}) from a 500 W super-high pressure mercury lamp through glass filters (Tokina, Y52 + HA50) for 2 h. After the formation of PAzo network, the cell was immersed in acetone to remove 1BZ6.

Preparation of PAzo/PDMS: PAzoTP in a cell was immersed in a mixture of HT-PDMS (M_n = 1170, 67 mol%), D_4V (33 mol%) and Karstedt's catalyst (10 ppm) for 72 h. The cell was heated at 75 ˚C for 2 h to allow formation of PDMS network through hydrosilylation reaction. The film was removed from the cell and washed with methanol.

Preparation of PAzo/PDDMA: PAzoTP in a cell was immersed in a mixture of DDMA (90 mol%), EGDMA (10 mol%) and 2,2'-azobisisobutyronitrile (1 mol% of the polymerizable molecules) for 24 h. Then, the thermal polymerization was performed at 60 ˚C for 3 h on a hot plate under argon atmosphere. The film was removed from the cell and washed with methanol.

Preparation of pristine PAzo: A mixture of A6AB6 (70 mol%), DA6AB (30 mol%), a photoinitiator (Irgacure 784, 2 mol% of the polymerizable molecules) was injected into a glass cell coated with rubbed polyimides in an isotropic phase (110 ˚C). After the mixture was cooled down (0.5 ˚C min^{-1}) to LC temperature (88 ˚C), photopolymerization (>540 nm, 2 mW cm^{-2}) was carried out for 2 h. The film was removed from the cell and washed with methanol.

Supplementary Figure



Supplementary Fig. 1: Photoinduced unbending behavior of films upon irradiation with visible light (>540 nm, 40 mW cm^{-2}) after photoinduced deformation with UV light to the bending angle of 60˚. Size of the films: 3 mm × 1 mm × 20 μm.

Supplementary Movies

Supplementary Movie 1: Photoinduced bending behavior of a PAzo/PDMS film upon irradiation with UV (365 nm , 10 mW cm^{-2}) and visible light (>540 nm, 40 mW cm^{-2}). Size of the film: 3 mm × 1 mm × 20 μm.

Supplementary Movie 2: Comparison of photoinduced bending behavior of PAzo/PDMS and pristine PAzo films upon irradiation with UV light (365 nm , 10 mW cm^{-2}). Size of the films: 3 mm × 1 mm × 20 μm.

Reference

1 A. S. Angeloni, D. Caretti, C. Carlini, E. Chiellini, G. Galli, A. Altomare, R. Solaro and M. Laus, *Liq. Cryst.*, 1989, **4**, 513.