Supplementary Information

Photomobile materials with interpenetrating polymer network composed of liquid-crystalline and amorphous polymers

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Sample preparation and experimental setup

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). PAzoTP was prepared by polymerization of A6AB6 and DA6AB. 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 polyimide at 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 and provide PAzoTP. IPN films were prepared by thermal polymerization of a methacrylate monomer (MMA, BMA or DDMA) and EGDMA in PAzoTP as follows. PAzoTP was immersed in a mixture of a methacrylate monomer (90 mol%), EGDMA (10 mol%) and 2,2'-azobisisobutyronitrile (1 mol% of the polymerizable molecules). Then, the thermal polymerization was performed at 60 °C for 3 h on a hot plate under argon atmosphere. A pristine PAzo film was prepared by photopolymerization of A6AB6 (70 mol%) and DA6AB (30 mol%) in a glass cell coated with rubbed polyimide at LC temperature (88 °C) for 2 h.

Morphology of films was observed by atomic force microscopy (AFM; Agilent, 5500) with a dynamic mode. Optical anisotropy of films was observed using polarizing optical microscope (Nikon, Optiphot). Polarized absorption spectra were measured with a spectrometer (Ocean Optics, USB2000+). The photoinduced bending and unbending of freestanding films were observed on a hot stage at 30 °C upon irradiation with UV light (366 nm, 10 mW cm⁻²) and visible light (>540 nm, 40 mW cm⁻²) from a high-pressure mercury lamp through glass filters (Tokina, U360 + HA50 for UV light; Y52 + HA50 for visible light). The alignment change of azobenzene moieties upon irradiation with UV light (365 nm, 5 mW cm⁻²) was observed using an optical system composed of a laser (633 nm), a polarizer, a sample, an analyzer and a detector. The director of the sample and the axis of the analyzer were set at 45° and 90° to the axis of the polarizer, respectively. 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.



Fig. S1 AFM phase images of films. a) A pristine PAzo film and b) PAzo/PMMA.



Fig. S2 POM images of films.



Fig. S3 Polarized UV-Vis absorption spectra of films. A_{\parallel} and A_{\perp} denote absorbance obtained with light polarized parallel and perpendicular to the director, respectively. Thickness of the films: 1.5 μ m.



Fig. S4 Stress–strain curves of PAzo/PMMA and PAzo films upon stretching to the direction parallel (//) and perpendicular (\perp) to the director axis of azobenzene moieties.

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.