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Direct Fabrication of Photomobile Polymer Materials with an Adhesive-Free Bilayer Structure by Electron-Beam Irradiation

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Materials

Synthesis of monomer

The azobenzene monomer, 6-[4-(4-ethoxyphenylazo)phenoxy]hexyl acrylate, was synthesized and purified according to a procedure similar to the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43-1.78 (m, 11H), 4.02-4.21 (m, 6H), 5.82 (dd, J = 10, 2 Hz, 1H), 6.13 (dd, J = 17, 10 Hz, 1H), 6.41 (dd, J = 17, 2 Hz, 1H), 6.97-7.00 (m, 4H). Elemental analysis: Calcd. for $C_{23}H_{28}N_2O_4$: C, 69.67; H, 7.12; N, 7.07 %. Found: C, 69.58; H, 7.18; N, 7.08 %. MS (FAB) found: *m/z* 397 $[M+1]^+$ (396.48 calcd for $C_{23}H_{28}N_2O_4$).

Synthesis of polymer

An azobenzene LC polymer (**PAz**) was prepared by bulk polymerization of the monomer (1.19 g, 3.00 mmol) with 2,2′-azobis(*N*-cyclohexyl-2-methylpropionamide) as an initiator (54.6 mg, 0.15 mmol). Firstly, the monomer containing the initiator was injected into a glass cell (size: 14 cm × 14 cm × 30 μm) on a hot plate at 100 °C. The polymerization was carried out in a preheated oven under vacuum for 24 h at 120 °C. After polymerization, the polymer was dissolved in tetrahydrofuran (THF) and precipitated in a large excess of methanol, and finally dried under vacuum. A yellow solid product was obtained with a yield of 94 %. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the polymer were measured by GPC (Japan Spectroscopy, model DG-980-50; column, Shodex GPC LF804 × 2 + LF804A; eluent, THF) using standard polystyrenes for calibration. The GPC curve of the obtained polymer is shown in **Fig. S1**.

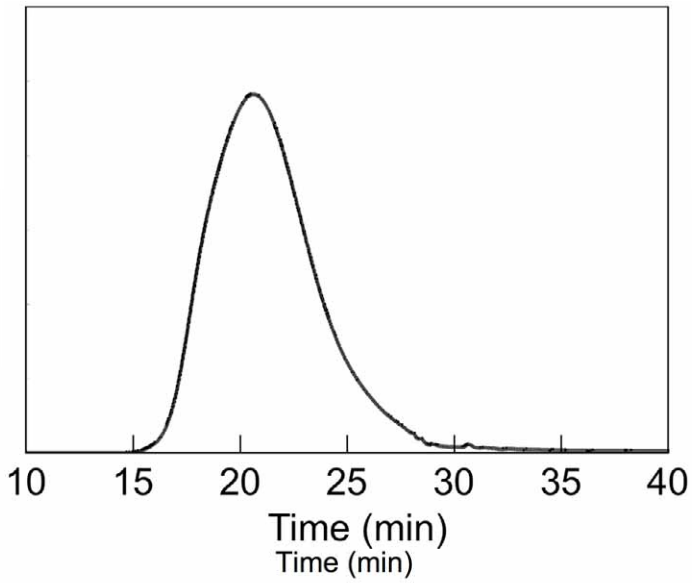

Figure S1. A GPC curve of the azobenzene LC polymer **(PAz)**.

Electron-beam (EB) irradiation

The **PAz** monolayer and **PAz/PE** bilayer (**PE**: polyethylene) films were irradiated with soft-EBs from an EB accelerator (Hamamatsu Photonics, EB-ENGINE®) at room temperature in a stream of nitrogen with a dose rate of 100 kGy/pass (current: 2 mA, pass speed: 80 mm/s, concentration of oxygen: <100 ppm).

Liquid-crystalline properties of polymer

The thermodynamic properties of the polymer were analyzed with a DSC (Seiko Instruments Inc., EXTRAR6000, DSC6220) at heating and cooling rates of 10 °C/min. At least three scans were performed to check the reproducibility. The mesomorphic properties were examined with a polarizing optical microscope (POM, Olympus. BX50F4) equipped with a hot stage (Mettler, FP-90 and FP-82). It was found that the polymer exhibited LC phases from 85 to 165 °C upon heating and from 162 to 81 °C upon cooling, and the DSC curve also exhibited a glass transition temperature (T_g) of **PAz** at approximately 60 °C before EB irradiation (**Fig. S2a**). After EB irradiation, the peaks of LC-isotropic phase transition disappeared, and the T_g fell to 40-50 °C (**Fig. S2b**).

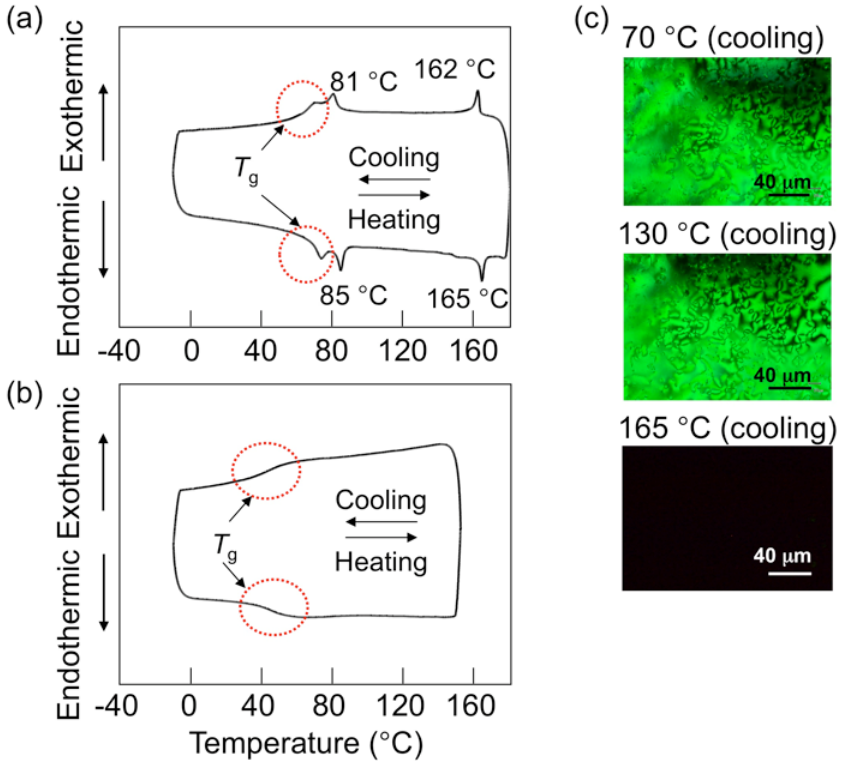

Figure S2. DSC thermograms of the azobenzene LC polymer. (a) **PAz**; (b) **PAz** after EB irradiation at a dose of 10 MGy; (c) polarizing optical micrographs of **PAz** at various temperatures.

Photoisomerizaiton of the EB-crosslinked PAz film

In the EB-crosslinked **PAz** film at 10 MGy, the isomerization of the azobenzene moieties was evaluated in films by UV-vis spectroscopy upon irradiation with UV light from a UV-LED irradiator (Keyence, UV-400, UV-50H) as shown in **Fig. S3**.

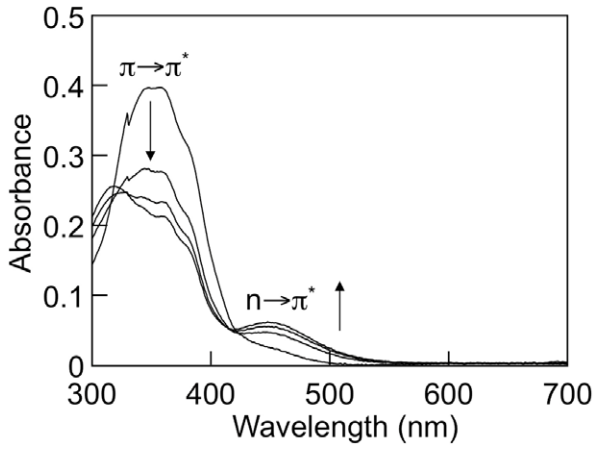

Figure S3. A change in UV-vis absorption spectra of the EB-crosslinked **PAz** film at 10 MGy by irradiation with UV light (365 nm, 10 mW/cm^2).

Photoinduced change in alignment of mesogens

A change in transmittance of the EB-crosslinked **PAz** films at 10 MGy (thickness: ~20 nm) was measured upon exposure to UV light (10 mW/cm^2) at 50 °C. The optical setup for the evaluation of the photoinduced change in alignment of azobenzene mesogens in films is shown in **Fig. 2a**. The intensity of a probe beam at 633 nm from a He-Ne laser (NEC, GLS5370) transmitted through a pair of crossed polarizers, with the sample film between them, was measured with a photodiode.

Recording of movement

The motions of films were recorded with a three-dimensional digital camera (Omron, VC-HRM20Z and VC1000).

Reference

[1] A. S. Angeloni, D. Caretti, C. Carlini, E. Chiellini, G. Galli, A. Altomare, R. Solaro, M. Laus, *Liq. Cryst.* **1989**, *4*, 513-527.