Electronic Supplementary Information

Liquid Crystal Polymer Based Single Layer Chemo-responsive Actuator

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References for ESI

Materials: RM257 and 5CB were purchased from TCI, Japan. Diethyl ether, hexane, xylene, ethylacetate, toluene, chloroform, acetone, methylene chloride (DCM), dioxane, pyridine, iso-propyl alcohol, ethanol and 1-hydroxycyclohexyl phenyl ketone were supplied by Sigma Aldrich. The polyimide solution with the commercial name of Luxon Aligner was obtained from Chisso Corporation, Japan. Milli-Q water (resistivity higher than 18.2 MΩ cm) was used in all experiments. All chemicals were used as received.

Actuator film preparation: The RM257/5CB mixtures in the vials at different ϕ values at 10 wt% intervals were prepared by dissolving them in DCM containing 1-hydroxycyclohexyl phenyl ketone (photoinitiator, 2 wt% against RM257 monomer) with magnetic stirring for 30 min, followed by the complete evaporation of DCM in a vacuum oven at room temperature. Aluminum foil was wrapped around the mixture vials to protect the mixtures from light. After evaporating the DCM, all transparent mixture solutions became white due to the recovery of the nematic state of 5CB at room temperature. To prepare the actuator film, the mixture solution was injected into the planar cell. To fabricate the planar cell, the glass slides were cleaned, dried and spin-coated with a PI solution at 1200 rpm for 1 min. The PI coated glass slides were dried at room temperature, and then baked in an oven at 120 °C. The baked PI-coated surface of the glass slides were rubbed uni-directionally with a velvet cloth and assembled into a cell by sandwiching Mylar films with the desired thickness as spacers at the edges with parallel PI rubbing directions. Before photopolymerization, the cell filled with a RM257/5CB mixture was inspected by polarized optical microscopy (POM) under crossed polarizers to confirm the uniform alignment of the RM257/5CB mixtures along the rubbing direction. The cell was irradiated for photopolymerization with ultraviolet (UV) light at 365 nm for 5 min. UV irradiation was carried

out using a UV instrument (Spot UV/Inno cures, Korea) operating at 100N, 100 W and $2000mWcm^2$ with a cell-to-UV light source distance less than 10 cm. The cell was opened after photopolymerization and kept in ethanol for 1 hr to remove any 5CB from the film. Supporting information Figures S2 and S3 present schematic diagrams of the entire preparation process.

Characterizations: POM images were taken using an optical microscope (Samwon, LSP-13, Korea) under crossed polarizers. The scanning electron microscopy (SEM, Hitachi S-5200, Japan) images were obtained at an accelerating voltage of 15kV. The sample surface for SEM was coated with platinum. Actuation of the actuator films was recorded using a Sony Handycam® (Sony, HDR-UX1, Japan). Differential scanning calorimetry (DSC) of the mixtures was performed on Setaram DSC (model 131–evo, France). The sample was sealed in an aluminum pan and heated in a nitrogen atmosphere over the temperature range, 20 to 140 °C at a heating rate of 3 °C/min. Wide angle X-ray scattering (WAXS) experiments were performed at the PLS-II 9A USAXS beamline of the Pohang accelerator laboratory (PAL) with a sample-to-detector distance of 199 mm and an X-ray wavelength of 0.62 Å. The two-dimensional (2D) WAXS patterns recorded on a CCD detector (Rayonix, USA) were scanned using the FIT2D software package to obtain one-dimensional (1D) patterns in the form of intensity vs. q (scattering vector, $q = (4\pi/\lambda) \sin(\theta/2)$, where λ is the wavelength of incident X-rays and θ is the scattering angle).
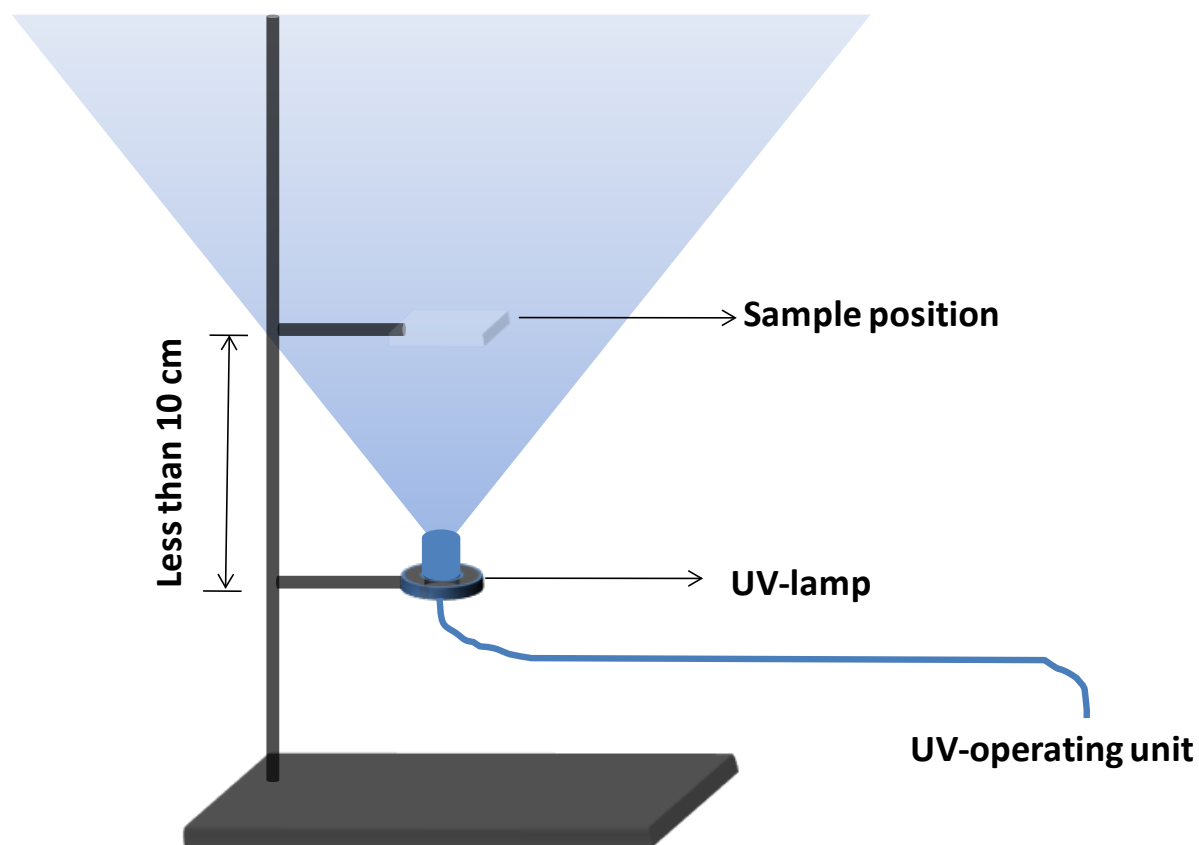
Fig. S1. Geometry of photopolymerization of mixtures in the LC cell.

(a)

(b)

(c)

(d)

(e)

(f)

Porous surface (with 5CB)

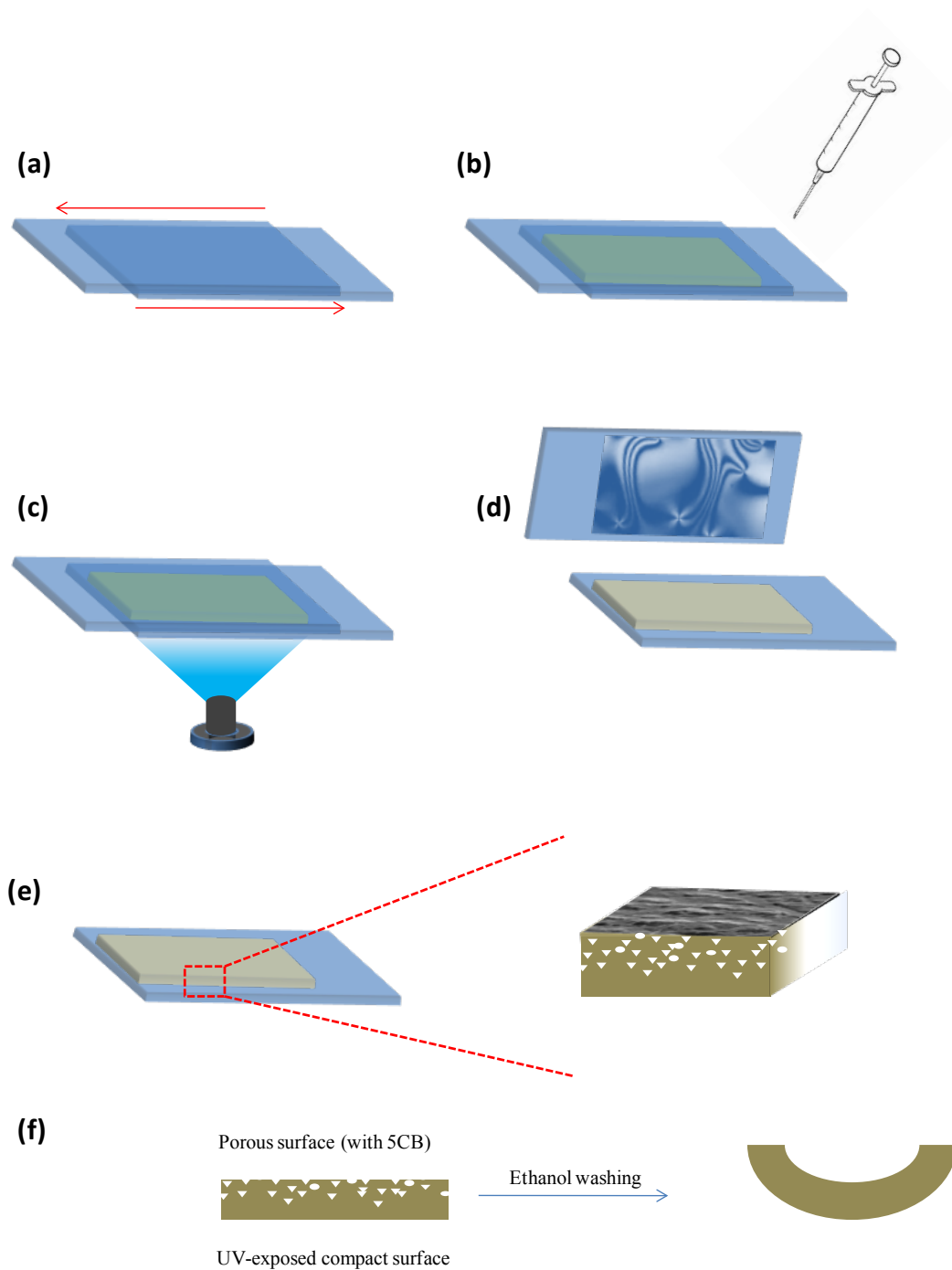Ethanol washing

UV-exposed compact surface

Fig. S2. Schematic illustration of the actuator film preparation; (a) an empty PI coated LC cell with arrows showing the rubbing directions, (b) mixture filling process in the LC cell, (c) photopolymerization, (d)) appearance of the cross-linked film on the slide glass after opening the LC cell where the photopolymerized film stayed on the UV-exposed slide glass and the 5CB-

wetted side on the opposite slide glass, (e) side view of the film on the slide glass showing an asymmetric porous structure, and (f) curling of the film after 5CB extraction by placing it in ethanol.

Phase behavior of RM257/5CB
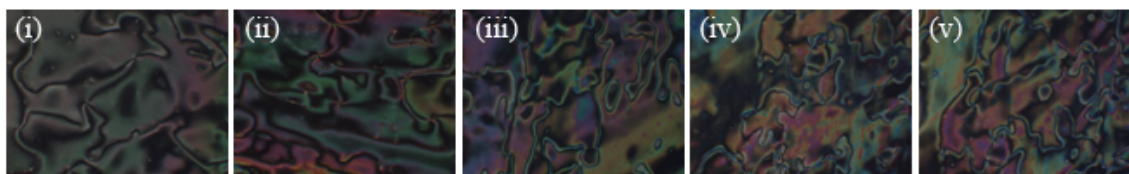
(a)

(b)
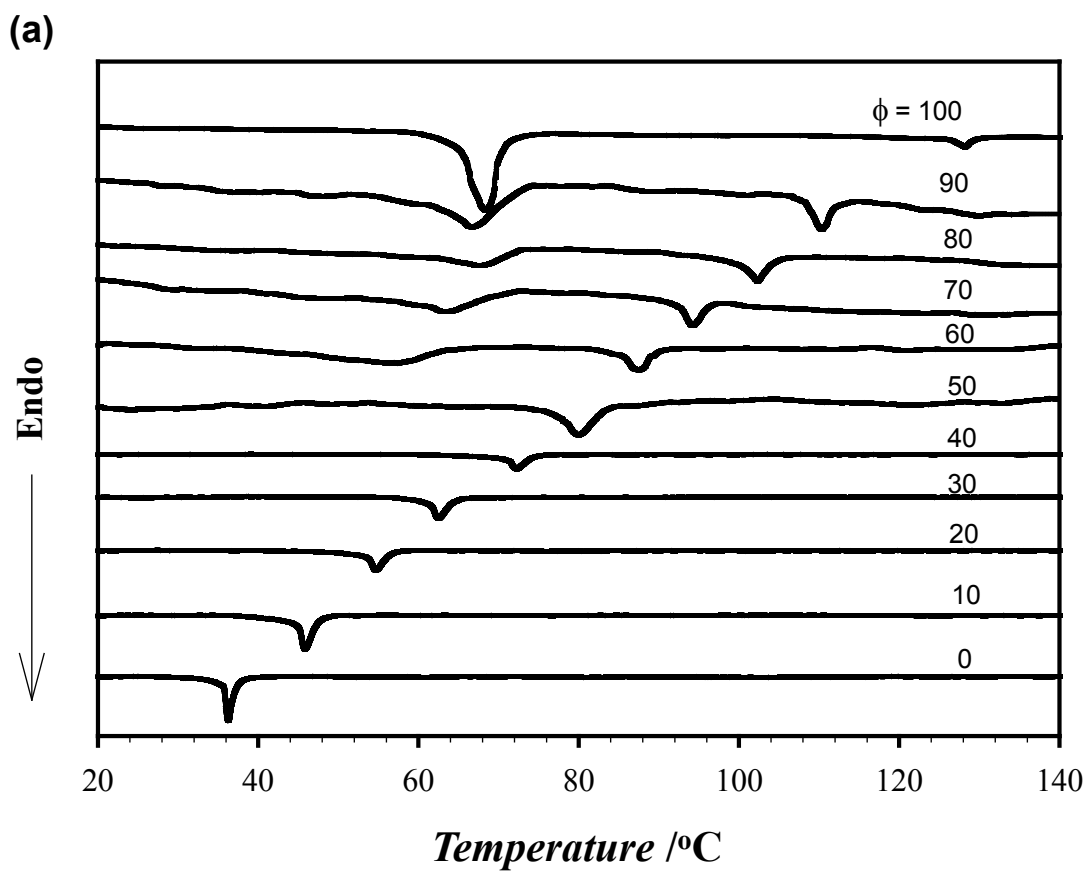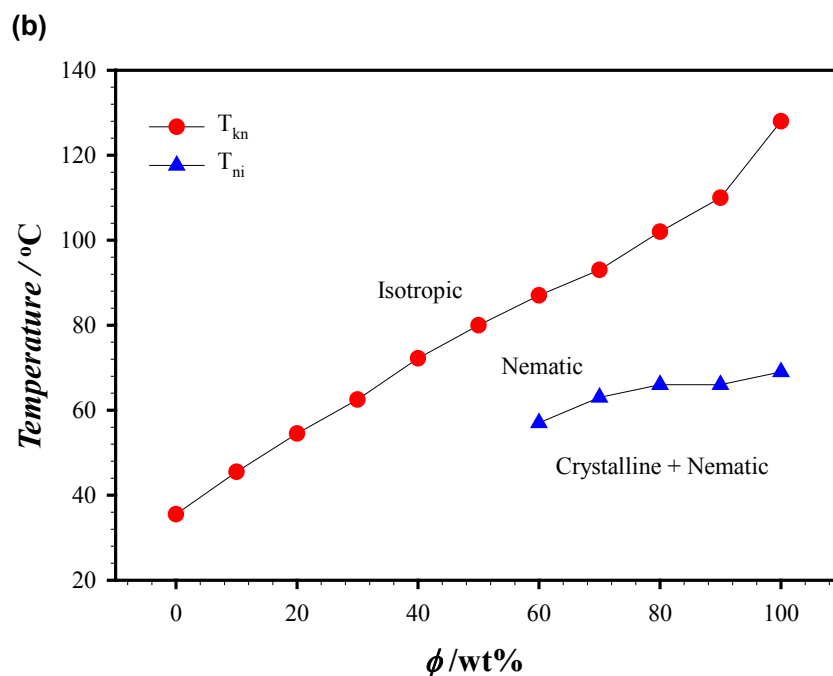
(c)

Fig. S3. (a) DSC heating thermograms at $\phi = 0$ to 100, (b) phase diagram and (c) POM images at $\phi =$ (i) 0, (ii) 10, (iii) 20, (iv) 30 to (v) 40 wt% under cross polarizers.

Fig. S3a shows the DSC thermograms of the RM257/5CB mixtures at $\phi = 0$ to 100 prior to photopolymerization. Two endothermic peaks at $\phi = 100$ (pure RM257) were observed at 70 and 128 °C, which were due to crystalline to nematic (T_{kn}) and nematic to isotropic (T_{ni}) transitions. The T_{kn} of 5CB (~ 22.5°C) was not observed because it takes much time for crystallization (beyond 15min) when temperature is lowered than 22.5°C. Since, in DSC measurement, 5CB was cooled to 18°C and subsequently heating run was started where insufficient time was provided for the crystallization of 5CB. Thus T_{kn} of 5CB didn't appear in

the DSC thermogram. The endothermic peaks were shifted continuously to lower temperatures with increasing ϕ. Fig. S3b shows these transition temperatures as a function of ϕ. The T_{kn} transition was observed only at $\phi = 100$ to 60 wt%, even though the T_{ni} transitions were observed at all mixing ratios. The increase in T_{ni} with increasing ϕ is consistent with the results reported by Stapert et al. using RM257/E7 mixtures.[1] The decrease in T_{kn} with decreasing ϕ was attributed to the melting temperature depression of RM257 by mixed 5CB, which is normally observed from binary crystalline/amorphous mixtures. Therefore, the mixtures at $\phi = 10$ to 50 show a single nematic phase and those at $\phi = 60$ to 90 wt% exhibit crystalline + nematic phases at room temperature. The solutions at $\phi = 0$ to 50 wt% on slide glasses were viewed by POM in the cross-polar state, as shown in Fig. S3c. The POM images at $\phi = 0$ to 50 wt% at room temperature were typical nematic marble textures, suggesting that the mixtures were a completely miscible nematic phase at these mixing ratios. The nematic marble texture is normally observed in thin samples, particularly for substrates that have not been rubbed or treated in any way.[2]

Curing experiments were performed using the RM257/5CB mixtures at $\phi = 10$ to 50 wt% at room temperature because these mixtures showed a uniform single nematic state and other mixtures at $\phi = 60$ to 100 wt% exhibited crystalline + nematic phases at room temperature. The film prepared from a RM257/5CB mixture at $\phi = 10$ wt% was non-uniform and adhered well to the glass slide after UV irradiation so that it was difficult to peel the film from the glass. On the other hand, the RM257/5CB mixture at $\phi = 50$ wt% was too viscous to fill into the cell. Therefore, the films at $\phi = 20$ to 40 wt% were used for further study.

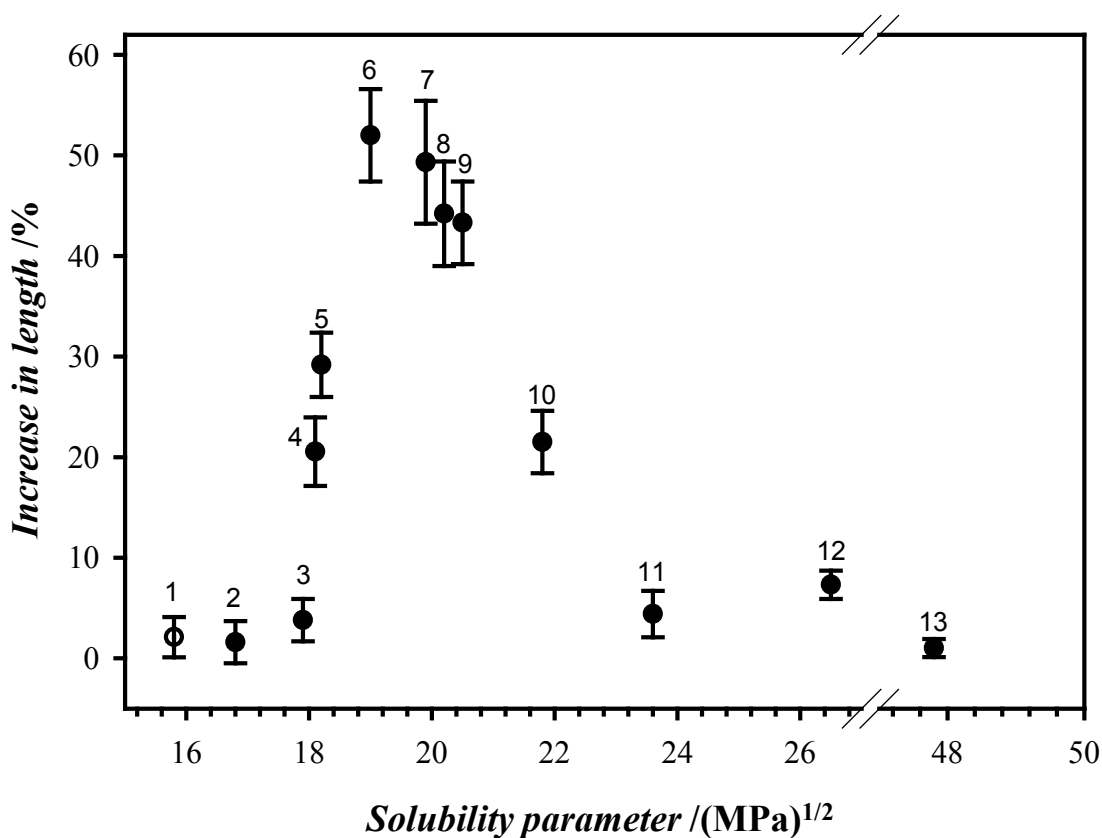**Solubility (swellability) of poly(RM257)**

Fig. S4. Increase in the length of poly(RM257) film in various solvents as a function of the solubility parameter; the film was fabricated by the photopolymerization of RM257 monomers without 5CB between two non-PI coated slide glasses at the isotropic state (75°C) for 5 min; the numbers in the graph represent the solvents of (1) diethyl ether, (2) hexane, (3) xylene, (4) ethylacetate, (5) toluene, (6) chloroform, (7) acetone, (8) methylene chloride, (9) dioxane, (10) pyridine, (11) iso-propyl alcohol, (12) ethanol and (13) water.

The photopolymerization of RM257 make a three-dimensional network structure due to two reaction sites in the diacrylate RM 257 monomer during polymerization. The cross-linked film can be swelled in the solvent and its degree of swelling is dependent on the solvent power, which

is normally represented by the difference in the solubility parameter ($\Delta\delta$) between the polymer and solvent. A small difference in solubility parameter represents a good solvent. The cross-linked and non-porous poly(RM257) film was fabricated by the photopolymerization of RM257 monomer in the isotropic state at 75°C for 5 min between two non-PI coated slide glasses. The cross-linked RM257 film was completely insoluble in any of the solvents tested but it did swell. A rectangular strip of the polymerized film (0.3×0.2 mm^2) was cut, kept on the cover slide, soaked in the desired solvent, viewed under a microscope and its length was measured before the solvent was evaporated. Fig. S4 depicts the % increase in the length ($\Delta L/L \times 100$) as a function of δ of the tested solvent.

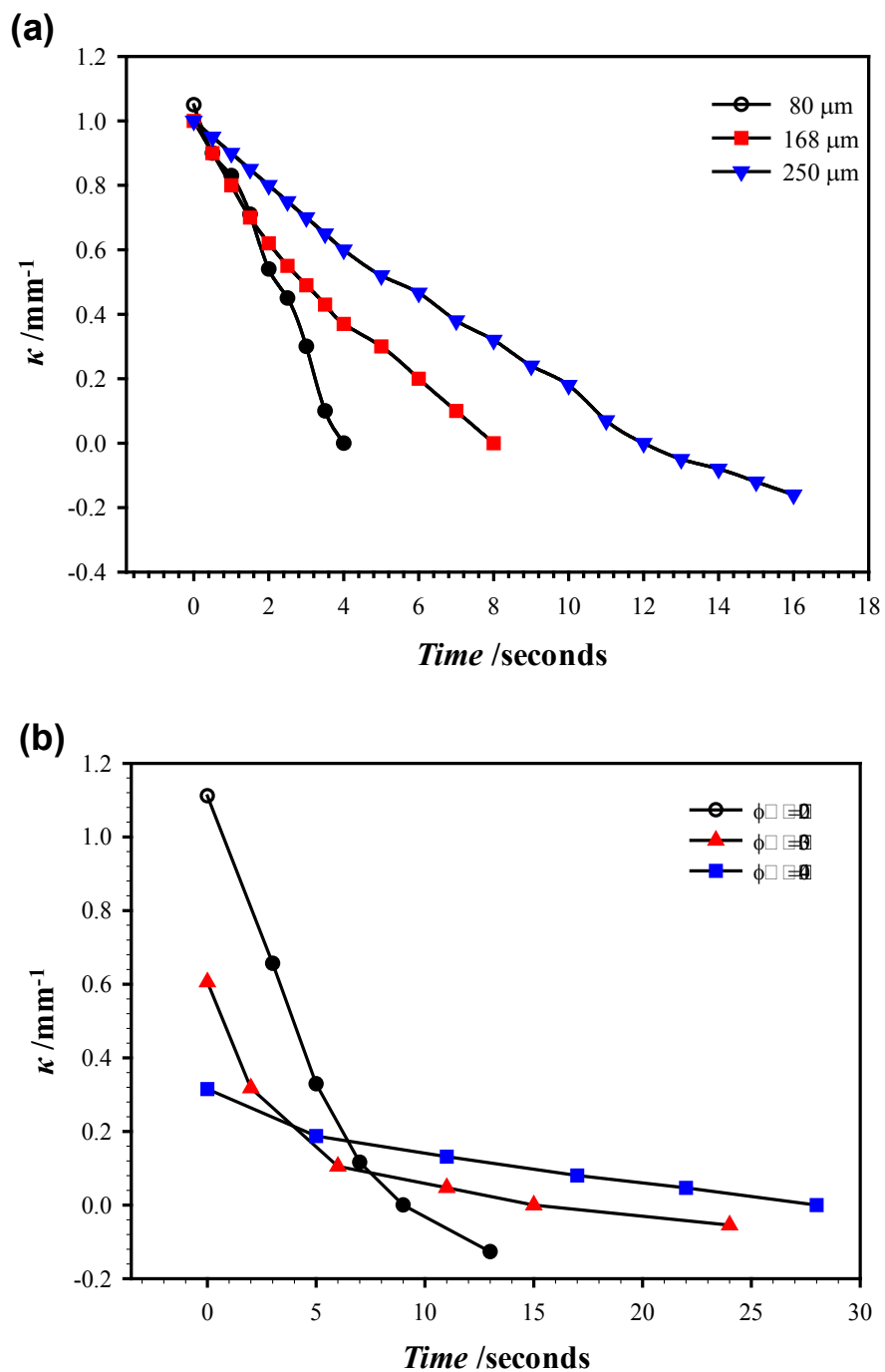**Effect of actuator thickness and mixture composition on actuation speed**

Fig. S5. (a) κ as a function of time at $\phi = 20$ wt% while changing the solvent from water to acetone for films with 80, 168 and 250 μm thicknesses and (b) κ as a function of time for the 150μm thick films fabricated at $\phi = 20$, 30 and 40 wt%.

Fig. S5a depicts κ as a function of time at $\phi = 20$ wt%, while changing the solvent from water to acetone for films with 80, 168 and 250 µm thicknesses. The κ was determined from the frames of the recorded video. The times for reaching the un-curling state ($\kappa = 0$) for the films with an 80, 168 and 250 µm thickness were 3, 7 and 12 seconds, respectively. The thin film showed faster actuation than the thick film, obviously because the speed of the solvent diffusion was fast and rigidity of the film was low for the thin film. Therefore, the actuation speed could be controlled by the film thickness, even though the high-responsive actuator with the thin film might be compensated for by the low mechanical properties. Fig. S5b illustrates κ as a function of time for the 150 µm thick films at $\phi = 20$, 30 and 40 wt% while dipping in acetone. The κ values for the films at $\phi = 20$, 30, and 40 wt% at time = 0 (in dry state) are 1.1, 0.6 and 0.3 mm^{-1}, respectively, indicating that the degree of the actuation decreased with increasing ϕ. A more porous structure would be generated with increasing ϕ so that high degree of actuation would occur with increasing ϕ. The times for reaching the un-curled state ($\kappa = 0$) in acetone were 8, 15 and 22 seconds at $\phi = 20$, 30 and 40 wt%, respectively, suggesting that actuation was slow while increasing the RM257 content in the curable mixtures.
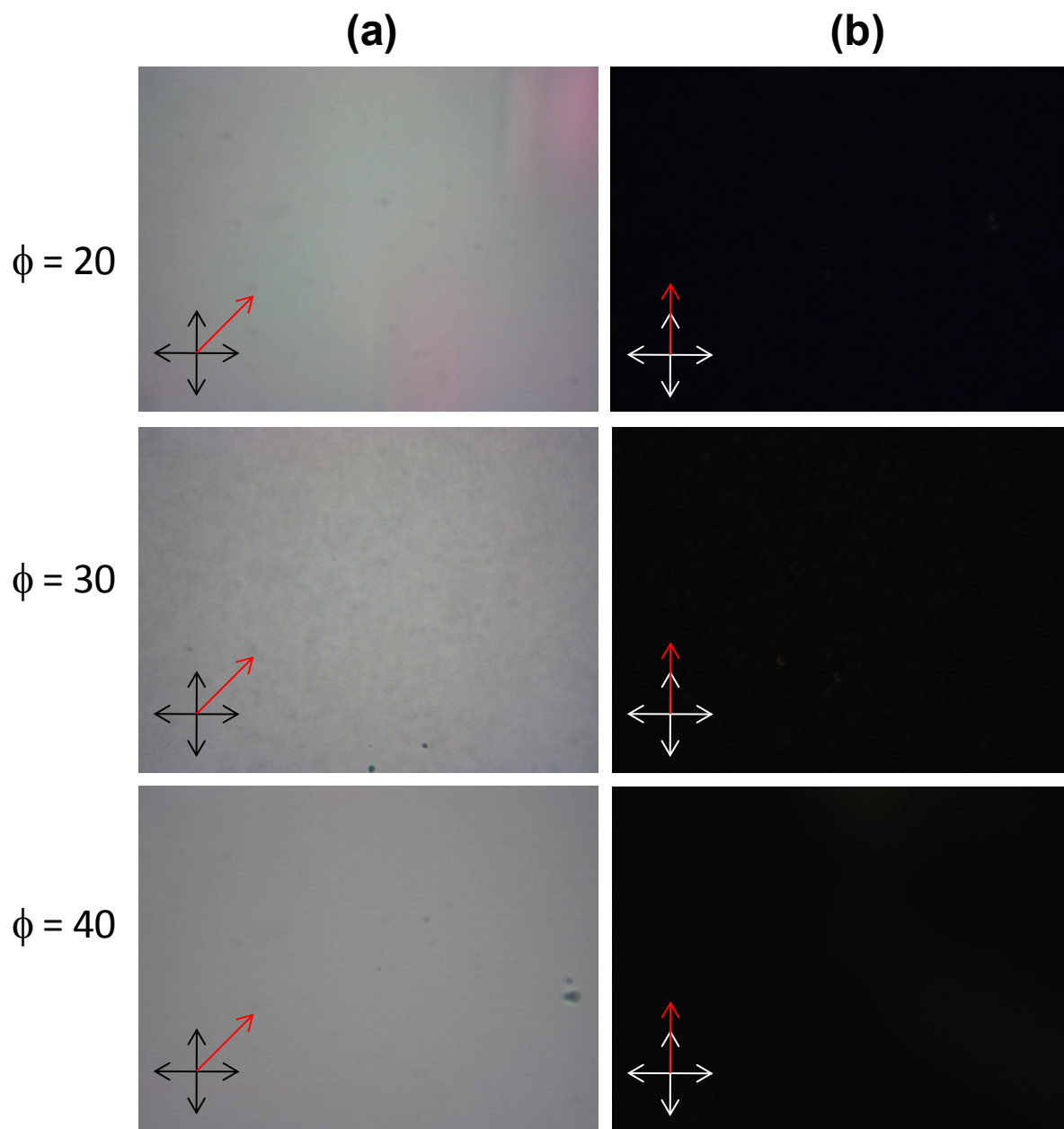
(a) **(b)**

$\phi = 20$

$\phi = 30$

$\phi = 40$

Fig. S6. POM images of different RM257/5CB mixtures in the LC cell before photopolymerization with their rubbing directions at (b) 45° and (b) 0° from the polarizer.
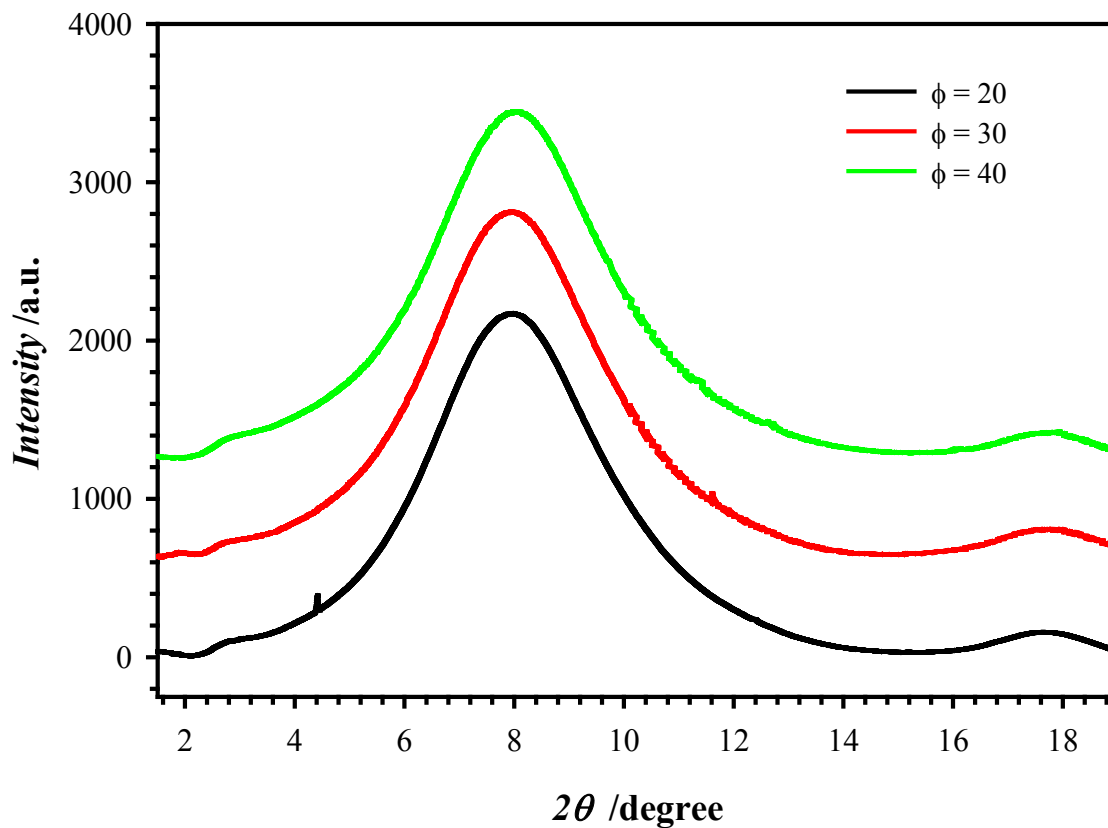
Fig. S7. Azimuthally averaged 1D WAXS patterns of different films deduced from 2D WAXS patterns.

References for SI

[1] H. R. Stapert, S. del Valle, E. J. K. Verstegen, B. M. I. van der Zande, J. Lub, S. Stallinga, *Adv. Funct. Mater.* **2003**, 13, 732.

[2] I. Dierking, in *Textures of Liquid Crystals*, Wiley-VCH Verlag GmbH & Co. KGaA, 2004, 51.