crosslinker are controlled, it is technically possible to prepare a gel membrane reflecting the specific color at a certain temperature. This method to prepare the interconnecting porous gels will give us the potential to study appropriate smart gels that may have interesting applications, such as in tunable optical filters, actuators, and sensors. Studies to confirm this are underway.

Experimental

Synthesis of Colloidal Crystals as Templates: To prepare the closest-packed colloidal crystals, a 15 wt.-% aqueous solution of silica spheres, having a diameter of 291 nm as determined from SEM measurements, was used. The growth of the crystal by the gravity sedimentation method was conducted in a flat Petri dish at 20 °C. The stable dried crystals were obtained within 1 week as the water evaporated, and then completely dried in vacuo at 60 °C. It is generally accepted that the crystalline arrays produced by the gravity sedimentation method have a cubic close-packed structure containing polycrystalline domains, similar to that of a natural opal. The thickness of the crystal can be easily controlled by the colloidal concentration and the iterative treatment. On the other hand, fine ordered crystals were created by the solvent evaporation method as follows: the colloidal suspension (ca. 15 wt.-%) was dropped onto a clean microscope slide and was placed in a thermostatic chamber at 90 °C, in which the solvent gradually evaporated. A high quality crystal can be prepared with a thickness of up to 1 mm.

Synthesis of Porous Hydrogels and Cylindrical Hydrogels: The thermosensitive gels were prepared by free-radical polymerization as follows. First, *N*-isopropylacrylamide (NIPA, 11.3 g), *N*, *N'*-methylene bis(acrylamide) (0.513 g) as a crosslinker, and benzoylperoxide (0.048 g), the initiator, were dissolved in degassed and nitrogen-saturated 1,4-dioxane to a final volume of 50 mL. The solution was then infiltrated into the colloidal crystals in a Petri dish, and the polymerization was conducted at 60 °C for 40 h. Afterwards, the samples were immersed in a 5 wt.-% HF aqueous solution to remove the SiO_2. The gels for a swelling measurement were prepared in micropipettes of 100 μm diameter. The resulting porous gels and the cylindrical gels were washed carefully with distilled water for 1 week.

Measurements: The swelling measurement was carried out by monitoring the diameter of the cylindrical gel in water. The temperature was controlled by using a temperature control system with circulating water. The reflection spectra were obtained by an Ocean Optics USB2000 fiber optic spectrometer

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[13] We did not use a macroporous gel to determine the swelling behavior. Therefore, a small difference in swelling size between the porous gel and cylindrical gel seems to be present, because the quantitatively different values were obtained in the wavelength of the peak of the reflection spectra from a porous gel as a function of temperature in Fig. 4b. Nevertheless, the experimental results qualitatively prove our description.

Anisotropic Bending and Unbending Behavior of Azobenzene Liquid-Crystalline Gels by Light Exposure

By *Tomiki Ikeda,* * Makoto Nakano, Yanlei Yu, Osamu Tsutsumi, and Akihiko Kanazawa*

Photoresponsive liquid-crystalline (LC) polymers have been extensively explored recently as highly functional and high-performance materials in information technology fields, because of their large anisotropy in optical and other physical properties.[1–5] In particular, cross-linked polymer LCs (PLCs) have attracted much attention for LC gels (LCGs) or LC networks (LCNs) due to their specific properties arising from the cross-linked polymer and LC behavior.[4–9]

Polymer gels may deform in response to a variety of external stimuli such as temperature, pH, ionic strength, electric field, and light.[10–12] Several successful examples have been reported on photoresponsive gels, such as volume phase transitions in *N*-isopropylacrylamide (NIPA)-based gels induced by light.[13–15] Mamada et al.[13] observed that the incorporation of triphenylmethyl moieties into the NIPA-based gel enabled the gel to expand in water by irradiation. However, the volume phase transition in those gels is due to the change in the osmotic pressure by the external stimuli, and the rate-determining step of the deformation is the diffusion process. Therefore, the response is too slow for various applications.[16]

Gels containing azobenzenes can expand or contract due to photoinduced structural changes of the azobenzenes. Upon photoirradiation, azobenzenes show *trans–cis* isomerization and exhibit a large change in the molecular length: the distance between 4- and 4′-carbons decreases from 9.0 Å (*trans*) to 5.5 Å (*cis*).[17] Eisenbach reported that polymers cross-linked with azobenzenes contract upon UV irradiation. However, the observed contraction was very small (0.15–0.25 %).[18] Recently, de Gennes et al. reported on theoretical studies on the possibility of a large deformation of LCGs,[16] and several groups demonstrated experimentally large deformations of LCNs induced by an electric field or temperature.[19,20] Finkelmann et al. reported a pioneering work on large contractions of LCNs containing azobenzene moieties by light.[21] Although their LCNs show excellent properties in comparison to previous LCGs or LCNs, there still remain some problems to be addressed for practical applications, i.e., response time and the type of deformation.

To prepare LCGs and LCNs showing large deformations and fast response, we focused our attention on LCGs and
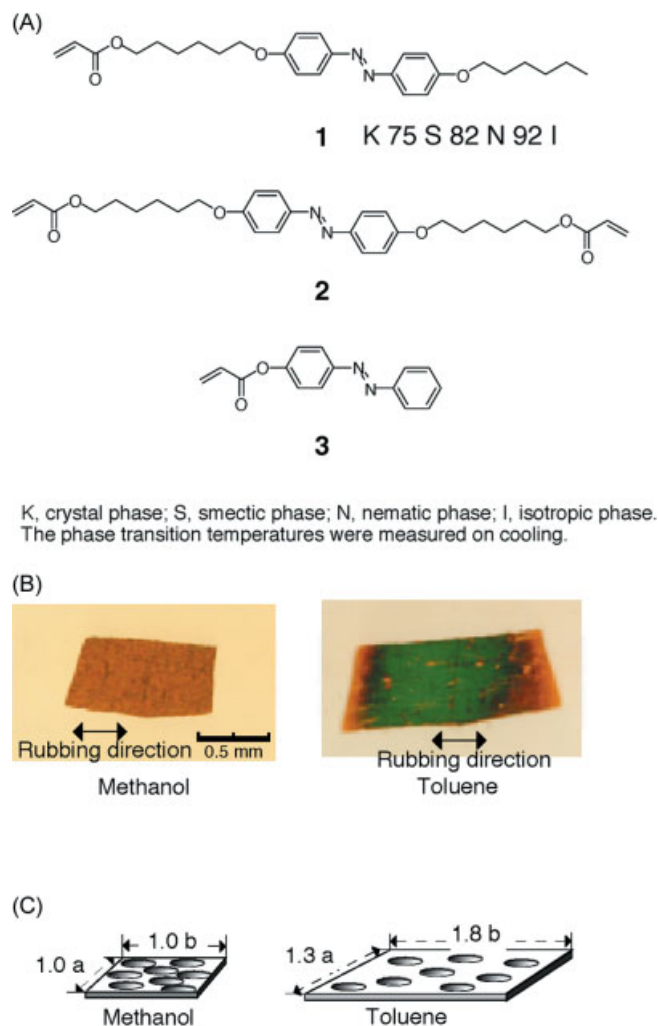
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LCNs composed only of azobenzene moieties. In previous studies, we found that the photoresponse of the PLCs consisting only of azobenzene moieties is much faster than that of copolymers composed of azobenzenes and non-photoactive mesogens.[3a] Therefore, it is expected that LCGs and LCNs composed only of azobenzene mesogens undergo fast deformation. Furthermore, in these LCGs and LCNs, due to large extinction coefficients of the azobenzene moiety, the depth profile for absorption of photons can be controlled just by choosing a suitable wavelength of actinic light. For instance, if absorption of photons occurs only in the surface of the film and *trans–cis* photoisomerization takes place only in the surface area, a bilayer structure with slabs of two different polymers that respond differently can be obtained; "bending" could then be induced, like in a bimetal. Since this mode of deformation is very advantageous for an artificial "hand", LCGs or LCNs that show bending upon photoirradiation are suitable for light-driven actuators. Furthermore, since only a part of the LCG or LCN is involved in the deformation in these materials, the bending could be much faster than other modes of deformation. Here, we report anisotropic bending and unbending of LCGs and LCNs induced by light.

The cross-linked polymer films were prepared by in-situ photopolymerization of an LC monomer containing an azobenzene moiety (**1**) and a diacrylate with an azobenzene moiety (**2**) at various ratios of **1** to **2** (Fig. 1). The cross-linked polymer films prepared with a high concentration of the cross-linking agent (20 mol-%) showed a glass transition temperature (T_g) at 85 °C and a LC phase up to 300 °C. The alignment of the azobenzene moieties in the cross-linked polymer films was examined by polarized UV-vis and IR absorption spectroscopy. It was revealed that the azobenzene moieties are preferentially aligned along the rubbing direction of the alignment layer in the cell used for the preparation of the cross-linked films. The cross-linked polymer films showed a swelling in good solvents, such as toluene and chloroform, but little change in size in poor solvents such as methanol and n-hexane, as shown Figure 1b. In addition, the swelling of the LCG films was anisotropic in good solvents: the enlargement of the LCG films was larger by a factor of 1.4 in the direction parallel to the rubbing direction of the alignment layer than in the direction perpendicular to the rubbing direction.

Exposure of the LCG film in toluene to UV light at 360 nm, which causes *trans–cis* photoisomerization of the azobenzene moieties, brought about bending of the LCG film towards the irradiation direction of the actinic light as shown in Figure 2a. Here, the LCG film was prepared from a mixture of **1** (80 mol-%) and **2** (20 mol-%) in the presence of 2 mol-% of the photoinitiator. At a light intensity of 3 mW cm^{-2}, the bending was completed in 20 s. When the bent film was exposed to visible light at 450 nm, which causes *cis–trans* back isomerization of the azobenzene moiety, unbending of the LCG film immediately took place and the initial flat film was restored in 30 s at the same light intensity. This bending and unbending of the LCG films could be re-

Fig. 1. Structures of the azobenzene LC monomers used in this study and anisotropic swelling of the LCG film. a) Structures of the azobenzene LC monomers. b) Anisotropic swelling of the LCG film in methanol (a poor solvent) and toluene (a good solvent). c) Schematic illustrations for the anisotropic swelling of the LCG film in methanol and toluene. The LCG film was prepared from a mixture of **A6AB6** (90 mol-%) and **DA6AB** (10 mol-%) containing 2 mol-% of a photoinitiator. The swelling in the good solvent was anisotropic: more enlargement of the LCG films was observed in the direction parallel to the rubbing direction of the alignment layer of the cells.

peated just by changing the wavelength of the irradiation light. It is worth mentioning here that the bending of the LCG films occurred only in the direction parallel to the rubbing direction of the polyimide alignment layer of the cell, and did not take place in other directions.

The optical properties of the LCG film during the bending and unbending processes were also examined by polarizing microscopy. It was clearly observed that the LCG film showed optical anisotropy at all stages of the bending and unbending processes (Fig. 2b). This means that the bending and unbending occur in the anisotropic phases.

These responses are different from the photoresponsive behavior of the LCNs reported by Finkelman et al. in two aspects.[21] First, the response of the present LCGs is faster by
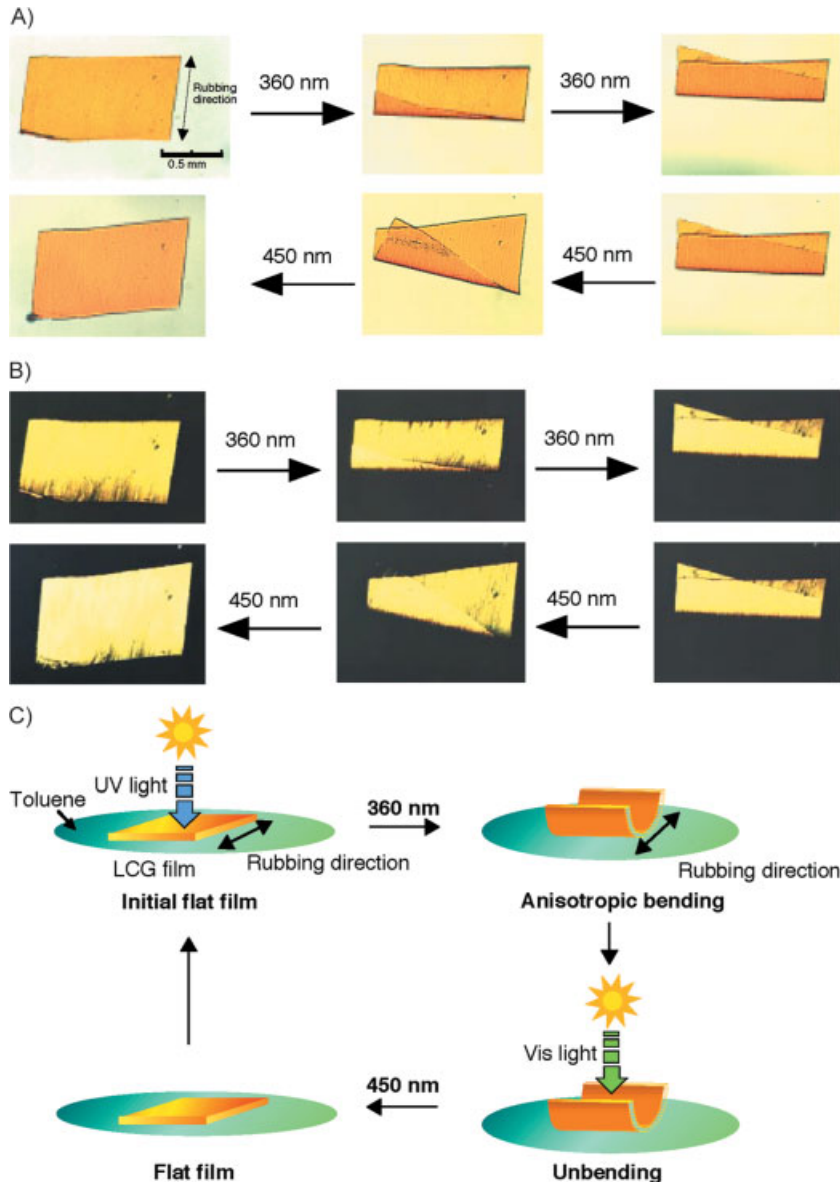
Fig. 2. Bending and unbending behavior of the LCG film in toluene. The LCG film was prepared from a mixture of **1** (80 mol-%) and **2** (20 mol-%) containing 2 mol-% of a photoinitiator. The LCG film bent toward the irradiation direction of UV light (360 nm) and reverted to the initial flat film completely upon irradiation of visible light (450 nm). The bending was always induced in one direction: the rubbing direction of the alignment layer of the cells used for the preparation of the LCG films. a) Photographs taken during bending and unbending processes. b) Polarizing micrographs observed during the bending and unbending processes. The LCG film showed optical anisotropy at all stages of the bending and unbending processes. c) Schematic illustration for anisotropic bending and unbending behavior of the LCG film.

oriented, and found that bending and unbending of the gels took place to some extent in toluene, but they were incomplete and isotropic; there was no preferential direction in bending.

Bending and unbending were observed in good solvents, such as toluene and chloroform, but not induced in poor solvents such as methanol and n-hexane. Interestingly, the cross-linked LC polymer films showed a bending toward the irradiation direction even in air (in the absence of any solvent), when the films were heated to 90 °C, which is above the T_g of the films as shown in Figure 3. The response of the cross-linked LC polymer films for bending in air was also fast: the bending was completed in 80 s and the bent film was restored to the initial flat film in 90 s. These findings seem to rule out the possibility that the bending of the LCG films is caused by the shrinkage of the slab of the polymer with *cis*-azobenzene moieties due to exclusion of solvent molecules, arising from the increased polarity of the azobenzene. In good solvents, the LCG films are swollen, which enables the azobenzene moieties to isomerize efficiently due to increases in free volume and segmental mobility of the polymers. These requirements could be fulfilled if the cross-linked LC polymer films are heated above T_g.

The mechanism of the photoinduced bending is thought to be as follows (Fig. 4). The thickness of the cross-linked LC polymer film is typically 10 μm. The extinction coefficient of the azobenzene moieties at 360 nm is large (2.6×10^4 L mol^{-1} cm^{-1}) and 99 % of the incident photons are absorbed by the surface within a thickness of < 1 μm. This means that upon photoirradiation at 360 nm, the *trans–cis* photoisomerization occurs only in the surface region, and in the bulk of the film the *trans* forms of the azobenzene remain unchanged. In other words, the volume contraction is induced only in the surface region of the cross-linked LC polymer film upon irradiation. Therefore, the bending is induced toward the incident direction of the actinic light. Furthermore, since the azobenzene moieties are aligned into one direction in the cross-linked films, the films could contract only in one direction upon *trans–cis* photoisomerization. Thus, the freestanding cross-linked LC polymer films undergo an anisotropic bending. For the bending and unbending of the cross-linked LC polymer films to be induced, the relaxation of

about two orders of magnitude than that of their LCNs (90 min). This may be understood in terms of a different mechanism of response of the present LCGs. Second, the mode of deformation is quite different between these two materials, i.e., contraction in LCNs by Finkelmann et al. and bending by us.

As a control experiment, we examined the photoresponsive behavior of isotropic gels made of 4-(phenylazo)phenyl acrylate (**3**) and **2**, in which azobenzene moieties are randomly
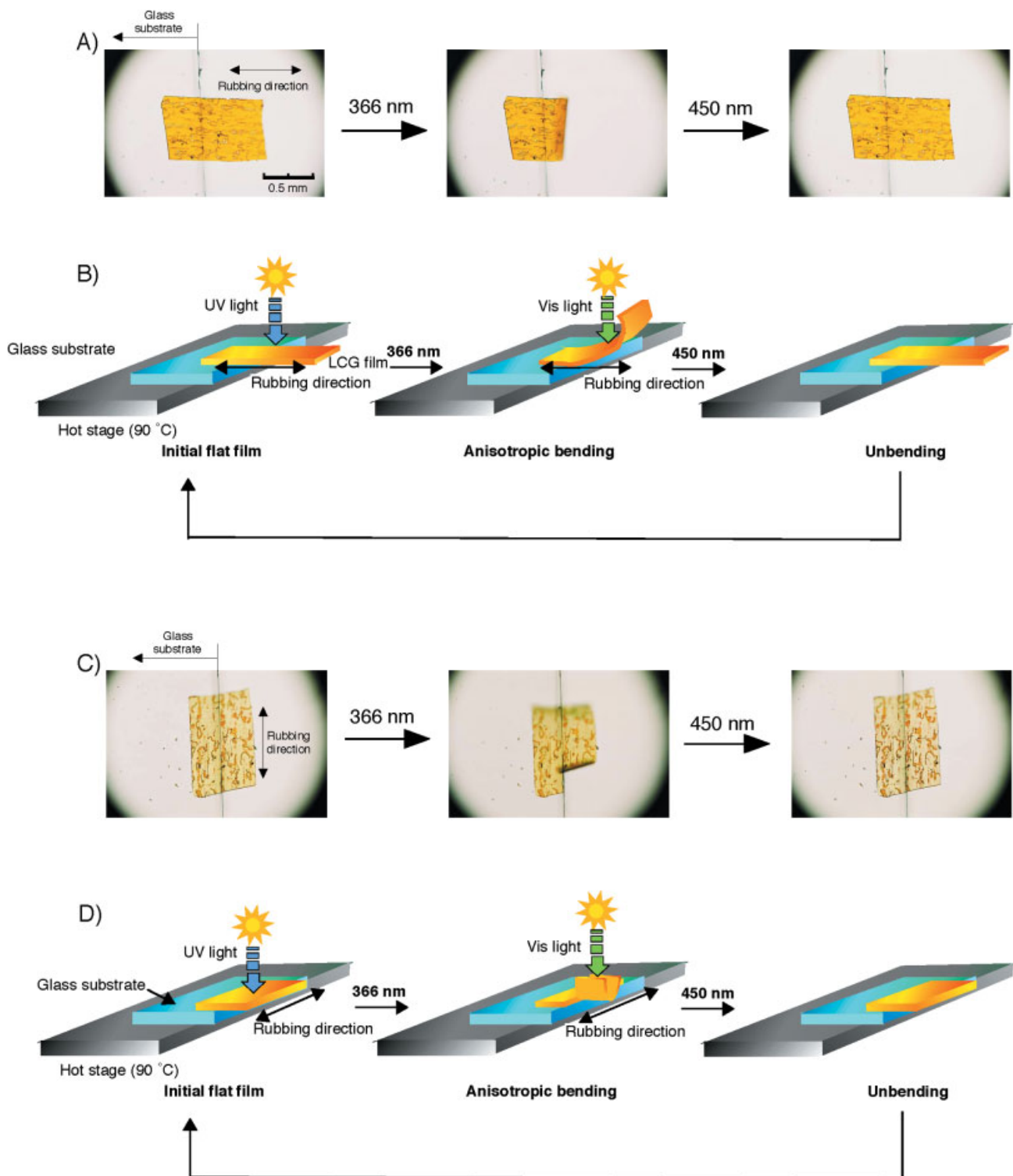
Fig. 3. Bending and unbending behavior of the LCN film at 90 °C in air. The LCN film bent toward the irradiation direction of UV light (366 nm) and reverted to the initial flat film completely upon irradiation of visible light (450 nm). The bending was always induced along the rubbing direction of the cell. A part of the film was fixed (pasted) on a glass substrate and irradiated. a) The rubbing direction is perpendicular to one side of the glass substrate. b) Schematic illustration of anisotropic bending and unbending behavior in (a). c) The rubbing direction is parallel to one side of the glass substrate. d) Schematic illustration for anisotropic bending and unbending behavior in (c). In (c), upon UV irradiation, the film was broken by bending along the rubbing direction.

polymer segments is necessary, which could be achieved by suspending the film into solvents or heating it to above T_g. The origin of the bending is an unbalanced contraction between the surface area and the bulk of the material. These photoresponsive materials enable light energy to be converted into specific mechanical work.
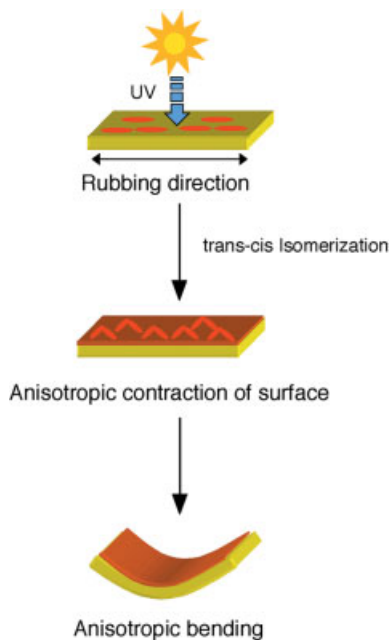
Fig. 4. Schematic illustration of the mechanism of the bending.

Experimental

Preparation of the sample: The azobenzene LCG films were prepared by in-situ photopolymerization of an LC monomer containing an azobenzene moiety (**1**) and a diacrylate with an azobenzene moiety (**2**) at various ratios of **1** and **2** (mol-%) (90:10–80:20). Both monomers were synthesized according to the method reported previously [22]. The mixture containing a photoinitiator (Ciba Specialty, Irgacure 784; 2 mol-%) was injected into a glass cell with polyimide alignment layers at 100 °C (in an isotropic phase). It was confirmed that the photoinitiator did not destabilize the LC phase at this concentration and no spontaneous thermal polymerization occurred during injection of the LC monomers into the cell. After the mixture in the cell was cooled down slowly (0.5 °C min^{-1}) to a polymerization temperature (85 °C), photoirradiation at > 540 nm (1.9 mW cm^{-2} at 547 nm) was performed with a 500 W high-pressure mercury lamp through glass filters (Toshiba, Y-52 + IRA-25) for 2 h. After polymerization, the cross-linked polymer film was taken off from the cell and washed thoroughly with chloroform to completely remove unreacted monomers. Finally, the cross-linked polymer film was dried under reduced pressure to remove the solvent.

Bending behavior in solvents: The cross-linked polymer films were cut into rectangular sections (1.3 mm × 0.8 mm × 10 μm), and placed horizontally in a vessel containing toluene (Fig. 2c). These LCG films were irradiated at room temperature at 360 nm from a Xe lamp (obtained through a monochromator (JASCO SM-5)). The bent films were exposed to visible light at 450 nm from the Xe lamp (obtained through the monochromator). The actinic light was irradiated from 4 cm above part of the film). The deformation behavior was observed by polarizing microscopy (Olympus BH-2) at room temperature.

Bending behavior in air: To explore the bending behavior of the cross-linked LC polymer films, the films were cut into rectangular shape (1 mm × 0.6 mm × 10 μm; in some cases 5 mm × 5 mm × 20 μm), and about one-third to one-half of the film was pasted to a glass substrate (Fig. 3c). The glass substrate with a film was placed on a hot stage (Mettler FP82HT and Mettler FP90), and kept at 90 °C (above T_g). Then the film was irradiated at 366 nm from a 500 W high-pressure mercury lamp through glass filters (Toshiba, UV-D36A + UV-35 + IRA25-S). The actinic light was irradiated from above, 4 cm away from the film.

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Lithium Niobate Inverse Opals Prepared by Templating Colloidal Crystals of Polyelectrolyte-Coated Spheres**

By *Dayang Wang* and *Frank Caruso**

Three-dimensional (3D), ordered macroporous materials with pore sizes in the submicrometer to micrometer range are of significant interest because of their application in separation processes,[1a] as light-weight structural materials,[1b] as catalytic supports and surfaces,[1c] as thermal and acoustic insulators,[1d] and as low-dielectric materials.[1e] Such materials have also received intense interest because of their importance in photonics,[2] where they can be used as photonic crystals for the manipulation of electromagnetic waves, for example, by localizing light and controlling spontaneous emission.[3]

The use of colloidal crystals as templates has proven to be a promising approach for the fabrication of 3D, highly ordered macroporous materials, or inverse opals.[4] Inverse opals are comprised of air spheres that are close-packed in a highly ordered 3D array, and are interconnected to each other by small

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