Is chemical crosslinking necessary for the photoinduced bending of polymer films?[†]

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Freestanding crosslinked liquid-crystalline polymer films obtained by self-assembly through intermolecular hydrogen bonding showed photoinduced bending and unbending. The structural change at the microscopic level, caused by *trans-cis* photoisomerization of the azobenzene moieties at the hydrogen-bonded crosslinks, is successfully converted into a macroscopic deformation in the liquid-crystalline polymer films.

Soft materials have attracted much attention because of their dynamic properties.¹ For effective muscle-like actuation, soft materials with stratified structures and high molecular orders are necessary. Crosslinked liquid-crystalline polymers (CLCPs) are superior soft materials that possess both the order of LCs and the elasticity of polymer networks.^{2,3} CLCPs exhibit a spontaneous contraction along the director axis when heated above nematicisotropic (I) phase transition temperatures.⁴ When azobenzene chromophores are incorporated into CLCPs, they can undergo the contraction isothermally because of the change in LC alignment caused by light.⁵ Furthermore, a three-dimensional deformation, bending, of CLCP films containing azobenzenes has been observed upon exposure to light.⁶ Due to the limitation of absorption of photons, a surface contraction caused by the photoinduced change in alignment of LCs contributes to the bending. By using photodeformation of these materials, one can convert light energy into mechanical work directly (photomechanical effects).^{3,5-7}

Hydrogen bonds have been used for the preparation of a wide variety of self-assembled soft materials, among which LC phases with well-defined structures have been formed by exploiting intermolecular hydrogen bonding.⁸ Various synthetic approaches for the construction of dynamically functional materials using hydrogen bonds have been demonstrated in such self-assembly systems as supramolecular LCs and polymers.^{8,9} However, there are few examples of supramolecular crosslinking of polymers by low-molecular-weight (LMW) crosslinkers.¹⁰ Crosslinked polymers by supramolecular interactions are expected to function as recyclable materials responsive to external stimuli, because LMW crosslinkers can be connected and disconnected reversibly.

Since the hydrogen bonds crosslink polymer chains to form three-dimensional polymer networks, if an azobenzene moiety as a photoresponsive group is introduced into the crosslinker, *trans-cis* isomerization of the azobenzenes may influence the crosslinking of the three-dimensional polymer networks. In this communication, we investigated the photoresponsive behavior of azobenzene CLCP films formed by self-assembly. We succeeded in fabricating recyclable CLCP films that could crosslink/de-crosslink reversibly using the hydrogen bonding at the crosslinks, and we showed photoinduced bending and unbending as well.

The structure of the LC copolymer (1) used in this study is shown in Fig. 1, which has both a carboxyl group and an azobenzene moiety. The mesomorphic properties of the copolymer 1 were studied by differential scanning calorimetry (DSC). The copolymer 1 exhibited a glass transition (T_s) at 38 °C, and an LC–I phase transition at 106 °C upon heating (Fig. 2). Crosslinkers 2 and 3 that are capable of recognizing hydrogen-bond donor molecules at the pyridyl ends were selected as hydrogen-bond acceptors (Fig. 1). A complex of the copolymer and the crosslinker was obtained from a THF solution containing equimolar amounts of the carboxyl group and the pyridine moiety. In the infrared (IR) spectra of the complexes of 1 + 2 and 1 + 3, the absorption bands corresponding to the hydrogen-bonded O-H stretch of the carboxyl groups were observed at 1930 and 2500 cm^{-1.11} On the other hand, in the single copolymer 1, no absorption due to the hydrogen bonding appeared. It was also found that when each

Hydrogen-bond donor



Hydrogen-bond acceptors



Fig. 1 Chemical structures of the hydrogen-bond donor (1) and acceptors (2 and 3) used in this study.

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Fig. 2 DSC thermograms of the copolymer and the complexes on heating (scan rate = 10 °C min^{-1}).

crosslinker was mixed with the copolymer **1**, the temperature range of the LC phase in the complexes became broader than that in the copolymer **1** (Fig. 2). It is observed clearly that the mesophases of the complexes are stabilized by the formation of the hydrogen bonding between **1** and the crosslinkers

Hydrogen-bonded azobenzene CLCPs were sandwiched between two sodium chloride (NaCl) plates with rubbing treatment. The cell thickness was controlled with silica spacers with a diameter of 20 μ m. Freestanding films were obtained after the NaCl substrates were dissolved in water. The optical anisotropy of the CLCP films was evaluated by polarizing optical microscopy. The regular maximum and minimum values with 90° separations showed that the azobenzene mesogens are preferentially aligned along the rubbing direction.

We observed the photoresponsive behavior of the hydrogenbonded CLCP films above their $T_{\rm gs}$ of 1 + 2 and 1 + 3. In 1 + 2, no bending was observed upon exposure to UV light at 366 nm and the film showed no deformation upon further visible-light irradiation at 60 °C (Fig. 3a). On the other hand, when the CLCP film of 1+3 was exposed to 366 nm light at 50 °C, the film bent toward the actinic light source along the alignment direction of the mesogens (Fig. 3b). The bent films reverted to the initial flat states when irradiated with visible light at >540 nm. Here, crosslinker **2** has no photoresponsive property, while crosslinker **3** shows



Fig. 3 Photoresponsive behavior of the hydrogen-bonded CLCP films of 1 + 2 (a) and 1 + 3 (b). Size of the films: $2 \text{ mm} \times 3 \text{ mm} \times 20 \text{ µm}$. UV light intensity, 18 mW cm^{-2} ; visible light intensity, 21 mW cm^{-2} .

photoisomerization behavior. The photoinduced bending and unbending of the hydrogen-bonded films of 1 + 3 is similar to that of the chemically-bonded films reported previously.⁶ These results indicate that a structural change caused by photoisomerization of the azobenzene moieties at the crosslinks plays an important role in the photoinduced bending of the hydrogen-bonded CLCP films. In other words, it means that the crosslinks formed by non-covalent bonds can convert the motion of the mesogens into a macroscopic change of the CLCP films.

Irradiation with UV light gives rise to *trans-cis* isomerization of the azobenzene mesogens in CLCPs. However, the CLCP films of 1 + 2 showed no bending upon UV-light irradiation. This is presumably because the photoisomerization of the azobenzene mesogens in the copolymer 1 induces no decrease in alignment order of the hydrogen-bonded LC structure. On the other hand, *trans*-azobenzenes in both the copolymer and the crosslinker isomerization of the azobenzenes in the CLCP films of 1 + 3. By photoisomerization of the hydrogen-bonded LC structure only in the film surface (Fig. 4). As the azobenzene mesogens are aligned parallel to the rubbing direction, an anisotropic contraction is generated along the alignment direction of the azobenzene moieties upon irradiation with UV light.

Next, the recyclability of the hydrogen-bonded CLCP films was investigated (ESI[†]). The chemically-bonded CLCP films were undissolved in various solvents. However, the hydrogen-bonded CLCP films were dissolved in THF. Reprecipitation from the THF solution in diethyl ether led to dissociation of the hydrogen bonding. We could reconstruct the CLCP films by self-assembly through hydrogen bonding and repeatedly induce the photoinduced bending of the reformed CLCP films.

In summary, freestanding hydrogen-bonded CLCP films containing azobenzenes have been obtained. The supramolecular crosslinking of the linear copolymers with LMW crosslinkers was



Fig. 4 Plausible mechanism of bending in the hydrogen-bonded CLCP films of 1 + 3. (a) Network structures of the hydrogen-bonded CLCP films consisting of the copolymers and the crosslinkers. Schematic illustration of molecular alignment in the hydrogen-bonded CLCP film before (b) and after (c) irradiation with UV light.

found to be a useful strategy for constructing the CLCP films. The structural change at the microscopic level is successfully converted to a macroscopic deformation of the hydrogen-bonded CLCP films by *trans-cis* photoisomerization of the azobenzene moieties at the crosslinks. This is the first example of a supramolecular photomechanical system based on hydrogen-bonded CLCP films, which converts light energy directly into mechanical work.

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