# Photoinduced Deformation of Crosslinked Liquid-Crystalline Polymer Film Oriented by a Highly Aligned Carbon Nanotube Sheet**

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Photodeformable polymeric materials have recently experienced vigorous development because of their potential applications in various fields, such as artificial muscle, photomobile soft actuator, and micro-optomechanical systems (MOMS).[1,2] Among them, crosslinked liquid-crystalline polymers (CLCPs) containing photochromic moieties such as azobenzene may represent one of the most studied systems, with a bending deformation owing to a photoinduced change in the molecular orientation of mesogens triggered by the *trans–cis* photoisomerization in azobenzene.[3–5] Various light-driven soft actuators including plastic motors,[6] inchworm-like walkers,[7] flexible microrobots,[8] high-frequency oscillators,[9] and artificial cilia[10] have been made from the CLCPs. For the above applications, it is critical to control the bending direction of the CLCPs which depends on the orientation format of the mesogens. For instance, a homogeneously oriented CLCP film bent towards the light source along the oriented direction of mesogens,[5] while a homeotropically oriented film bent away from the light source.[11]

To achieve the orientation in a liquid-crystalline (LC) system, the surface of the substrate is usually modified to provide an anchoring action for LC molecules during fabrication. Of many methods, the preferred modification technique is mechanical rubbing. Typically, an aligned polyimide (PI) layer with parallel grooves is firstly generated by mechanical rubbing along one direction, and the grooves are then used to orient the LC molecules.[12] However, there remain several challenges, such as the production of broken debris and structural damage during fabrication and the accumulation of electrostatic charge on the surface during use, which have largely limited the application of the CLCPs.

On the other hand, carbon nanotubes (CNTs) have been widely investigated for their extraordinary mechanical and electrical properties as well as good absorption in the visible/

near-infrared (NIR) region. It has been reported that the dispersion of CNTs in a thermoresponsive CLCP created a light-controllable network, which enabled a contraction upon irradiation by NIR light.[13] In this case, the CNT functions as a nanoscale heat source to absorb the NIR light and further convert it to thermal energy, which induces a thermal phase transition of the CLCP from LC to isotropy with a thermal contraction. However, both sensitivity and stability are very low for such an indirect photoactuation. In addition, it remains difficult to control and improve the orientation of mesogens in the CLCP due to the random dispersion of CNTs, and the other important properties such as mechanical strength also need to be improved in this fabrication.

Herein, we report the development of a new and general method to prepare photodeformable CLCP/CNT nanocomposite films by using highly aligned CNT sheets.[14] A photosensitive CLCP containing azobenzene has been carefully investigated as a demonstration. It was found that the aligned nanostructure of the CNT sheet could effectively orient the CLCP mesogens along the length of the CNTs without using any other aligning layer. The resulting nanocomposite film underwent bending and unbending by alternate irradiation with UV and visible light. Furthermore, the introduction of aligned CNTs remarkably increased the mechanical strength and provided electrical conductivity for the CLCP film.

The chemical structures and properties of two monomers, **A11AB6** and **A9Bz9**, and the crosslinker **C9A**, are shown in Scheme 1. The monomers and crosslinker were synthesized and purified according to the literature.[15] The synthetic details, ^{1}H NMR spectra, and differential scanning calorimetry (DSC) thermograms are presented in the Supporting Information. The fabrication of the CLCP/CNT composite film is shown in Figure 1. Firstly, a CNT array was grown on silicon by chemical vapor deposition.[16] Secondly, uniform CNT sheets were pulled out of the array by dry spinning and stabilized on glass substrates.[14] Thirdly, an LC cell was made of two CNT-sheet-covered glass slides with the CNT sheet inside. Fourthly, a molten mixture of **A11AB6**, **A9Bz9**, and **C9A** (molar ratio 1:1:3) containing 1 mol% photoinitiator (Irgacure 784) was injected into the LC cell at 90°C (in an isotropic phase), and then slowly cooled to a polymerization temperature of 77°C (in a nematic phase) at a rate of 0.1°C min$^{-1}$. The CLCP/CNT composite film was obtained after photopolymerization at a wavelength of 547 nm (2 mW cm$^{-2}$) under a 500 W high-pressure mercury lamp through a glass filter for 2 h. The LC cell could be further opened to produce a freestanding composite film.

Figure 2a shows a typical scanning electron microscopy (SEM) image of a CNT array on silicon. The CNTs are highly
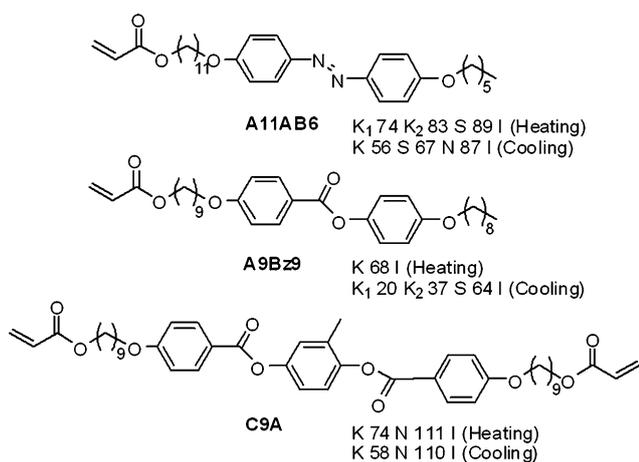
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**Scheme 1.** Chemical structures and properties of the two monomers and crosslinker. K, S, N, and I correspond to the crystal, smectic, nematic, and isotropic phases, respectively.
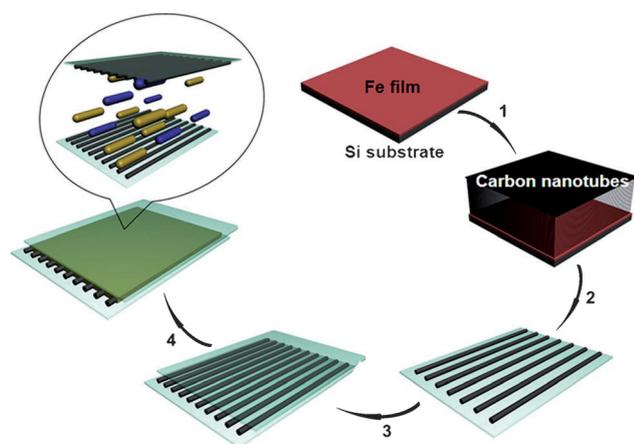


**Figure 1.** Preparation of an oriented CLCP/CNT nanocomposite film in four steps: 1) growth of a CNT array by chemical vapor deposition; 2) formation and stabilization of the CNT sheet on a glass substrate; 3) preparation of the LC cell by using two CNT-sheet-covered glass slides; and 4) injection of the molten mixture including the monomers, crosslinker, and photoinitiator into the LC cell.
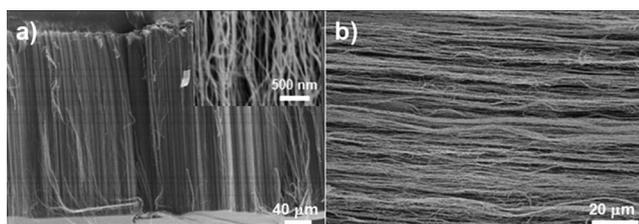


**Figure 2.** SEM images of a) a CNT array (inset, high magnification) and b) a CNT sheet.

aligned with each other and vertical to the substrate. High-resolution transmission electron microscopy indicates a multi-walled structure in the CNT with a diameter of approximately 10 nm (Figure S5 in the Supporting Information). Figure 2b shows a CNT sheet stabilized on the glass substrate. The CNTs are highly aligned along the pulling direction at the nanoscale.

The anisotropic orientation of mesogens was evaluated by tracing the transmittance of the CLCP/CNT composite film, which was sandwiched between two crossed polarizers at room temperature. Typical polarized optical micrographs are shown in Figure 3a. The highest transmittance occurred at an
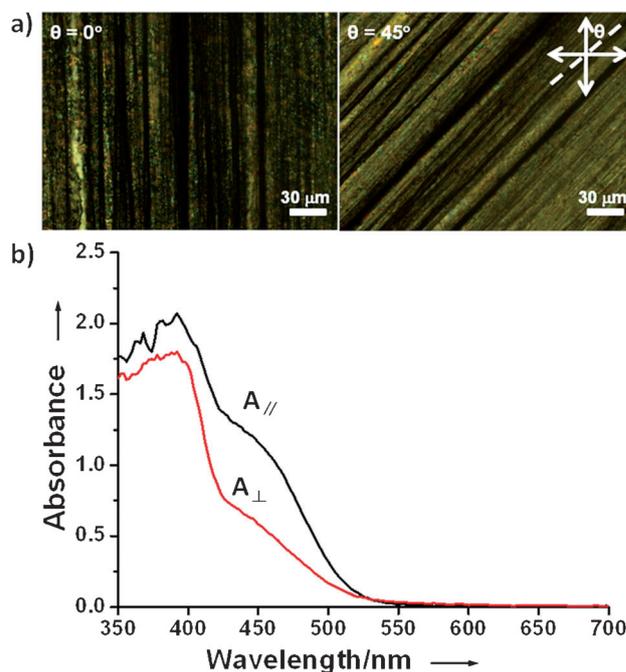


**Figure 3.** a) Polarizing optical micrographs and b) polarized absorption spectra of the CLCP/CNT composite film. The white arrows indicate the directions of optical axes of the two polarizers, while the dashed white line shows the CNT-aligned direction. $A_{\parallel}$ and $A_{\perp}$ are the absorbances measured with the light polarized parallel and perpendicular to the CNT-aligned direction, respectively.

angle of 45° between the polarization direction of either polarizer and the CNT-aligned direction, whereas the lowest transmittance appeared when the polarization direction was parallel to the CNT-aligned direction. Therefore, a periodic change of dark and bright images was observed by rotating the composite film with an interval of 45°. This result reveals that the mesogens are preferentially oriented parallel to the CNT-aligned direction.

Furthermore, the dichroism in the optical absorption spectra of the CLCP/CNT composite film was measured with the light polarized to be parallel and perpendicular to the CNT-aligned direction (Figure 3b). It is clear that the absorption of the composite film measured under parallel polarization ($A_{\parallel}$) is higher than that under perpendicular polarization ($A_{\perp}$). This phenomenon further indicates that the azobenzene mesogens are preferentially oriented along the CNT-aligned direction. Both polarized optical micrographs and polarized absorption spectra verified that the highly aligned CNTs are able to induce the orientation of mesogens in the CLCP.

The CLCP/CNT composite film exhibited a rapid and reversible deformation under alternate irradiation by UV and visible light (Figure 4). Upon exposure to UV light (wave-
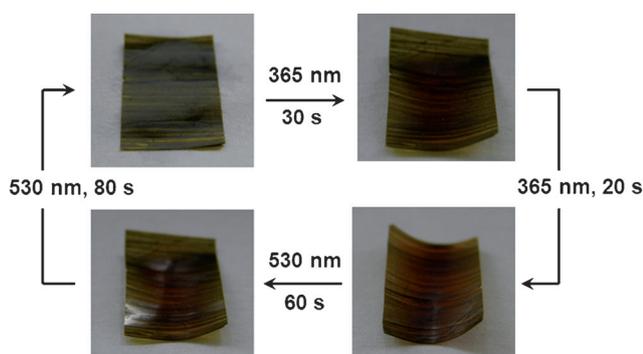
***Figure 4.*** Photographs of a CLCP/CNT composite film during one bending and unbending cycle after alternate irradiation by UV and visible light at room temperature. The intensities of the UV light at 365 nm and visible light at 530 nm were 100 and 35 mWcm$^{-2}$, respectively.

length 365 nm), the composite film bent toward the incident light along the oriented direction of the mesogens, that is, the CNT-aligned direction. This actuation is derived from the structure change in the composite film. The *trans*-to-*cis* photoisomerization of the azobenzene moieties results in a reduction in orientation order of the CLCP mesogens along the CNT-aligned direction, and subsequently in an anisotropic contraction in the surface layer.[5] The anisotropic contraction of the irradiated surface contributes to the anisotropic bending of the composite film. After exposure to visible light at 530 nm, the bent film completely recovered its initial morphology due to the reversible *cis*-to-*trans* isomerization of the azobenzene moieties. This photoinduced bending and unbending could be repeated over 100 cycles without obvious fatigue.

The CLCP/CNT composite film also showed an anisotropic mechanical property. The stress–strain curves of the composite film were measured both parallel and perpendicular to the CNT-aligned direction (Figure S6 in the Supporting Information). The results are summarized in Table 1. Two pure CLCP films with one oriented by conventional mechanical rubbing and the other without orientation were also studied and compared. The CLCP/CNT composite film exhibited a tensile strength of 31.2 MPa along the CNT-aligned direction, whereas the strength in the perpendicular

direction was 6.4 MPa. Clearly the composite film demonstrates better mechanical properties in the parallel direction than the perpendicular direction. On the other hand, the tensile strength of the composite film was higher than that of the oriented pure CLCP film in the parallel (15.7 MPa) and perpendicular (5.5 MPa) directions. Table 1 also demonstrates that the composite film along the CNT-aligned direction exhibits higher strength than the unoriented pure CLCP film (8.5 MPa). These results indicate that the highly aligned CNT sheet not only orients but also reinforces the CLCP.

Compared with conventional mechanical rubbing, the incorporation of aligned CNTs also provides the composite film with high electrical conductivity, for example 270 Scm$^{-1}$, along the CNT-aligned direction at room temperature (Figure S7 in the Supporting Information). The high conductivity can prevent the electrostatic accumulation observed in the other CLCPs, and greatly enhances the sensitivity and stability of the composite film in deformation. As previously mentioned, the reversible deformation was rapidly repeated for over 100 cycles without any fatigue. The electrical conductivity of the composite film may be further increased after optimization. The excellent electrical property also enables various other applications, such as deformable optoelectronic and electronic devices.

In summary, we have reported a novel method to fabricate a deformable CLCP composite film by using highly aligned CNTs to orient LC mesogens through a facile melting process. A rapid and reversible photoinduced deformation has been achieved by alternate irradiation by UV and visible light. Compared with CLCPs prepared with a conventional mechanical rubbing method, the CLCP/CNT composite film shows a much improved mechanical strength and high electrical conductivity. As a result of the combined properties, the CLCP/CNT composite film could be widely used as a new high-performance actuation material to drive actuators and microrobots.

***Table 1:*** Mechanical properties of the CLCP/CNT composite film measured parallel (‖) and perpendicular (⊥) to the CNT-aligned direction and of the oriented and unoriented pure CLCP films.[a]

|  | Tensile strength [MPa] | Elongation [%] |
|---|---|---|
| composite film (‖) | 31.2 | 2.7 |
| composite film (⊥) | 6.4 | 5.6 |
| oriented pure film (‖)[b] | 15.7 | 4.0 |
| oriented pure film (⊥)[b] | 5.5 | 6.2 |
| unoriented pure film | 8.5 | 3.6 |

[a] The oriented and unoriented pure CLCP films were prepared by photopolymerization of a mixture of **A11AB6**, **A9Bz9**, and **C9A** in an LC cell without the use of aligned CNT sheet, and the glass substrates were covered with and without the rubbed PI inside, respectively. [b] The oriented pure CLCP film was measured with the tensile direction parallel (‖) and perpendicular (⊥) to the rubbed direction of the PI.

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