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Unusual Reversible Photomechanical Actuation in Polymer/Nanotube Composites**

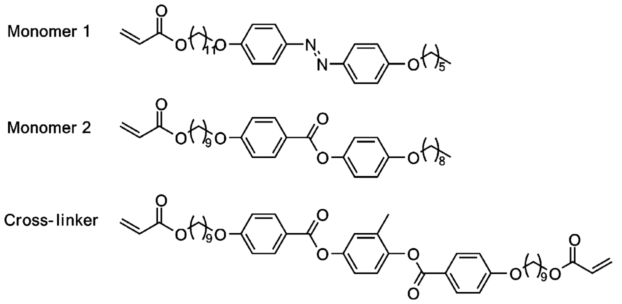
*Xuemei Sun, Wei Wang, Longbin Qiu, Wenhan Guo, Yanlei Yu, and Huisheng Peng**

Photodeformable polymer materials have recently attracted increasing attention owing to their promising applications in a wide variety of fields, such as artificial muscles, micromachines, and sensing devices.[1,2] Among these materials, liquid-crystalline polymers containing photoresponsive components, such as azobenzene, are probably one of the most studied systems.[2,3] Azobenzene-containing liquid-crystalline polymers (ALCPs) showed a reversible photodeformation that is typically induced by isomerization of azobenzene between *trans* and *cis* under alternate ultraviolet (UV) and visible-light irradiations.[4,5] Generally, ALCPs cannot deform reversibly under irradiation of the same light,[1–5] though it is necessary for many applications where the switches between two different lights are not available or allowed.

Carbon nanotubes have been widely studied for their extraordinary physical properties, such as good absorption in the visible/near-infrared region, high mechanical strength of 100 GPa, and electrical conductivity of 10^5 S cm^{-1}.[6] Furthermore, nanotubes were found to obviously affect the structure and property of incorporated organic molecules by noncovalent interactions.[7] Therefore, nanotubes had been successfully incorporated into thermoresponsive liquid crystalline polymers (LCPs) to produce a reversible contraction upon irradiation by the near-infrared light.[5,8] In this case, the nanotube mainly functioned as a nanoscale heat source, which absorbed the light and converted it into thermal energy with a thermal contraction. However, important as they are, the sensitivity and stability are relatively low in the case of an indirect photoactuation. Furthermore, the nanotubes are randomly dispersed in LCPs without post-treatment and could not be used to induce and control the orientation of LCPs.

Recently, nanotubes have been highly aligned into sheets or yarns at macroscopic scale, and the resulting bulk material retained the excellent property of individual nanotubes.[9,10] Herein, we further present a general but simple method to synthesize ALCPs by using the aligned carbon nanotubes to orient azobenzene mesogens. Specifically, nanotube arrays were first synthesized by a chemical vapor-deposition process. Aligned nanotubes in a strip format were then pulled out of the array according to our previous reports,[7,10] followed by the addition of precursor solutions for the desired ALCP. Finally, the ALCP/nanotube composite could be easily produced after in situ photopolymerization. The resulting nanocomposite showed an unusual reversible deformation, which had been realized by the use of UV light alone. This photomechanical actuation released an unexpected high stress of near 260 times of the strongest natural skeletal muscle.[11] Considering other remarkable properties, such as high mechanical strength of about 1 GPa and high electrical conductivity of 10^2–10^3 S cm^{-1}, we have demonstrated it for a remote electric switch.

The precursors include two monomers and a cross-linker with 1 mol % of a photoinitiator for the photopolymerization. The chemical structures of the two monomers and cross-linker are shown in Scheme 1. The nanotube strip was obtained from a nanotube array with a height of about 300 μm, and the distance of less than 20 nm among the nanotubes were investigated. The used nanotubes showed a multiwalled structure with a diameter of about 10 nm. Figure 1 a,b show typical SEM images of an ALCP/nanotube composite strip at low and high magnifications, respectively. Compared with a pure nanotube strip in Figure 1 c, the aligned structure of nanotubes had been well-maintained, which was further confirmed by transmission electron microscopy (Supporting Information, Figure S1). The ALCP molecules are mainly oriented on the nanotubes and among their voids.[7]



Scheme 1. Chemical structures of the two monomers and cross-linker.

The ALCP/nanotube composite strip reversibly and rapidly responds to the UV irradiation. Figure 2 exhibits the reversible bending of an ALCP/nanotube composite strip before and after UV irradiation. The UV source could be

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[*] X. Sun, L. Qiu, W. Guo, Prof. H. Peng
State Key Laboratory of Molecular Engineering of Polymers,
Department of Macromolecular Science
and Laboratory of Advanced Materials, Fudan University
Shanghai 200438 (China)
E-mail: penghs@fudan.edu.cn
W. Wang, Prof. Y. Yu
Department of Materials Science, Fudan University (China)

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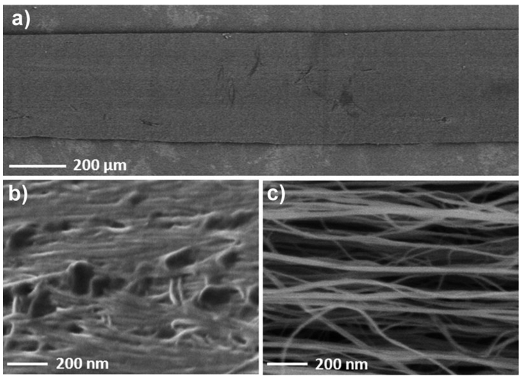

Figure 1. Scanning electron microscopy (SEM) images of pure nanotube and ALCP/nanotube composite strips. a) A composite strip at low magnification; b) the composite strip in (a) at high magnification; c) a pure nanotube strip at high magnification.

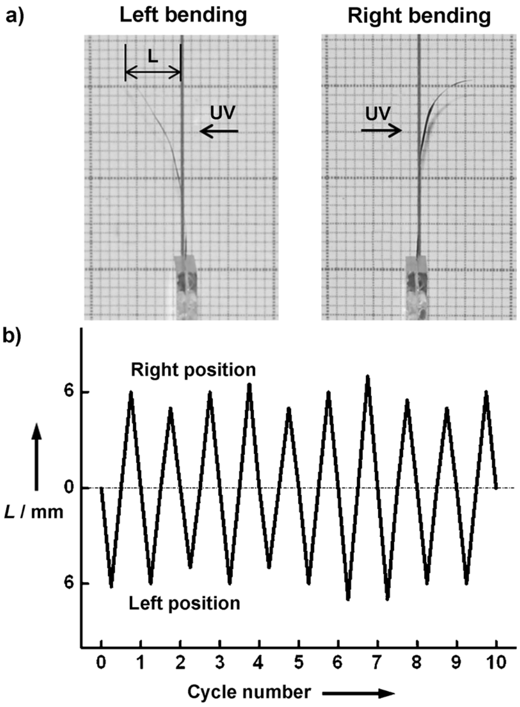

Figure 2. Reversible deformation of an ALCP/nanotube composite strip under the same UV light. a) Photographs of the tunable direction during the photomechanical deformation; b) the reversible deformation characterized by tracing the bent distance from the upright line.

located at the right or left in Figure 2a. Obviously, the composite strip was mainly bent away from the UV source. For instance, when the UV light was irradiated from the right, it bent to the left; when the UV light was at the left side, the composite strip switched back to the right. A bending cycle of left-right-left was completed in two seconds. The reversible deformation could be repeated over one hundred cycles, and the high sensitivity and stability was maintained; Figure 2b shows the initial ten cycles of the reversible deformation. Note that the composite strip showed a transmittance of almost 0 in the wavelength range of 300–800 nm (Supporting Information, Figure S2), so UV light could be effectively used. The deformation speed was very rapid (two seconds) under the irradiation typically used for UV light (50–100 mW cm^{-2}). A further increase of exposure time beyond two seconds did not obviously improve the deformation. No obvious dependence of the deformation on strip thickness and width was observed in the studied range.

It is well-known that UV light may induce a *trans–cis* isomerization of an azobenzene unit and even a phase transition from liquid-crystalline to isotropic.[12] Both size and alignment of azobenzene units are reduced with a volume change during the process. The volume change mainly occurs at the irradiated surface of an ALCP material, as more than 99 % incident photons are absorbed by the irradiated top surface (thickness of less than 1 µm below). An ALCP material can bend to or away from the UV source, depending on the oriented structure of azobenzene mesogens.[12] A homogeneous structure with azobenzene mesogens parallel to the irradiated surface favors the bending to UV source as the irradiated surface contracts. As a contrast, a homeotropic structure with azobenzene mesogens normal to the irradiated surface produces a bending away from the UV source as the irradiated surface expands. Therefore, the azobenzene mesogen in this composite should be perpendicular to the nanotube-aligned direction, which was confirmed by the polarized UV/Vis absorption spectroscopy. The composite strip shows a low absorption when the polarization degree of measurement light is either 0 or 90° relative to the aligned direction of nanotubes (Figure 3a). As a comparison, a pure ALCP film with a homogeneous structure exhibits much larger absorption for the polarization parallel to mesogen orientation than the normal polarization.[13]

Small-angle X-ray scattering (SAXS) was further used to confirm the oriented structure of azobenzene mesogens in the composite strip (Supporting Information, Figure S3).[13,14] When the azobenzene mesogens were aligned in a vertical

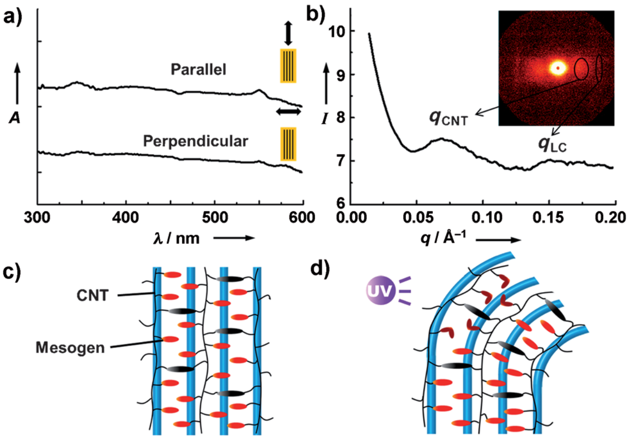

Figure 3. Mechanistic study on the ALCP/nanotube composite. a) Polarized UV/Vis spectra. Polarization is parallel and perpendicular to the nanotube-aligned direction. b) Small-angle X-ray scattering profile (inset: two-dimensional pattern) showing that the mesogens are oriented in a direction perpendicular to the nanotube-aligned direction. c) Illustration of an ALCP/nanotube composite; d) illustration of the deformation of the ALCP/nanotube composite under UV light.

direction, two sharp arc-shaped reflections appeared at the top and bottom in the SAXS pattern with $q_{\mathrm{LC}} \approx 0.15$ Å^{-1}. When the nanotubes were aligned in the vertical direction, two dense reflection areas were observed at the left and right in the SAXS pattern with a $q_{\mathrm{CNT}} \approx 0.07$ Å^{-1}. Figure 3b showed a typical SAXS profile of a composite strip with two peaks at about 0.07 Å^{-1} and 0.15 Å^{-1}, which corresponded to the reflections of nanotubes and mesogens, respectively. The two-dimensional pattern in Figure 3b further indicated that the mesogens were aligned in a direction perpendicular to the nanotube length (Figure 3c; Supporting Information, Figure S4). Figure 3d further shows the structure evolution of the composite strip during the deformation.

For a pure ALCP with homeotropic structure, a *cis–trans* transition of azobenzene unit is responsible for the recovery of its shape under a visible light. However, the reversible mechanism of ALCP/nanotube composite strip is different as the same UV light was applied to the opposite direction of composite strip without the use of visible light. Therefore, the deformation reversibility should be derived from the unique alignment of nanotubes and may be summarized as below. For the first UV irradiation on the right side, for instance, the azobenzene units at the right side in the strip showed a transition from *trans* to *cis*, while those at left remained almost unchanged in conformation as the strip thickness was much higher than 2 μm. For the second UV irradiation on the left, the azobenzene units at the left side showed a *trans–cis* transition, which produces a force to recover the strip shape. During the recovery process, the azobenzene units at the right side should be returned to *trans* in conformation. Otherwise, upon the UV irradiation at the right again, no deformations could be observed as azobenzene units could not change their conformations. Similarly, after the third UV irradiation, the azobenzene units at the left also recover from *cis* to *trans*. Therefore, the reversible deformation can be repeated for hundreds of cycles without obvious decay.

To further understand this unusual photodeformable reversibility under UV irradiation, the right and left sides of a composite strip were alternately irradiated for half an hour by UV light each time. It generally took less than a second to induce the photodeformation of composite strip upon irradiation by UV light. In other words, all available azobenzene units had been transformed from *trans* to *cis* after half an hour. The composite strip maintained a good reversibility in deformation after more than ten cycles. Therefore, reversible conformation changes of azobenzene units must occur during the repeated photodeformations. To understand the driving force of the reversible conformation in azobenzene units under UV light, Raman spectroscopy was used to study the interaction between ALCP molecules and nanotubes through a comparison of D and D* bands with pure nanotubes (Supporting Information, Figure S5). For the pure nanotubes, the D and D* bands appeared at about 1325 and 2645 cm^{-1}, respectively. Here D band corresponds to defects originated from the structural imperfections and associated with the disordered sp^3 hybridized carbon network, while D* band reflects a breathing vibration mode by which all atoms of a graphene sheet undergo an in-plane movement. The D and D* bands in the ALCP/nanotube composite shifted to 1328 and 2655 cm^{-1}, respectively. This result indicates a strong π–π interaction between ALCP molecules and nanotubes.[15] Therefore, the aligned nanotubes strongly interact with azobenzene units and induce their conformation to switch back when the nanotubes are recovered by the expansion from the opposite side under UV irradiation in structure and shape. As a comparison, no reversible deformation had been observed for either a pure ALCP or nanotube strip under the same conditions. The reversible isomerization between *trans* and *cis* has been further confirmed by FTIR spectroscopy. The same plane of a composite strip was traced during the deformation process (Supporting Information, Figure S6). The characteristic peak that is assigned to the asymmetric C–N stretching mode between 1250 and 1260 cm^{-1} is closely related to the different conformation of *trans* and *cis*.[16] It was located at 1255 and 1251 cm^{-1} in the conformation of *trans* and *cis*, respectively. Obviously, this peak shifted from 1255 to 1251 cm^{-1} after UV irradiation at the studied face and then switched back to 1255 cm^{-1} after another UV irradiation at the opposite face. In other words, a reversible isomerization between *trans* and *cis* occurred during the reversible deformation.

Deformable liquid-crystalline polymers have been widely explored for various applications, such as artificial muscles.[5] To this end, it is critically important to further improve their mechanical strength, which are typically tens of megapascals or lower. Carbon nanotubes have been recognized as the strongest material yet discovered and proposed to reinforce the other materials.[9,17] Thus, highly aligned nanotubes were introduced to improve the mechanical property of ALCP. Figure 4a compares stress–strain curves of an ALCP/nanotube composite strip and a pure ALCP strip under the same condition. The composite strip achieves a tensile strength of about 1 GPa, compared with about 16 MPa of the pure ALCP (Supporting Information, Figure S7) and more than ten times of the other high-strength liquid-crystalline polymers.[15] The excellent mechanical properties of composite strip were further investigated by tracing the produced stress according to the experimental setup in Figure 4b. A composite strip was fixed and tightly pulled with a load of 30 MPa. Upon irradiation by UV light, the stress gradually decreased. The released stress achieved a value of 26 MPa, which is much higher than 0.1 MPa of the strongest natural skeletal muscle and typically several megapascals of the other artificial muscles.[2,11] It should be noted that no stress had been released from a pure nanotube strip under the same

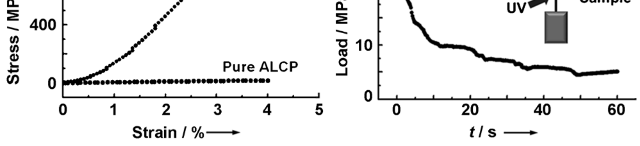

Figure 4. a) Stress–strain curves of pure ALCP and ALCP/nanotube composite strips. b) Mechanical stresses produced by a composite strip during the deformation under UV light.

condition, so the expansion of irradiated surface should be responsible for the stress change, while the aligned nanotubes further increase the released stress. On another hand, this result also further confirms that the photoactive mesogens are oriented in the direction normal to the strip surface.

The introduction of nanotubes had also provided an electrical conductivity for the ALCP composite strip, for example about 350 S cm^{-1} along the CNT length at room temperature (Supporting Information, Figure S8). Furthermore, the conductivity can be increased under UV irradiation and recovered to the original value after removal of UV irradiation. The conductivities of a composite strip were improved by 2 % under UV irradiation. The reversible change of conductivity may be realized in less than a second for over one hundred cycles with stable values. According to the three-dimensional hopping conduction mechanism of aligned nanotube strips (Supporting Information, Figure S9),[7,10] the resistance of a composite strip is mainly composed of two parts; that is, the resistance of individual nanotubes and contact resistance among nanotubes. As the resistance of individual nanotubes remained almost unchanged, the increased conductivity should be derived from the decreased contact resistance among nanotubes. In other words, the distance among nanotubes slightly decreased during the UV irradiation with the *trans–cis* transition, which pulled the neighboring nanotubes to be a little closer. However, it is difficult to directly detect the slightly decreased thickness of composite strip by optical microscopy or scanning electron microscopy.

This electrically conductive ALCP material is promising for many unique applications. We have demonstrated it as a remote electric switch with a high efficiency. Figure 5 a shows the experimental setup. The composite strip was bent to contact the left conductive wire to connect the left electric circuit upon UV irradiation from the right. It can be returned to the original upright state to disconnect the left electric circuit upon UV irradiation from the left, or further bent to contact the right conductive wire to connect the right electric circuit by slightly increasing the irradiation time. The above connections and disconnections could be repeated for more than a hundred cycles without obvious decay for the measured current in both electric circuits when a constant voltage was applied. Figure 5 b shows the stable operation of this photomechanical electric switch between connection and disconnection of the left electric circuit.

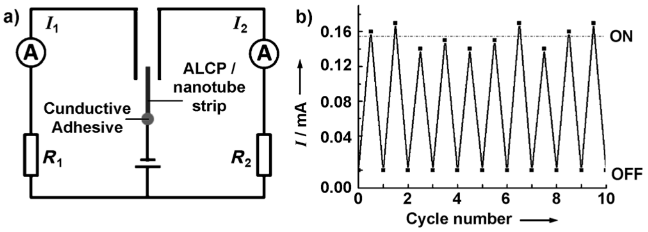

Figure 5. Application of the electrically conductive ALCP/nanotube composite strip for a remote electric switch. a) Illustration of the experimental setup. b) The reversible switch between connection and disconnection for the left electric circuit in (a).

In summary, an ALCP/nanotube composite strip shows rapid and reversible deformation under UV irradiation alone. The aligned nanotube structure also provides the composite strip with much higher mechanical strength than pure ALCPs and very high electrical conductivity, which is not available for other liquid-crystal materials. This work sheds further light on and promotes the design and practical applications of a new high-performance actuation material to drive actuators and microrobots.

Experimental Section

Aligned nanotube strips with lengths of up to meters were spun from a nanotube array, which was synthesized by a chemical vapor deposition.[10] The synthetic details of monomer 1, monomer 2, and cross-linker are described elsewhere.[10c] A mixture of monomer 1, monomer 2, and cross-linker (molar ratios of 1:1:3) with 1 mol % of a photoinitiator, bis(cyclopentadienyl)bis [2,6-difluoro-3-(1-pyrryl)-phenyl]titanium, dissolved in dimethyl formamide (concentration of 10 mg mL^{-1}) was dropped onto the nanotube strip in the dark, followed by evaporation of the solvent. The resulting composite strip was sandwiched between two glass slides and slowly cooled down (-0.1 °C min^{-1}) from a melting (90 °C) to polymerization temperature of 77 °C. The ALCP/nanotube composite could be then prepared by an in situ photopolymerization which was performed at 545 nm (2 mW cm^{-2}) by a 500W high-press mercury lamp for 2 h. The resulting composite strip typically showed lengths of 2–2.5 cm, widths of 200–500 μm, and thicknesses of 2–5 μm.

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