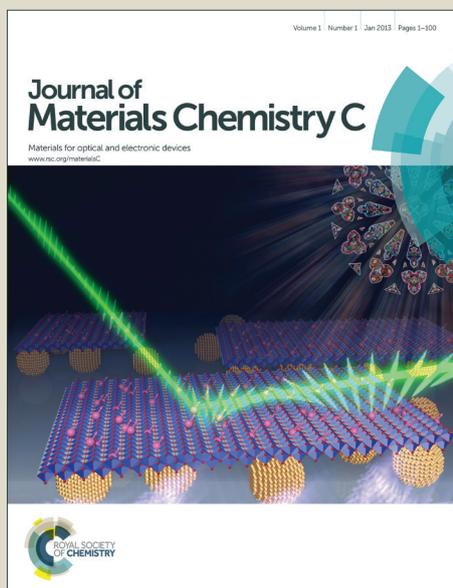


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Cite this: DOI: 10.1039/c0xx00000x

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Communication

Enhancement of Mechanical Stability in Hydrogen-bonded Photomobile Materials with Chemically Modified Single-walled Carbon Nanotubes

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Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

Uniaxially aligned azobenzene liquid-crystalline polymers crosslinked by hydrogen bonding can deform in response to actinic light. The polymers can be precisely shaped due to high processability of hydrogen-bonded polymers. The mechanical properties of the polymer fibers were improved by introducing single-walled carbon nanotubes as a filler material. Because of weak hydrogen bonding, starting materials can be recovered, reused and recycled, which is very useful in view of chemical resources utilization.

Crosslinked azobenzene liquid-crystalline polymers (CALCPs) are a class of materials that exhibit macroscopic deformation in response to actinic light.¹ These materials contain aligned mesogenic units as well as azobenzene with a crosslinked structure as shown in Figure 1. The polymers deform reversibly upon exposure to actinic light, based on the reversible trans-cis isomerization of azobenzene in the LC polymers, which results in photoinduced phase transition² or reduction in order parameters of mesogens, leading to a subsequent anisotropic deformation thanks to a strong coupling between the molecular order and the crosslinked polymer structures.^{3,4} CALCPs have been intensively investigated due to their large photomechanical effects, which have enabled the fabrication of unique devices such as rotors,⁵ cilia,⁶ lenses,⁷ inch worm⁸ and robotic arms.⁹ We previously reported the preparation of uniaxially aligned azobenzene LC polymer films crosslinked by hydrogen bonding.¹⁰ These films show photoinduced deformation just as in CALCPs and exhibit unique features such as high processability and recyclability originating from the hydrogen-bonded polymers; however, they are not mechanically stable enough for various applications. This work focuses on enhancing the mechanical stability of the hydrogen-bonded azobenzene LC polymers by introducing single-walled carbon nanotubes (SWNTs) as a filler.

SWNTs are well-known materials that can improve the mechanical properties of polymers.¹¹ It has been reported that crosslinked LC polymers containing SWNTs can deform in response to IR/NIR light because SWNTs effectively absorb IR/NIR light and convert it into thermal energy, which induces a LC-isotropic phase transition of the matrix LC polymers.¹² On the other hand, SWNTs tend to aggregate due to strong van der Waals forces among them, which limits an effective loading-level of SWNTs in polymer-composite applications.¹³ We enhance dispersive properties of SWNTs by chemical modification to reduce the van der Waals interactions among them.¹¹

IR and Raman spectra of the SWNTs were measured before and after modification. The chemically modified SWNTs (O-SWNTs) showed two IR absorption peaks at 1650 and 3500 cm^{-1} due to hydrogen bonding of carboxylic acid and an increase in the Raman peak at 1550 cm^{-1} due to the disorder mode (D-band)

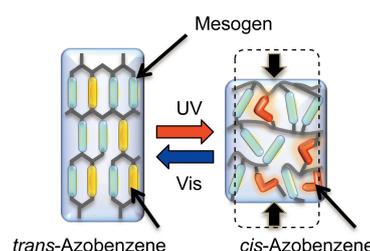


Fig. 1 Schematic illustration of anisotropic deformation of CALCP in response to actinic light.

of SWNTs compared to that for pristine SWNTs (P-SWNTs) (Figure S1).¹⁴ Furthermore, X-ray photoelectron spectroscopy (XPS) of O-SWNTs revealed a broad shoulder around 289 eV, which suggests that carboxylic acid is generated on the SWNT surfaces by chemical modification (Figure S2).¹⁵ The effect of chemical modification on the dispersion behavior of SWNTs was investigated using the azo polymer (PAAC) shown in Figure 2(A). PEAP is capable of recognizing hydrogen-bond donor molecules at the pyridyl ends and selected as

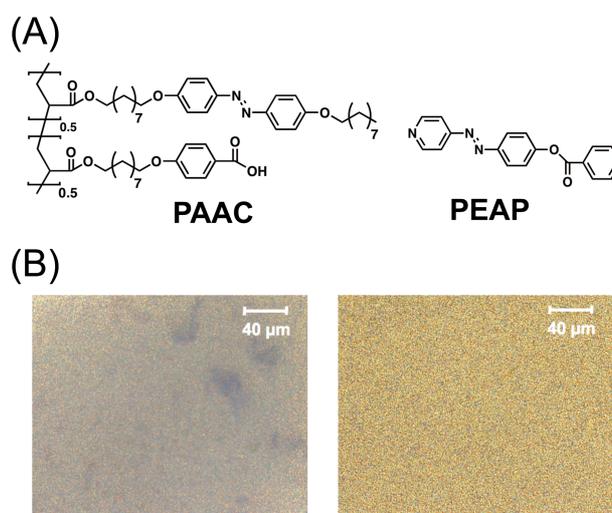


Fig. 2 (A) Chemical structures of the azobenzene LC copolymer (PAAC) and hydrogen-bonding acceptor (PEAP) used in this study; (B) optical micrographs of PAAC-PEAP mixtures (PAAC-P) containing 0.1 wt% P-SWNTs (left) and 0.1 wt% O-SWNTs (right).

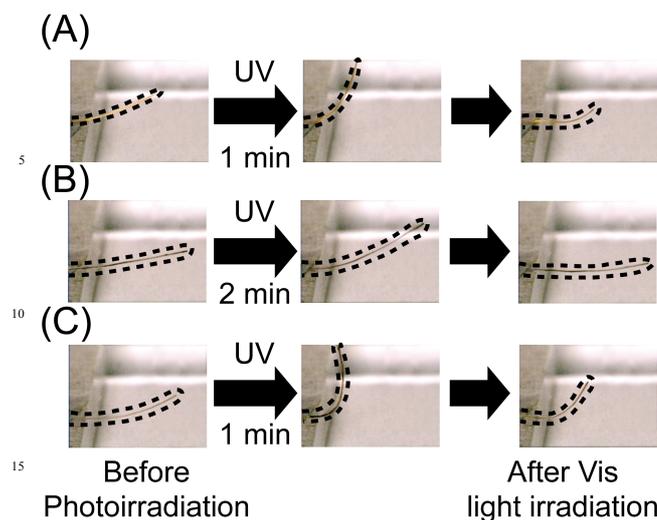


Fig. 3 Composite fibers exhibiting photoinduced reversible bending behavior: (A) PAAC-P; (B) P/OS-1; (C) P/OS-0.1. Fiber size: 14 mm (length) \times 0.1 mm (diameter). Irradiation with 366 nm light (25 mW cm^{-2}).

a hydrogen-bond acceptor. The mesomorphic properties of the copolymer (PAAC) and the PAAC-PEAP mixture (PAAC-P) were determined by differential scanning calorimetry (DSC) and the results are shown in Figure S3. It is clear that PAAC hydrogen-bonded with PEAP (PAAC-P) shows a more stabilized LC phase as evidenced by a wider temperature range for the LC phase.¹⁰ Low molecular weight surfactants were not used to aid dispersion of SWNTs because of their tendency to act as plasticizers, which may lower the mechanical properties of the polymer matrix.¹⁶ Figure 2(B) shows optical micrographs of the composites with 0.1 wt% P-SWNTs and 0.1 wt% O-SWNTs cast on a glass substrate. The P-SWNTs form dark domains due to aggregation, while the composite containing 0.1 wt% O-SWNTs (P/OS-0.1) shows a homogeneous dispersion of O-SWNTs in PAAC-P. The concentration of SWNTs is not sufficient enough to confirm their effect in the polymer matrix by IR spectroscopy; however, the micrographs suggest that the presence of carboxylic groups on the SWNT surfaces is likely to enhance the dispersive property of SWNTs in the composite. In addition, P/OS-0.1 exhibits similar photoreactivity to the copolymer without SWNTs (PAAC-P) when irradiated with 366 nm light (Figure S4).

Photoinduced deformation of the composites was confirmed for fibers. The fibers were prepared from composites with O-SWNT concentrations of 0, 0.1 and 1 wt%, respectively. The fibers were easily prepared by the method previously reported¹⁷ and exhibited high optical anisotropy along the fiber axis (Figure S5); while long fibers could not be drawn from the composite containing 1 wt% SWNTs (P/OS-1) because it became so stiff and brittle. Figure 3 shows the change in the macroscopic shape of the composite fibers under actinic light irradiation. When the composite fiber was exposed to UV light at 366 nm, the fiber bent toward an actinic light source along the fiber axis and the bent fibers reverted to the initial flat state upon irradiation with visible light at $>540 \text{ nm}$. Photoinduced bending of the composite fibers was reversibly induced by changing the wavelength of the actinic light, similar to CALCP fibers covalently crosslinked.¹⁸ However, the photoinduced bending of the composite fiber was slower than that of the copolymer fiber without SWNTs (PAAC-P), which suggests that the stiffness of the fiber affects the photoinduced deformation behavior. The results of thermo mechanical analysis are shown in Figures 4 and S6. Tensile testing was performed to evaluate the effect of O-SWNT on the mechanical properties of the hydrogen-bonded copolymer fiber.

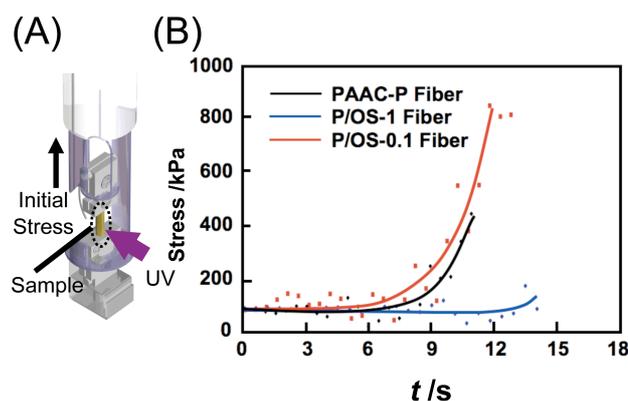


Fig. 4 (A) Schematic illustration of the mechanical measurement setup. (B) Mechanical force generated in the fibers by photoirradiation. Initial stress: 75 kPa, light intensity: 25 mW cm^{-2} .

Compared to the fiber without SWNTs (PAAC-P), the P/OS-0.1 fiber showed an enhancement in Young's modulus (Figure S6): P/OS-0.1 exhibited a tensile strength of 9.5 MPa, which is 1.6 times larger than PAAC-P. Improvement in the tensile strength and Young's modulus of the composite could result from the strong interactions between the polymer matrix and O-SWNTs. The strain-at-break of the samples, an indicator of the material flexibility, was lower on addition of a high concentration of SWNTs, which shows that the inclusion of SWNTs at a high concentration makes the polymer more brittle. The stress generated in the fibers by UV light irradiation was also measured, although it was difficult to measure the generated force in a single fiber because of the measurement limit of the contraction mode. Therefore, three pieces of fibers were bundled together side by side and both the top and bottom of the fibers were adhered together using epoxy glue. The bundled fibers were then fixed by clamping both ends of the fibers and heated to $90 \text{ }^\circ\text{C}$, which is higher than the glass transition temperature (T_g). Initial stress was loaded to the bundled fibers to maintain a constant length. Upon irradiation with UV light, the stress increased and reached to 850 kPa when the fiber was broken, which was twice as large as that of the copolymer fiber without SWNTs (Figure 4(B)). Meanwhile, P/OS-1 showed the lowest value, indicative of difficulty in preparation of P/OS-1 fibers.

It is worth mentioning that PAAC and PEAP can be recovered by solvent extraction because of the weak hydrogen bonding, reused and recycled, which is very useful in view of chemical resources utilization.

In summary, azobenzene LC polymer fibers, crosslinked by hydrogen bonding, containing chemically modified SWNTs were prepared, which exhibit reversible bending behavior upon exposure to actinic light. The tensile stress and mechanical force generated by irradiation with UV light much increased by incorporation of a small amount of SWNTs, which is quite advantageous in various applications of these materials.

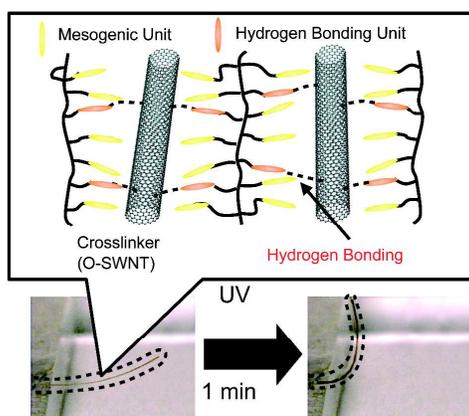
Notes and references

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¹¹⁰ Electronic Supplementary Information (ESI) available: Experimental setup, IR, Raman, XPS spectra of SWNTs, DSC thermograms of the copolymer, UV-vis absorption spectra of the samples, polarizing optical

microscopy images of the sample and stress-strain curves of the composite fibers. See DOI: 10.1039/c000000x/

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A graphical and textual abstract for the contents pages



Hydrogen-bonded photomobile liquid-crystalline polymer fibers with chemically modified single-walled carbon nanotubes were prepared and their photomobile properties were investigated.