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Photoinduced Deformation of Polymer Fibers with Anthracene Side Groups

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We prepared photomobile polymer fibers with anthracene side groups and explored their photomechanical properties. Upon irradiation with UV light, the fiber bent toward an actinic light source. The degree of bending and photoreaction were strongly affected by temperature. The fiber can dose the deformation without macroscopic change at room temperature and release them on heating.

Photomechanical effects that directly converts light energy into mechanical work are of great interest.[1] This effect can apply to light-driven mechanical devices with noncontact supplying and rapid manipulating.[2] When a polymer system is used as a matrix for the photoreaction, we can form them into precise shape and size with high flexibility. In the past decades, various types of polymers exhibiting photomechanical effect have been reported. These polymers usually contain photochromic compounds, which change their shape reversibly in a single molecule. Among them, photodimerization has attracted much attention for photomechanical effect because the dimerization induces migration of the photoactive moiety and a large deformation is expected. In addition, the reacted compounds are thermally stable, allow stepwise measurement of the photoreaction, and are easy to trace by spectroscopy. Photodimerizable polymers were used for shape memory polymers.[3] Zhao et al. first reported photoinduced bending of a supramolecular film driven by photodimerization of coumarin moieties.[4]

Anthracene is a conventional photoreactive compound that undergoes [4 + 4] intermolecular dimerization upon irradiation with UV light.[5] Bardeen et al. have demonstrated photomechanical effect of anthracene in the crystal forms.[6] However, the effect of photodimerization of anthracene on the polymer system has not been explored so far. In this work, we prepared polymer fibers from a simple polymer as shown in Figure 1 and explored their photoresponsive behavior.

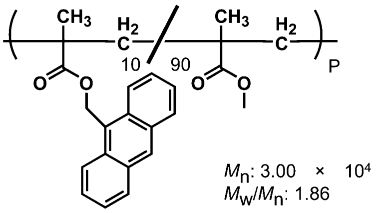

Figure 1. Chemical structure, molecular weight, and polydispersity of compounds used in this study.

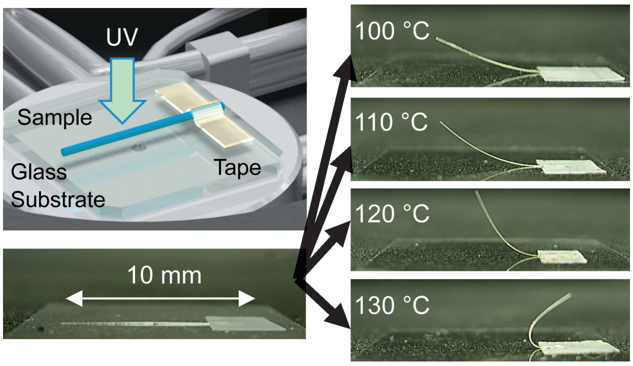

Figure 2. Macroscopic deformation of the fiber: schematic illustration of experimental setup and photographs of the fiber exhibiting bending behavior on irradiation with UV (365 nm, 150 mW cm^{-2}) light for 30 min at different temperature. Diameter: 200 µm, length: 10 mm.

Based on differential scanning calorimetry, the glass transition temperature of the anthracene polymer was determined to be approximately 120 °C, and no extra properties were detected below 200 °C. The fiber was fabricated with the method that was previously reported.[7] Polarizing optical micrographs indicate that the fiber showed optical anisotropy along its axis and that the diameter of it is approximately 200 µm (See Supporting Information, Figure S1[11]). The macroscopic photoresponsive behavior of the fiber was observed by placing it on a glass substrate fixed with tape at one end (Figure 2). Irradiation with UV light (150 mW cm^{-2}) from the top of the fiber caused it to bend toward the actinic light source. In addition, the bending angle of the fiber increased with an increase in temperature under photoirradiation. Especially, the fiber bent over 90° when it was heated above the glass transition temperature, 130 °C.

The bent fiber was undissolved in chloroform and maintained its shape in the dark for over one month, indicating that the photoreaction formed crosslinking among the backbones of the polymer. It has been reported that with increasing temperature the mobility of the polymer segments also increases with a great enhancement of photomechanical effects.[8] Since the effect of temperature on photodimerization is not clear, we investigated the effect of the photochemical reaction on fiber deformation by absorption spectroscopy (Figure 3a). Thin films on a quartz substrate were prepared (<1 µm), as the fiber is difficult to directly measure due to its shape. Changes in absorbance of the polymer due to photoirradiation were found: the anthracene peak around 350–400 nm decreased slowly and did not recover. We define the degree of photodimerization (ΔP) as

$$\Delta P = \frac{A_0 - A_{\mathrm{UV}}}{A_0} \times 100 \qquad (1)$$

where A_0 and A_{UV} indicate the absorbances at 367 nm before and after photoirradiation, respectively. Figure 3b shows the change in ΔP of the film as a function of supplied energy under different

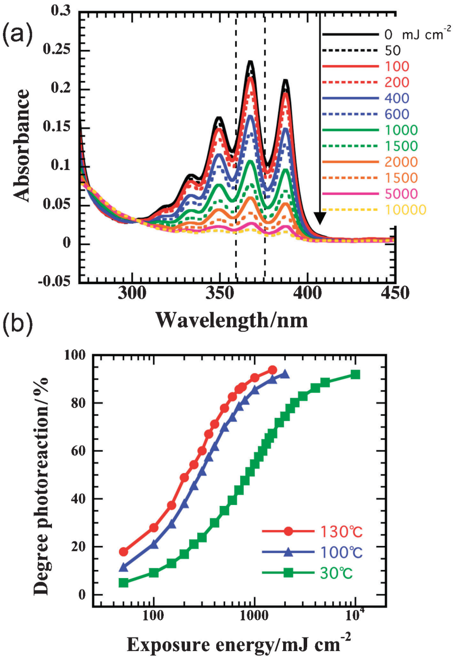

Figure 3. Change in absorbance upon irradiation with 365-nm light at room temperature (a) and degree of the photoreaction (ΔP) calculated by the change in absorbance at 367 nm under different temperatures.

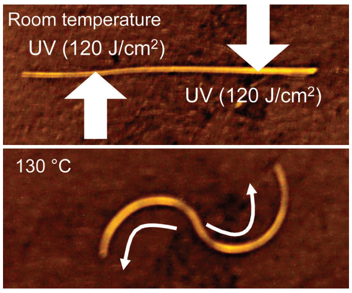

Figure 4. Photographs of the programmed fiber at room temperature and at above glass transition temperature (130 °C). White arrows in the top of the photograph indicate the direction of light source.

temperatures. The photodimerization occurred more effectively when the temperature increased, suggesting that the enhancement of the mobility increased photoreactivity as well as macroscopic deformation.

In addition, the photoreaction clearly reached 100% even in a glassy phase without a photostationary state though the bending of the fiber was small. It can be presumed that the movement of the polymer backbones, that defines the fiber shape, is suppressed at room temperature even if the photoreaction proceeds to a high ratio. To confirm this hypothesis, we tried to dose the photoinduced deformation as distortion of polymer backbone. Both ends of the fiber were fixed and irradiated with UV light from the arrow direction as shown in Figure 4. The fiber showed little bending at this time. Then the fiber was heated above the glass transition temperature to enhance the mobility of the polymer backbones. It bent and deformed into a winding shape (Figure 4 bottom). This result strongly indicates that the fiber memorizes the deformation by distortion at low temperature and that we can program a precise shape into the polymer in advance by photoirradiation.

As the polarization of light can be controlled with a wave plate or polarizer, photoselectivity of light-driven compounds may enhance the motion of photomobile materials. Recently, unique motion in response to polarization direction of actinic light has been reported in liquid-crystalline (LC) azobenzene elastomers.[9] We have revealed that anthracene derivatives in the LC polymer showed axis-selective photoreaction, which affects the whole alignment of LC systems. Anthracene has a preferable absorptive direction of the electric field vector of the incident beam, with anisotropic photodimerization.[10] Taken together, the deformation behavior of the fiber might be improved through incorporation into LC elastomers that we are currently investigating.

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