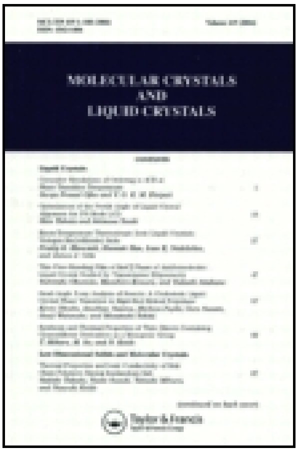

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Preparation and Macroscopic Deformation of Liquid-Crystalline Polymer Fibers Crosslinked with Anthracene Side Chains

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Anthraccene liquid-crystalline (LC) polymer fibers were synthesized and their photomechanical properties were explored. The polymer fiber bent toward a light source upon exposure to UV light due to photodimerization of anthracene moieties. They contracted with decrease in optical anisotropy along their fiber axis when they were heated above their LC-isotropic phase transition temperature.

Keywords anthracene; liquid-crystalline polymers; fiber; photodeformation; photodimerization

Introduction

Light-driven actuation (LDA) generates mechanical work from light energy through photomobilie materials by controlling their motions and energy supplying. It makes mechanical devices much simple and lightweight for their remote-controlling characteristics. Therefore, LDA has been intensively investigated for past decades and such mechanical devices as lens [1], motor [2] and airplane [3] have been proposed. Recently, Bardeen *et al.* proposed novel LDA system using anthracene as a photoactive moiety [4]. Anthracene is a conventional photoreactive compound that can undergo [4+4] intermolecular dimerization upon irradiation with UV light. The change in structure in anthracene is sufficiently large to demonstrate macroscopic movement in a crystal state. In the previous work, we apply this mechanism for polymer LDA to introduce high processability and flexibility. When the polymer was formed into a fiber shape and illuminated with a UV lamp, it bent toward the actinic light source due to [4+4] photodimerization of anthracene moiety and subsequent deformation of polymer backbone [5]. Lastly, we synthesized anthracene polymers containing flexible side chains and reported that the photoreactivity at room temperature was enhanced. The deformation was investigated using a thermomechanical analyzer, which revealed that the polymers undergo fast expansion and slow contraction in response to UV light, due to the thermal expansion and photodimerization of the anthracene moiety, respectively though

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the degree of deformation is low. It is well known that crossliked liquid-crystalline polymers (CLCPs) with uniform alignment show large deformation when they are heated across their phase transition temperature because the spatial conformation of a polymer backbone is coupled with the liquid-crystalline structure. CLCP can utilize various photoreaction to enhance their actuation properties. They deform upon exposure to actinic light by incorporating photoactive moieties that can change mesomorphic property of the CLCPs [6, 7]. Photocrosslinkable moiety such as benzophenone [8] and phenyldiacrylate ester [9] has been used to prepare the polymers. However, anthracene has not been explored so far neither photoactive compound nor photocrosslinker in this system. In this work, we apply CLCPs for anthracene polymer to enhance the photomechanical effect. We synthesized anthracene liquid-crystalline polymers and explored their photo- and thermoresponsive behavior.

Experimental

Materials

Figure 1 shows the chemical structure of the copolymers used in this study. It has been reported that the photoactive unit in **P2** showed a LC phase at homopolymer [10]. The Copolymers were synthesized by radical polymerization in tetrahydrofuran (THF) solution using azobisisobutyronitrile (AIBN) as an initiator. The number-average molecular weight (Mn), polydisperse index (PDI) were determined for the anthracene polymer using gel permeation chromatography (GPC) with polystyrene standards for calibration. The copolymerization ratio was confirmed by 500 MHz ^{1}H nuclear magnetic resonance spectroscopy (NMR; Bruker DRX500). The mesomorphic properties of the polymer were analyzed using differential scanning calorimetry (DSC; Seiko I&E SSC-5200 and DSC220C) at heating and cooling rates of 10°C/min and a polarizing optical microscope (POM; Olympus BX51P) equipped with a hot stage (Linkam TH-600PM). The composition, Mn, PDI and thermal properties of the relevant copolymers are also described in Figure 1.

Preparation and Characterization of the Polymer Fibers and Films

The polymer fiber was prepared according to previously reported method [11]. A small amount of polymer was heated above T_g (>150°C) on a glass substrate placed on a hot

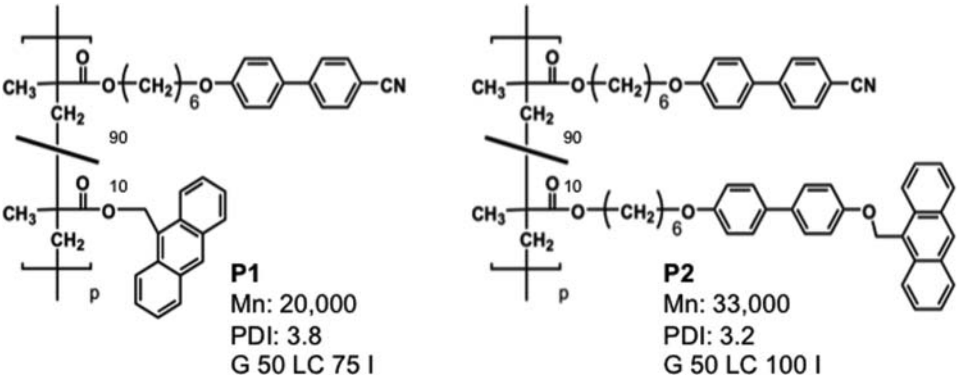

Figure 1. Chemical structure, Mn, PDI, and mesomorphic properties of polymers used in this study. Key: G, glassy, LC, liquid-crystal phase, I isotropic.

stage. The fibers were drawn by dipping the tip of a pick and pulling it. The optical anisotropy of the fiber was observed with a POM. An absorption spectrum was measured with a UV-vis spectrometer (Hitachi U-3010) using a thin spin-coated polymer film from a THF solution. Photoinduced change in macroscopic shape of the fibers was observed upon irradiation with UV light at 365 nm from a UV-LED irradiator (Keyence UV-400 with UV-50H and Dynatech LS500H) and recorded with a digital camera. The degree of contraction of the fibers was measured with a thermomechanical analyzer (TMA: Seiko SS6100) using the static stretch mode under photoirradiation. The fiber was fixed at both ends on the apparatus with instant glue and loaded at 3 mN as initial stress. We used the

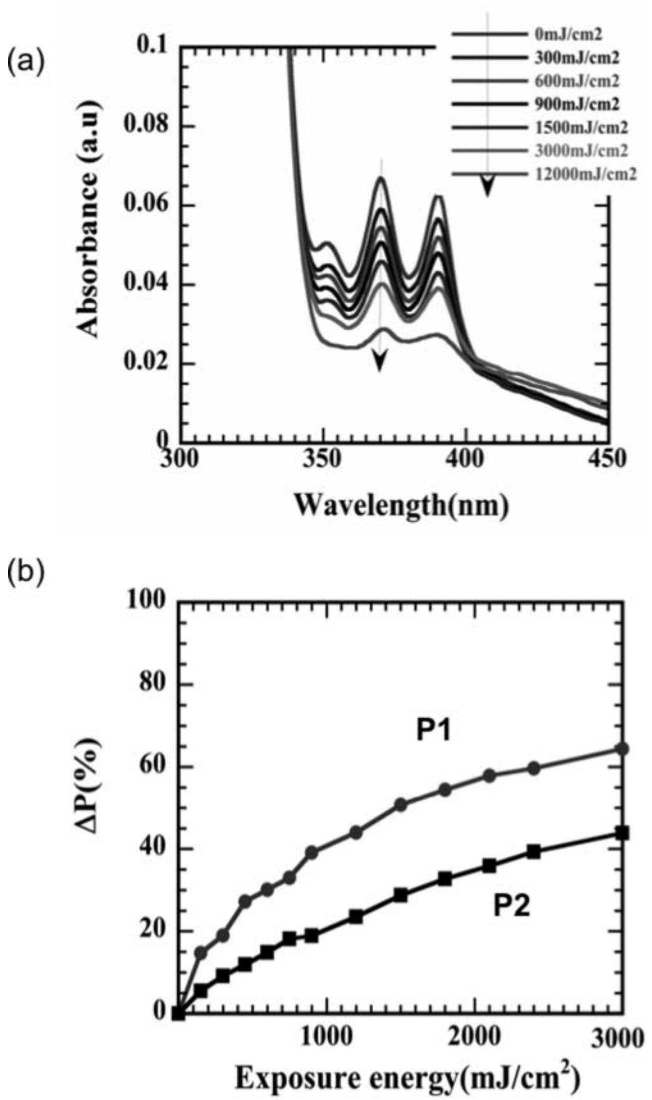

Figure 2. Change in absorption spectrum of P1 film upon exposure to UV light (a) and change in degree of photoreaction (ΔP) of the polymers as a function of exposure energy (b).

fibers with high anisotropy with 200-μm diameters for TMA that were evaluated with a POM.

Results and Discussion

Photomechanical Effect

Figure 2(a) shows change in absorption spectrum of the **P1** film under photoirradiation. Absorbance around 360 nm is decreased upon exposure to UV light due to [4+4] photodimerization of anthracene moieties. The degree of photodimerization (ΔP) is defined as following equation

$$\Delta P = \frac{A_0 - A_{UV}}{A_0} \times 100(\%), \tag{1}$$

where A_0 and A_{UV} indicate the absorbance at 367 nm before and after photoirradiation, respectively. The change in ΔP of the polymers at room temperature as a function of supplied energy is plotted in Figure 2(b). It was found that the photoreactivity of **P2** film is lower than that of **P1** film.

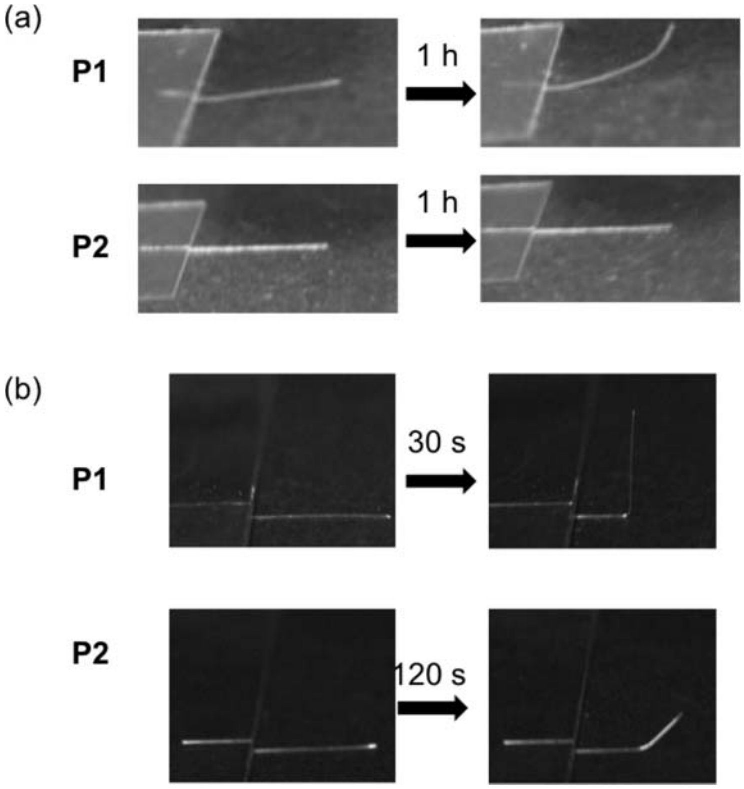

Figure 3. Photographs of the polymer fibers irradiated with UV light at 800 mW/cm^2 (a) and 2.2 W/cm^2 (b).

Photoinduced change in macroscopic shape of the polymer fibers at room temperature was observed under an experimental setup as follows: the fiber was fixed on a glass substrate and irradiated with a UV-LED from above. Upon exposure to UV light at 800 mW/cm^2, the **P1** fiber bent toward the actinic light source while **P2** showed no response (Figure 3(a)). On the other hand, both polymer fibers bent toward the actinic light source when they were irradiated at 2.2 W/cm^2. The deformation of **P1** fiber greatly enhanced with the bending angle reached nearly 90° for 30-s irradiation. However, the bending angle of the **P2** fiber could not reached 90° even it was irradiated with UV light for 120 s, 4r times longer than that of **P1**, resulting in **P2** fiber showed slow and small bending in comparison to **P1** fiber (Figure 3(b)).

Figure 4 shows change in length along the fiber axis under themomechanical analysis, For evaluating the photomechanical properties, the degree of contraction upon exposure to

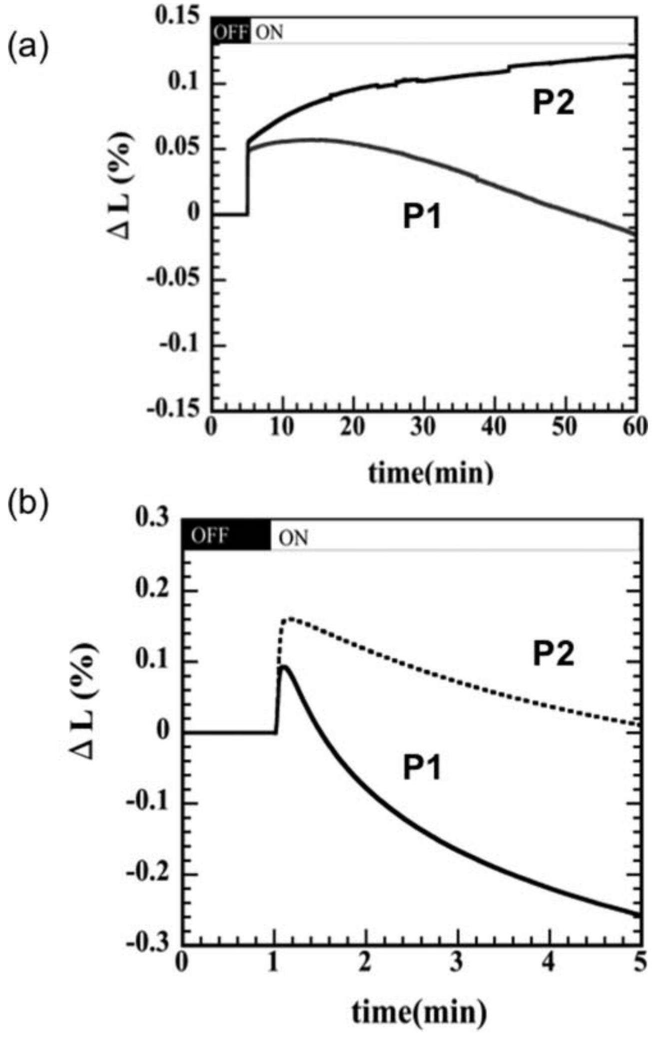

Figure 4. Degree of deformation along the fiber axis (ΔL) of the polymer fibers upon exposure to UV light at 800 mW/cm^2 (a) and 2.2 W/cm^2 (b).

UV light was defined as follows,

$$\Delta L = \frac{L_{UV} - L_0}{L_0} \times 100(\%). \tag{2}$$

where L_0 and L_{UV} represent the lengths of the film before and after photoirradiation, respectively. Upon exposure to UV light at 800 mW/cm^2, **P1** showed fast expansion and subsequent slow contraction resulting from thermal expansion and photodimerization respectively, while **P2** only showed fast expansion (Figure 4(a)). On the other hand, both fibers showed large contraction when they were irradiated with UV light at 2.2 W/cm^2 (Figure 4(b)). The change in value of ΔL was larger than previous report, indicating that LC phase can enhance the photomechanical effect. In addition, the effect of light intensity on ΔL was agreed with the change in macroscopic shape. These results suggests that the mobility of anthracene side chain plays an important role on photoreactivity and subsequent deformation of the polymers.

Thermal Effect

We observed change in optical anisotropy of **P1** fiber on heating. Figure 5 represents polarizing optical micrographs of a **P1** fiber under the experiment. The fiber shows a

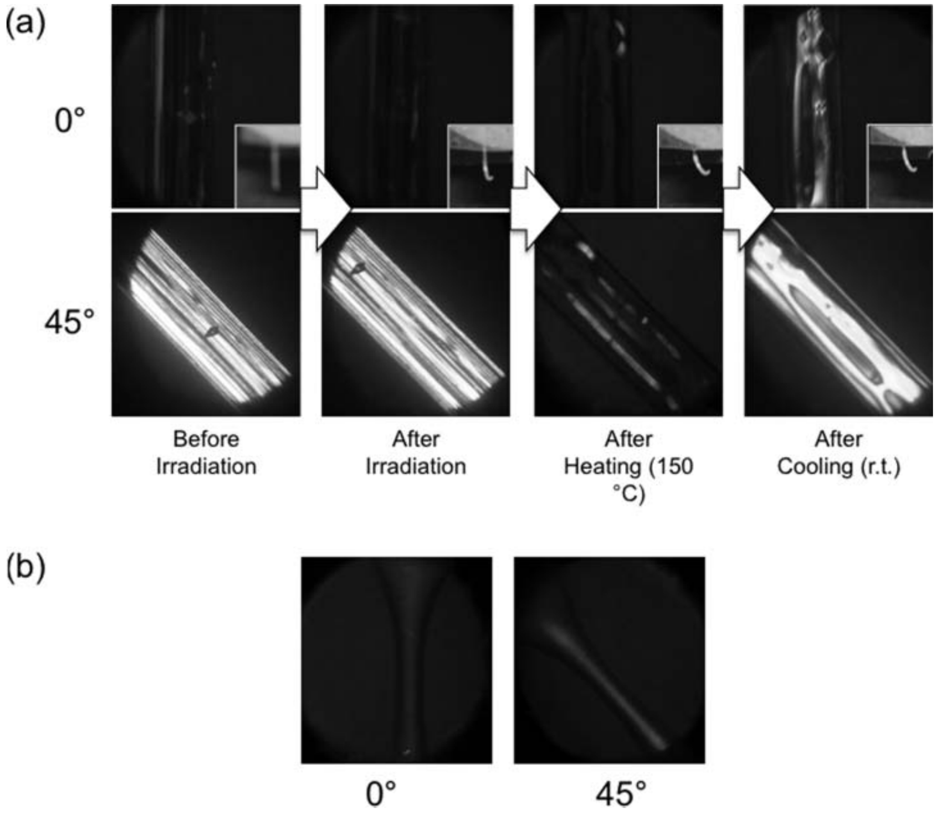

Figure 5. Polarizing optical micrographs (POM) of the **P1** fiber exhibiting a change in optical anisotropy on heating (a) and POM of the **P1** fiber after the same experiment of (a) without photoirradiation. The inset in (a) displays a macroscopic shape of the fiber under the same condition.

uniform change in birefringence upon rotating the sample to 45° position with respect to the polarization direction of a probe beam. The inset of the POM image displays the macroscopic shape of the fiber under relevant scheme. The fiber kept the anisotropy after photoirradiation. In addition, the photoreacted, bent polymer fibers became insoluble to organic solvent. These results indicate that the fiber shows high anisotropy along the fiber axis even after photocrosslinking. When the fiber was heated above 150°C, LC-isotropic phase transition temperature, the fiber contracted along the fiber axis with decrease in birefringence. The optical anisotropy partly reverted when the fiber was cool down to their LC temperature though no reversion of macroscopic shape was observed. On the hand, when we used the fiber without photoirradiation, it could not fix their optical anisotropy under the same experiment (Figure 5(b)). It can be presumed that the polymer fiber fixed their uniaxial alignment by crosslinking structure of anthracene moieties. However, unlike to other photoactive CLCPs, photodeformation of anthracene polymers did not couple with change in molecular order of liquid-crystalline polymers.

Conclusions

LC polymers containing anthracene side chains were synthesized. The fibers bent toward UV light source on irradiating with UV light due to photodimerization of anthracene moieties. They contracted with decrease in optical anisotropy along their fiber axis when they were heated above their LC-isotropic phase transition temperature.

Acknowledgements

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