Thermal Response Behavior of a Photo-Crosslinked Liquid Crystalline Polymer and a Side Chain Liquid Crystalline Polymer

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Liquid crystalline polymers (LCPs) have attracted much attention because of their macroscopic deformation to external stimuli such as heat or light-irradiation. Among them, thermal responsive polymers, in which their macroscopic structures are controlled by heat treatment, are one of the most attractive materials. Although the thermal responsive materials by thermal phase transition were developed in wide for the application to the electronic devices and sensors, few examples have been applied to practical uses because of their high transition temperatures. In this paper, the development of LCPs with low deformation temperatures was investigated aiming for the application to functional fibers responding to body temperature. The phase transition temperature was found to depend on the content of crosslinking unit, and the film deformation was controlled by the one-side photo-irradiation to change the degree of crosslinking between two sides.

Keywords: Actuator, Liquid crystalline polymer, Phase transition, Photo-crosslinking, Thermal responsibility

1. Introduction

Recently, stimuli-responsive materials in which reversible expansion and contraction or bending and tightening induced by external stimuli, such as heat, light, electricity, and magnetism have been intense interest because of their potential for their uses in artificial muscles, actuators, and chemical sensors [1-4]. In 1997, P. G. de Gennes et al. demonstrated the flexible molding of liquid crystalline elastomers (LCEs) by temperature controlling, light-irradiation, and applying electricity and magnetism for application to artificial muscles [5]. In addition, we previously reported that the photo-induced volume control using polymers including an azobenzene unit, in which phase transition between nematic and isotropic phases induced by UV-irradiation, was achieved [6].

Regarding to the molecular design for the fabrication of stimuli-responsive materials, there are two key factors. One is the cross-link formation between polymer chains. It is expected that the cross-linking realizes the preparation of

monodomain alignment, which achieves a free-standing actuator. In the past, based on the photo-induced cross-linking, reversible deformation of complex 3D structures of materials was performed [7,8]. The other is the adjustment of the length of side chains of polymers, which affects the phase transition temperature [9]. For example, it was revealed that relatively low phase transition temperature at less than 40 °C was displayed using cyanobiphenyl units having short alkyl chains such as C₆ and C₈ chains [10].

Although the application of the thermal or light responsive materials for fibers and films aiming to electronic devices and sensors was reported, to the best of our knowledge, there is no example of the fabrication of daily necessities such as clothes. In this report, we purposed the development of functional fibers using LCEs, which display thermal responsiveness at around human body temperature. We expected that the air permeability of the clothes formed by such fibers would be controlled by the deformation of the thermal responsible LCEs. That

is, when our body temperatures increase because of exercises or sickness, clothes are ventilated due to the contraction of LCEs in the fibers. To this end, we designed liquid crystal polymers (LCPs), **CBPA** and **CAPE**. Figures 1a and 1b show chemical reactions in the syntheses of the polymers. The former is prepared by copolymerization of methacrylic acid alkoxybiphenyl (**C3M-CB** and **C6M-CB**), bis(methacrylic acid hexyloxy)biphenyl (**BMHBP**), and butyl methacrylate (**BM**), and the latter is copolymerized by bis(hydroxylhexyloxy)-biphenyl (**BHHBP**), phenylsuccinic acid (**PSA**), and hydroxyhexyloxy coumaric acid (**6HCA**). For **CBPA**, **BMHBP** is included as a cross-linking unit. In addition, C₃ and C₆ alkyl chains in **C3M-CB** and

C6M-CB are adopted as side chains for the lowering the phase transition temperature. Moreover, **MB** is introduced because of the possibility for improvement of flexibility and lowering phase transition temperature of polymers. In the case of **CAPE**, **PSA** is introduced for the construction of a helical structure in the polymer chains. Furthermore, **6HCA** having a coumarate unit is adopted as a reactive site by photo-irradiation after the molding because it would bind to each other in head-to-head and head-to-tail manners to form a cyclobutane ring [11] as shown in Fig. 1c. Herein, we evaluated the thermophysical properties with different molar ration of monomers.

Fig. 1. Chemical reactions in syntheses of **CBPA** (a) and **CAPE** (b), and photocycloaddition reaction of coumaric acid in head-to-head and head-to-tail manners (c).

2. Experimental

2.1. Apparatus

For differential thermal analysis (DTA), a thermogravimetry/differential thermal analyzer (DTA-60, Shimadzu Corporation) was used at heating rate of 1 °C/min. For differential scanning calorimetry (DSC), a differential scanning calorimeter (Thermo plus EVO2, Rigaku Corporation) was used at a heating rate of 5 °C/min using 5 mg of samples. Polarizing microscopy (PO) observations were performed by using a microscope (CX31PF, OLYMPUS). UV-vis absorption spectra were recorded on a spectrometer (V-550, JASCO) in the range of wavelength at 200–800 nm. ¹H-NMR (400MHz) spectra were measured on a Bruker UlreaShield Plus 400 spectrometer. The spectra were referenced to a proton signal of tetramethylsilane (0 ppm) in DMSO-*d*₆ and CDCl₃. The heating of LCPs was performed by a hot stage (FP82HT, METTLER) with a thermos system controller (FP90, METTLER) to set temperatures above 5 °C from the phase transition temperature in each sample.

2.2. Reagents

All commercially available reagents were used as received from TCI or Wako Pure Chemical Industries, Ltd. *N,N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried over molecular sieves 4A before use. Other solvents were used without purifications.

2.3. Preparation of films

All sample films were prepared by compression after samples were sandwiched between polypropylene films with heating at 100 °C for **CBPA** and 70 °C for **CAPE**.

2.4. Photo-irradiation to films

To obtain cross-linked materials, films were irradiated by UV light using a Xenon lamp with a filter cutting off wavelength less than 320 nm. The one side of films were exposed to the UV light.

2.5. Syntheses of polymers

2.5.1. General procedure of synthesis of **CBPA**

C6M-CB (668 mg, 2.84 mmol), **C3M-CB** (590 mg, 2.84 mmol), and AIBN (14.7 mg, 89.0 mmol) were dissolved in THF (5.0 mL). After stirring at 50 °C for 1.5 h, 55 °C for 0.5 h, 60 °C for 0.5 h, 70 °C for 3 h, 75 °C for 1 h, 90 °C for 0.5 h, the solution was added to methanol dropwise for reprecipitation. After the filtration, product was

dried under vacuum for overnight. **CBPA-2** (1.09 g) was obtained as a white solid.

2.5.2. General procedure of synthesis of **CAPE**

BHHBP (4.51 g, 11.7 mmol), **6HCA** (1.29 g, 3.89 mmol), **PSA** (2.27 g, 11.7 mmol), Zn(AcO)₂ (23.4 mg, 128 μmol), and Sb₂O₃ (23.4 mg, 80.3 μmol) were placed to a 100 mL round-flask. After the mixture was stirred and heated at 180 °C for 1h under vacuum, reaction temperature increased to 200 °C at the ratio of 20 °C/h. After stirring at 200 °C for 4.5 h, the mixture was cooled to room temperature under vacuum. The crude product was dissolved in THF and the solution was added to water dropwise for reprecipitation. After the filtration, **CAPE-3** (7.33 g) was gave as a white solid.

3. Results and discussion

3.1. Syntheses of polymers

CBPA [12] and **CAPE** [13,14] were synthesized by radical polymerization using AIBN as a radical initiator and by polycondensation under solvent-free condition, respectively, through modification of the previously reported methods. To investigate the effect of molar ratio of monomers for the thermal responsibility of polymers, we synthesized series of **CBPA** and **CAPE** with different monomer

Table 1. Molar ratio of monomers for series of **CBPA**.

Polymer	C3M-CB	C6M-CB	BMHBP	BM
CBPA-1	—	1	—	—
CBPA-2	1	1	—	—
CBPA-3	1	1	2	—
CBPA-4	5	5	1	—
CBPA-5	25	25	1	—
CBPA-6	100	100	1	—
CBPA-7	150	150	1	—
CBPA-8	25	25	1	25

Table 2. Molar ratio of monomers for series of **CAPE**.

Polymer	BHHBP	PSA	6HCA
CAPE-1	1	1	0.091
CAPE-2	1	1	0.11
CAPE-3	1	1	0.33
CAPE-4	1	1	0.2
CAPE-5	1	1	1
CAPE-6	1	1	2

composition ratios. The molar ratio of the monomer component of **CBPA** and **CAPE** are summarized in Tables 1 and 2, respectively. Note that, for **CBPA-3** and **CBPA-8**, gel-like products were obtained after the polymerization.

3.2. Thermal analyses of series of **CBPA**

Thermal analyses of the series of **CBPA** were performed by DSC measurements. Figures 2 and 3 show DSC curves of each sample and typical polarizing microscopy (PO) images of samples observed on the hot stage at temperatures inserted in the images. For **CBPA-1** and **CBPA-2**, which are a homopolymer of **C6M-CB** and a copolymer including **C3M-CB** and **C6M-CB**, a peak was observed at ca. 90 °C during both of raising and lowering temperature processes. Based on PO images obtained at 101 and 102 °C (Fig. 3a), it was found that the peak in DSC curve was corresponded to the liquid crystal phase transition. In the cases of **CBPA-4–7**, several peaks were observed in the scanning range. On the basis of PO observations, we considered that peaks detected at ca. 100 °C were assigned to the liquid crystal phase transition, which are slightly higher compared to those of **CBPA-1** and **CBPA-2**. Figure 3b shows PO images of **CBPA-4** as an example. This result suggests that

Fig. 2. DSC curves during the process of raising (left) and lowering (right) for the series of **CBPA**.

Fig. 3. PO images of films formed by **CBPA-1** (a) and **CBPA-4** (b).

addition of a small amount of **BMHBP** in polymer raise the liquid crystal phase transition temperature probably because of increasing molar weight of polymers due to the cross-linking. Other endothermic peaks indicate the presence of several thermal stable phases within the liquid crystal phase as shown in Fig. 3b (25 and 104 °C). On the other hand, in the cases of **CBPA-3** and **CBPA-8**, no peak was observed during temperature scanning. These are probably due to, for the former, a large amount of the cross-linking unit, and the relatively higher flexibility induced by the **BM** unit for the latter. Although it was found that LCPs including the cross-linking unit exhibits the liquid crystal phase transition, their temperatures are considerably higher than human body temperature.

3.3. Macroscale thermal responses of series of **CBPA**.

We investigated the thermal responsibility of the series of **CBPA** in macroscale. After the preparation of films using LCPs by heating compression-molding, we performed heating experiment of the films on the hot stage in which temperature was set to above 5 °C from each phase transition temperature detected by DSC. Films obtained from **CBPA-1** and **CBPA-2** were fragile and melted during heating, and the gelled **CBPA-3** was too hard to form a film. For **CBPA-4–7**, off-white flexible films were formed. Although the flexibility of the film was improved by the addition of the cross-linking unit, these films melted with heating. As an example, photo images of the film formed by **CBPA-5** without and with heating at 108 °C were shown in Fig. 4a. In the case of a film of **CBPA-8**, although gel-like product was obtained by polymerization, the flexible film was formed and it

Fig. 4. (a) Photo images of the film formed by **CBPA-5** before (left) and after (right) heating at 108 °C for 10 sec. (b, c) Photo images of the film formed by **CBPA-8** without and with heat at 105 °C for 10 sec (b), and that after stretching without and with heat at 105 °C for 20 sec (c).

exhibited heat resistance at least 105 °C (Fig. 4b). After cooling of the film to room temperature, it was artificially stretched to form a curled film. As shown in Figure 4c, the shape of the film was changed to that before stretching, which is indicated that the film exhibited shape memory character with heating by including the **BM** unit in the polymer.

3.4. Thermal properties of CAPE

Next, we performed thermal analyses using the series of **CAPE** in which the mixing molar ratios of **6HCA** was set to be from 50% to 9%. In Fig. 5, DTA curves of the samples are shown. In the cooling process of the samples of **CAPE-1–4**, two peaks at around 50 °C and 60 °C were observed. As an example, Fig. 6a shows PO images of **CAPE-3** obtained on the hot stage set at 30, 52, and 58 °C. From the images, it was revealed that the peak at higher temperature is due to the liquid crystalline phase transition. With increasing the molar ratio of **6HCA**, the liquid crystal phase transition temperature was shifted to lower. Unfortunately, we did not understand completely on the phase transition at lower temperature because PO images

Fig. 5. DTA curves during the process of raising (left) and lowering (right) for the series of **CAPE**.

Fig. 6. PO images of films by **CAPE-3** (a), **CAPE-5** (b), and **CAPE-6** (c).

and motional changes of films in macroscale were not observed. In DTA curves of **CBPE-5**, only one peak at ca. 48 °C was detected. This is due to the liquid crystal phase transition as shown in Figure 6b. For **CAPE-6**, quite weak peaks at 43 °C and 60 °C were observed. The latter is corresponded to the liquid crystalline phase transition (Fig. 6c). From these experiments, it was found that the presence of the **6HCA** unit affected to lowering the temperature of liquid crystal phase transition although, unfortunately, the temperatures are higher by ca. 20 °C in comparison with human body temperature.

3.5. Cross-link formation of series of CAPE by UV-irradiation

Next, we performed the cross-link formation of the series of **CAPE** by UV-irradiation using their thin films. Before UV-irradiation, the films were stretched in one direction to set to be ca. 50 μm thickness in order to form the film with uniaxially oriented polymer chains. These films were demonstrated UV-irradiation with light at 320 nm. Monitoring the cross-link formation was performed by measurements of absorption of the films. As an example, Fig. 7 shows UV spectra of the film formed by **CAPE-3** before and after UV-irradiation for up to 180 min. Before the UV-irradiation, the absorption at around 320 nm, which is due to π - π^* transition of the coumarate unit, was observed. The absorbance decreased with UV-irradiation, and after the irradiation for 180 min, it disappeared. This indicates the formation of a cyclobutane ring by the connection of the coumarate unit, in which the expected chemical reactions were shown in Fig. 1c although it was too difficult to refer to reaction types,

Fig. 7. UV spectra of the film formed by **CAPE-3** before and after UV-irradiation at 320 nm for up to 180 min.

that is, head-to-head and head-to-tail manners. As a result, we concluded that crosslinked materials were obtained by the UV-irradiation.

3.6. Macroscale observations of thermal response of the film before and after cross-linking

We performed heating experiments of the film before and after the cross-linking. The left image of Fig. 8a shows a photo image of the non-crosslinked film of **CAPE-3** fixed on the hot stage by a tape. We stretched the film to one direction before the cross-linking as shown in the middle of Fig. 8a. After heating at 65 °C for 45 sec, the stretched film was shrunk in the vertical direction, and its shape changed to that before stretching (the right image of Fig. 8a), which is indicated that shape memory characteristic was exhibited. On the other hand, Fig. 8b exhibits the photo image of the film, which was performed the UV-irradiation to one side of the film with the light at more than 320 nm for 90 min, before and after heating at 65 °C for 90 sec on the hot stage. Surprisingly, the film showed a curled structure, in which the UV-irradiated side was bent inward with heating. These results suggested that cross-linked polymers shrank more efficiency compared to that without the cross-linking by heating treatment compared to that without the cross-linking because of effective entropy elasticity.

Fig. 8. Photo images of the films formed by **CAPE-3** before (a) and after (b) the cross-linking without and with heat at 65 °C for the time inserted.

4. Conclusion

In order to decrease the phase transitional temperature to human body temperature, two types of liquid crystalline polymers, **CBPA** and **CAPE**, including cross-linking units and short alkyl chains with different molar ratios of monomers were

synthesized. In the cases of **CBPA** having a small molar ratio of **BMHBP**, which is a cross-linking unit, it was found that, based on thermal analyses and PO observations, the phase transitional temperature was detected at more than 100 °C, which is significantly higher than the temperature of human body. In addition, **CBPA** having a **MB** unit exhibited a shape memory characteristic. For series of **CAPE**, the phase transition was observed at lower compared to that of **CBPA** due to cross-linking using a **6HCA** unit. In addition, it revealed that a film formed by **CAPE**, in which UV light irradiation was performed to one side, was curled because of the differentiation of the contraction of polymers before and after the cross-linking. Although it is necessary to design the polymer structure more precisely to achieve the phase transition at human body temperature, we found characteristic structural changes of LCPs in macroscale.

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