Photoinduced Change in Phase-Separated Structure of a Binary Film Composed of 4-[Bis(9,9-dimethylfluoren-2-yl)amino]-4'-nitroazobenzene and Poly(vinyl acetate)

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In due course of our studies on photomechanical effects observed for azobenzene-based photochromic amorphous molecular materials, photoinduced change in phase-separated structure of an amorphous binary film composed of title materials has been investigated in the present study. When the phase-separated film was irradiated with a linearly polarized laser beam, the circular domains in the film extended in the direction parallel to the polarization direction of the incident laser beam. The rate of such photoinduced extension was found to increase with increasing temperature. The result seemed to be contrary to the results of the temperature dependences of other photomechanical effects observed for photochromic amorphous molecular materials we have previously reported. Azo-molecules were suggested to exist both in the domains and in their surroundings and it is of importance to consider the both effects of azo-molecules existed in the domains and in their surroundings for phase-separated binary systems.

Keywords: Photomechanical effect, Binary film, Phase separation, Azobenzene, Photochromic amorphous molecular material, Poly(vinyl acetate)

1. Introduction

Organic materials that exhibit photo-triggered structural changes and photoinduced motions, namely photomechanical effects, have been attracting attentions. Azobenzene-based photochromic materials are the promising candidates for such photomechanical materials because they exhibit trans-cis photoisomerization reactions with large structural changes and cooperation of such motions in molecular levels upon photoirradiation is expected to lead to photomechanical shape changes and movements in bulk scale. Typical photomechanical behaviors were demonstrated in early stage using azobenzene-based liquid-crystalline polymer films and fibers that exhibited bending motions upon photoirradiation [1,2]. Photomechanical shape changes of colloidal spheres composed of azobenzene-conjugated polymers have recently been reported [3,4]. Photoinduced surface relief grating (SRG) formation observed for azobenzene-based polymer films upon interference irradiation with coherent laser beams is also one of the photomechanical effects, that are believed to be due to mass transport induced at the surface area of the films upon irradiation [5–8]. Photo-triggered alignment changes of microphase-separated nanostructures and changes in phase-separated patterns of thin films using azobenzene-containing block copolymers are also the subjects of interest [9–12].

We have been studying the creation of low molecular-mass photochromic materials that readily form amorphous glasses above room temperature, that we referred to as photochromic amorphous molecular materials [13–19]. Among these studies, we have investigated to find novel photomechanical behaviors using azobenzene-based photochromic amorphous molecular materials and to elucidate their mechanisms. For example, we have demonstrated photoinduced SRG formation using the azobenzene-based
photochromic amorphous molecular materials, indicating that they are the novel candidates for SRG-forming materials [20–22]. We have also reported that amorphous molecular fibers exhibited photomechanical bending motions and that the bending direction could be controlled by just altering the polarization direction of the incident beam [23,24]. Photoinduced mass flow at the surface of the amorphous films, photoinduced movements of the glass fragments on the substrate [25,26], and photoinduced shape changes of the particles fixed in agar gel [27] have also been reported. We believe that trans–cis photoisomerization reactions of azo-materials took place upon irradiation to soften the material to be mobile, and simultaneously anisotropic mass transport and/or vibration were induced in the direction parallel to the polarization direction of incident laser beam, resulting in the above photomechanical behaviors of azobenzene-based photochromic amorphous molecular materials depending upon the polarization direction of the incident beams. In addition to the above single component systems, we have also investigated photomechanical behaviors observed for binary systems. We have reported that the mixed film of 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFlAB) and a quaternary ammonium salt exhibited photoinduced phase separation and that SRG composed of the quaternary salt could be obtained by interference irradiation of the mixed film followed by immersing to hexane [28]. In addition, we have reported the preliminary results of photomechanical effect observed for binary films of BFlAB and poly(vinyl acetate) (PVAc) obtained by spin-coating method [29]. The film exhibited phase-separation by annealing and the resulting phase-separated structures were changed upon irradiation with a polarized laser beam. That is, the circular domains extended in the direction parallel to the polarization direction of the incident laser beam and each domain was finally divided into two domains.

2. Experimental

NO$_2$-BFlAB was prepared by the method described in our previous paper [22]. PVAc was purchased commercially (Aldrich, Average $M_w$: 113,000) and purified by reprecipitation before use. The binary film of NO$_2$-BFlAB and PVAc with a thickness of ca. 100–200 nm was prepared by spin-coating method (1500 rpm) onto a transparent glass substrate from a 1,2-dichloroethane solution of NO$_2$-BFlAB and PVAc (2:8 w/w) at room temperature. Phase separation behaviors were observed by using optical microscope (Optiphot X2, Nikon) fitted with a hot stage (TH-600PM, Linkam). Changes in phase-separated structures were observed using the microscope upon irradiation with a polarized laser beam (488 nm, 10 mW, CYAN-488-100 CDRH, SpectraPhysics Inc.) from the bottom of the sample through the glass substrate.

3. Results and discussion

A homogeneous amorphous film of NO$_2$-BFlAB–PVAc with a ratio of 2:8 (w/w) was obtained by spin-coating method (Fig. 1a). When the film was gradually heated, phase separation began to take place at ca. 200 °C and was obviously recognized at around 220 °C (Fig. 1b) to give phase-separated pattern with circular domains. On further heating, dissolution took place to disappear the phase-separated structure at ca. 270 °C. When the sample was cooled, phase separation again took place below ca. 270 °C as shown below (Fig. 2a) although the resulting amount of domains and domain size were different from those obtained on the heating process. The resulting phase-separated structure maintained at room temperature. Such
phase-behaviors were similar to those observed for binary films of BFlAB–PVAc [29]. Hereafter, we used such phase-separated NO$_2$-BFlAB–PVAc film obtained by annealing the spin-coated film for investigation of the photomechanical behaviors.

Fig. 1. Optical microphotographs of the NO$_2$-BFlAB–PVAc film (a) as prepared by spin-coating method at room temperature and (b) at 220 °C on heating. Scale bar: 5 µm.

As well as the phase-separated BFlAB–PVAc films [29], photoinduced change in the present phase-separated structures of NO$_2$-BFlAB–PVAc film was observed. When the annealed film (Fig. 2a) was irradiated with a polarized laser beam at 80 °C, the domains gradually extended in the direction parallel to the polarization direction of the incident laser beam and each domain was finally divided into two domains upon irradiation as shown in Fig. 2b.

Fig. 2. Change in phase-separated structure of the NO$_2$-BFlAB–PVAc film (a) before and (b) after 4 hour-irradiation with the linearly polarized laser beam at 80 °C. Polarization direction of the laser was parallel to the horizontal direction of these photographs. Scale bar: 5 µm.

The rate of such photoinduced deformation of domain structures were investigated. Figure 3 shows the change in average relative length of the long axis of domains (RL) vs. irradiation time. The RL values were found to gradually grow upon irradiation. The growing rate of RL was found to increase with increasing temperature. We have reported that the photoinduced SRG formation took place using azobenzene-based photochromic amorphous molecular materials and the modulation depth of obtained SRG became larger with decreasing temperature because lowering the temperature reduced the fluidity of the materials preventing collapse of the SRG by surface tension [21]. Similarly, we have also reported that the elongation of the glass particles of azobenzene-based photochromic amorphous molecular materials fixed in agar gel took place upon irradiation with a linearly polarized laser beam and the rate of elongation increased with decreasing temperature due to increase in fluidity with increasing temperature to make the particles to shrink by surface tension [27]. Therefore, the present result that the growing rate of RL increased with increasing temperature seemed to be contrary to the results of the temperature dependence of photoinduced SRG formation and elongation of the glass particles in agar gel. It is noted that the growing rate of RL at 120 °C (Fig. 3d) looked considerably larger than those below 100 °C (Fig. 3a-c).

Fig. 3. Change in RL of the domains in the NO$_2$-BFlAB–PVAc film upon irradiation with the linearly polarized laser beam at (a) 60 °C, (b) 80 °C, (c) 100 °C, and (d) 120 °C.

In addition, the domain structure after irradiation with linearly polarized laser beam at 120 °C was found to be different from those below 100 °C. As described above, each domain was finally divided into two domains upon irradiation at relatively lower temperature (Fig. 2b). In contrast, each domain extended smoothly without division in the direction parallel to the polarization direction of incident beam at 120 °C (Fig. 4). Thus, some phase transition might take place between 100 °C and 120 °C.
In order to gain further information, the temperature dependence of growing rate of RL of domains for NO$_2$-BFIAB–PVAc film was compared with that for BFIAB–PVAc film. Figure 5 shows the temperature dependence of RL of domains after 30 min-irradiation with linearly polarized laser beam for both NO$_2$-BFIAB–PVAc and BFIAB–PVAc films. As well as NO$_2$-BFIAB–PVAc film, the growing rate of RL of domains for BFIAB–PVAc film was also found to increase with increasing temperature. In addition, the rate for BFIAB–PVAc film was somewhat larger than that for NO$_2$-BFIAB–PVAc film especially at ca. 100 °C. Since glass transition temperature ($T_g$) and melting temperature of BFIAB (97 °C and 167 °C, respectively) [16] were lower than those of NO$_2$-BFIAB (117 °C and 228 °C, respectively) [22], the phenomena were suggested to be related with their thermal properties such as glass transition. Although the mechanism of the present photomechanical behaviors has been not clear at present, the present photomechanical behaviors could be explained as follows based on the idea that the azo-molecules existed both in domains and in their surroundings. It is conceivable that the contents of azo-molecules were larger for domains than for the surroundings. Since $T_g$ of pure PVAc (ca. 40 °C) is lower than those for the present azo-materials, the surrounding phase was thought to be softer than the domain phase. When the phase-separated films were irradiated with linearly polarized laser beam, the azo-molecules existed in the circular domains vibrate and/or transport in the direction parallel to the polarization direction of the incident beam to push the surroundings, resulting in extension of the domains. With regard to the surroundings, it is thought the presumed increase in fluidity with increasing temperature reduce the repulsion force against the extension of the domains, resulting in the increase of extension rate of domains with increasing temperature. Similarly, the growing rate of RL of domains was larger for BFIAB–PVAc film than for NO$_2$-BFIAB–PVAc film due to lower $T_g$ of BFIAB than NO$_2$-BFIAB. Thus, the present results suggested that the azo-molecules existed not only in the domains but also in their surroundings and that both azo-molecules in the domains and in the surroundings play an important role for the present photomechanical behaviors.

**Fig. 4.** Optical microphotograph of the NO$_2$-BFIAB–PVAc film after 30 min-irradiation with the linearly polarized laser beam at 120 °C. Polarization direction of the laser was parallel to the horizontal direction of the photograph. Scale bar: 5 μm.

**Fig. 5.** Temperature dependence of RL of the domains after 30 min-irradiation with the linearly polarized laser beam. (a) NO$_2$-BFIAB–PVAc film, (b) BFIAB–PVAc film.

### 4. Conclusion

Photomechanical behavior has been observed for the phase-separated film of NO$_2$-BFIAB–PVAc obtained by spin-coating followed by annealing. It was found that the circular domains in the film extended in the direction parallel to the polarization direction of the incident laser beam and that the rate of photoinduced extension increasing with increasing temperature. In addition, the rate for BFIAB–PVAc film was somewhat larger than those for NO$_2$-BFIAB–PVAc film. The present study suggested that the azo-molecules existed not only in the domains but also in their surroundings and that both azo-molecules in the domains and in their surroundings played an important role for the photomechanical behaviors observed for binary systems. The present photomechanical behaviors are complexly intertwined with related factors and we will continue further detail studies.

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