

Photoinduced Phase Transition of Hybrid Films of Azobenzene-based Photochromic Amorphous Molecular Materials and Poly(vinyl acetate)

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Homogeneous hybrid films of azobenzene-based photochromic amorphous molecular materials, 4-[bis(4-methylphenyl)amino]azobenzene (BMAB) and 4-[phenyl(biphenyl-4-yl)amino]azobenzene (PBAB), together with poly(vinyl acetate) (PVAc) were obtained by spin-coating method. Both BMAB–PVAc and PBAB–PVAc films exhibited reversible phase separation–resolution phenomena by thermal treatments. When the resulting phase-separated films were irradiated with 488 nm-laser beam at appropriate temperature, phase transition was found to take place to form homogeneous films.

Keywords: Azobenzene-based photochromic amorphous molecular material, Poly(vinyl acetate), Phase separation, Photoinduced phase transition

1. Introduction

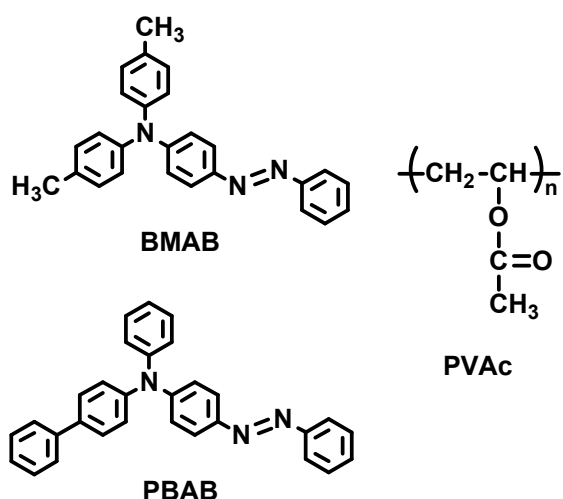
Creation of photo-responsible materials and systems has been a recent subject of interest. One of the most attractive examples is a series of photomechanical materials that exhibit mechanical motions triggered by photoirradiation. A variety of photomechanical behaviors have been reported such as photoinduced bending motions of azobenzene-based liquid crystalline polymer films and fibers [1,2], reversible photomechanical shape changes of needle- and plate-shaped microcrystals of photochromic compounds [3,4], and photo-induced surface relief grating (SRG) formation of azobenzene-based amorphous polymers [5–8].

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 [9–13], and in due course of the studies, we have demonstrated a variety of novel photomechanical behaviors using azobenzene-based photochromic amorphous molecular materials and to elucidate their mechanisms including photoinduced SRG formation [14–16], photomechanical bending motions of photochromic molecular fibers [17,18], photo-

induced movements of the glass fragments placed on the substrate [19,20], and photoinduced shape changes of the particles fixed in agar gel [21]. Not only such single component systems, we have also investigated photomechanical behaviors observed for hybrid systems. We have reported that the hybrid film of 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFIAB) with a quaternary ammonium salt exhibited photoinduced phase separation and that SRG composed of the quaternary salt could be obtained by interference irradiation of the homogeneous hybrid film followed by immersing to hexane [22]. In addition, we have reported the photomechanical behaviours observed for hybrid films of azobenzene-based photochromic amorphous molecular materials, BFIAB and 4-[bis(9,9-dimethylfluoren-2-yl)amino]-4'-nitroazobenzene (NO₂-BFIAB), together with poly(vinyl acetate) (PVAc) [23, 24]. These homogeneous films obtained by spin-coating method 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.

In the present study, we have newly investigated the thermal behaviors and photoresponses of hybrid films using other photochromic amorphous molecular materials, 4-[bis(4-methylphenyl)amino]azobenzene (BMAB) and 4-[phenyl(biphenyl-4-yl)amino]azobenzene (PBAB), together with PVAc. Although the photoinduced shape changes of phase-separated structures could be observed for neither BMAB–PVAc nor PBAB–PVAc films, we have found that their phase-separated films exhibited phase transition to become homogeneous by photoirradiation.



2. Experimental

BMAB and PBAB were prepared by the methods described in our previous papers [12,25]. PVAc (average molecular weight: 100,000) was purchased commercially and used after reprecipitation by using toluene/hexane. Sample films were prepared by spin-coating onto a transparent glass substrate from 1,2-dichloroethane solution of appropriate amounts of BMAB or PBAB and PVAc. Optical microscopy was performed with an Optiphot X2 (Nikon) microscope fitted with a TH-600PM hot stage (Linkam). Photoinduced phase transition was monitored by means of optical microscopy in situ upon irradiation with a laser beam (488 nm, 10 mW, CYAN-488-100 CDRH, SpectraPhysics Inc.) from the bottom of the sample.

3. Results and discussion

We have already reported that BMAB and PBAB form readily amorphous glasses with glass-

transition temperatures (T_g s) of 27 °C and 47 °C, respectively [12,25]. PVAc was confirmed to be in amorphous state at room temperature and to exhibit glass transition around 40 °C by differential scanning calorimetry.

Sample hybrid film of BMAB–PVAc (2:8 w/w) was prepared by spin-coating method onto a transparent glass substrate. The resulting film was homogeneous as shown in Fig. 1a. When the film was gradually heated, phase separation seemed to begin at ca. 120 °C and the phase-separated structure with circular domains was obviously observed at ca. 150 °C (Fig. 1b). On further heating, resolution was observed to become homogeneous again above 170 °C (Fig. 1c). When the homogeneous film was cooled, phase-separation again took place (Fig. 1d). Thus, the film was found to exhibit reversible phase transition by thermal treatments.

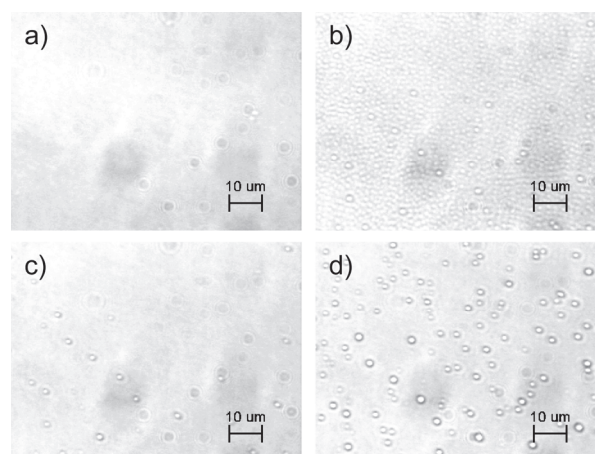


Fig. 1. Optical microphotographs of BMAB–PVAc (2:8 w/w) film a) as prepared at room temperature, b) at 150 °C on heating process, c) at 170 °C on heating process, d) at 150 °C on cooling process.

In the next stage, response of the phase separated film upon irradiation with a laser beam (488 nm, 10 mW) was investigated. When the film was irradiated at room temperature, no structural change was observed for 5 h. On the other hand, photoinduced phase transition to become smooth homogeneous film was observed at higher temperature. That is, when the phase separated film obtained by annealing at 170 °C followed by cooling was irradiated at 120 °C, the phase separated structures disappeared as shown in Fig. 2. When the irradiation stopped, the phase separation gradually took place again.

In order to gain further information about the

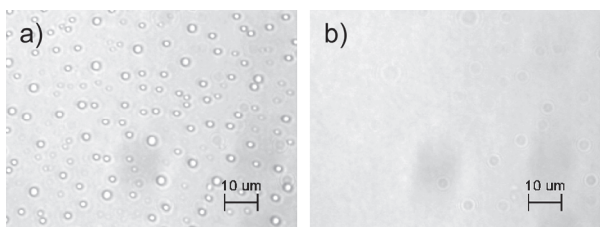


Fig. 2. Optical microphotographs of the BMAB–PVAc (2:8 w/w) film obtained by annealing at 170 °C. a) Before photoirradiation at 120 °C. b) After photoirradiation at 120 °C.

photoinduced phase transition, the hybrid film of BMAB and PVAc with a ratio of 5:5 (w/w) was prepared. When the spin-coated film was heated, phase separation took place and phase-separated structure was obviously observed at ca. 150 °C. On further heating, the sample could not maintain the film state above ca. 170 °C and gathered to become island shapes due to increasing fluidity. When the phase-separated film obtained by annealing at 150 °C was irradiated at 120 °C, a part of phase-separated structure seemed to disappear but the phase transition did not complete as shown in Fig. 3. Since the sample maintained the film state upon irradiation without gathering to become island shapes, the temperature of the sample was not suggested to rise to 170 °C. Therefore, the present photoinduced phase transition observed for BMAB–PVAc (2:8 w/w) film was not caused by photo-thermal effect but by photochromic reaction of BMAB. It is thought that solubility of cis-BMAB molecules to PVAc was larger than that of trans-BMAB molecules and that the photoirradiation induced to decrease the concentration of trans-BMAB and to form more soluble cis-BMAB resulting in resolution to disappear the phase-separated structures. With regard to BMAB–PVAc (5:5 w/w) film, the concentration of trans-BMAB might not decrease enough to solve into PVAc by irradiation, therefore, the phase transition did not complete.

As well as BMAB–PVAc film, PBAB–PVAc film was also found to exhibit such photoinduced phase transition. As shown in Fig. 4, phase separated structure of the PBAB–PVAc (2:8 w/w) film obtained by annealing above 190 °C disappeared by photoirradiation at 160 °C. Thus, the photoinduced phase transition of the phase-separated film to homogeneous one seemed to be general phenomenon for hybrid films of azobenzene-based photochromic amorphous molecular materials together with PVAc. With

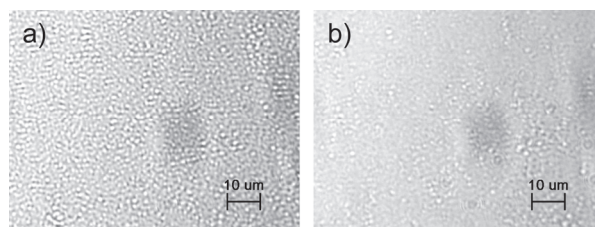


Fig. 3. Optical microphotographs of the BMAB–PVAc (5:5 w/w) film obtained by annealing at 150 °C. a) Before photoirradiation at 120 °C. b) After photoirradiation at 120 °C.

regard to BFIAB–PVAc and NO₂-BFIAB–PVAc films, photomechanical change in phase separated structure depending on the polarization direction of incident beam was observed at around 80 °C as described above [23,24]. However, at higher temperatures, there is a possibility that BFIAB–PVAc and NO₂-BFIAB–PVAc films also exhibit similar photoinduced phase transition like as observed in the present study. Further studies are in progress.

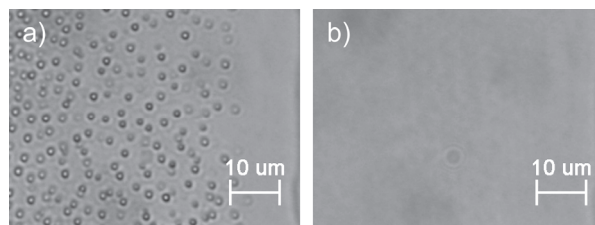


Fig. 4. Optical microphotographs of the PBAB–PVAc (2:8 w/w) film obtained by annealing above 190 °C. a) before photoirradiation at 160 °C. b) after photoirradiation at 160 °C.

4. Conclusion

In due course of our studies of the creation of photo-responsive hybrid materials including azobenzene-based photochromic amorphous molecular materials, new hybrid films of BMAB–PVAc and PBAB–PVAc were prepared. It was found that these films exhibited thermally reversible phase separation–resolution phenomena and that the phase-separated films of these films exhibited phase transition to form homogeneous film by photoirradiation. It was suggested that the photoinduced phase transition was not caused by photo-thermal effect but by photochemical one.

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