

Phase separation and photo-induced deformation of domain structures of azobenzene-based photochromic amorphous molecular materials–poly(vinyl acetate) hybrid films

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ABSTRACT

Hybrid films of azobenzene-based photochromic amorphous molecular materials and poly(vinyl acetate) were found to exhibit thermally reversible phase separation to produce dissipative patterns with circular domains. Deformation of such domain structures could be induced by irradiation of the phase separated film using a relatively high-T_g material with polarized laser beam.

Keywords: *Photomechanical effect, Phase separation, Polarized laser beam, Azobenzene-based photochromic amorphous molecular material, Poly(vinyl acetate)*

1. INTRODUCTION

Photomechanical effects observed for photochromic materials have been attracted a great deal of attention from both viewpoints of fundamental science and practical applications. The effect is believed to induce reversible mechanical motions in bulk scale caused by cooperation of the motions in molecular levels upon photo-irradiation. Films and fibers of azobenzene-based liquid-crystalline polymers have been reported to exhibit bending motions by light irradiation [1-4]. Needle- and plate-shaped microcrystals of diarylethene-, anthrathene-, and azobenzene-based photochromic compounds have also been reported to exhibit reversible shape changes by photo-irradiation[5-7]. In addition, photo-induced surface relief grating (SRG) formation using azobenzene-based polymer films has attracted attention as one of the photomechanical effects [8-14]. Such SRG formation is believed to take place due to mass transport from the bright area to the dark area upon exposure of interference laser beams.

We have been performing studies on creation of photochromic amorphous molecular materials, namely low molecular-mass photochromic materials that readily form amorphous glasses above room temperature [15-19]. In due course of these studies, we have demonstrated that azobenzene-based photochromic amorphous molecular materials exhibited

several photomechanical effects related with photo-induced mass transport, including photo-induced SRG formation [20-29], photomechanical bending of the molecular fibers [30,31], photo-induced mass flow at the surface of the amorphous film [32], movements of fragments of photochromic molecular glasses upon photo-irradiation [32,33], etc. It has been suggested that the photo-induced mass transports were induced in the direction parallel to the polarization direction of the incident laser beam. It is thought that *trans-cis* and *cis-trans* photo-isomerization reactions of the molecules play an important role for photo-induced mass transport; however, the mechanism of the photo-induced mass transport has not been clear yet. It is of interest and of importance to create a variety of photomechanical systems using azobenzene-based photochromic amorphous molecular materials and to investigate their behaviors upon photo-irradiation.

In the present study, we have found that the hybrid films of azobenzene-based photochromic amorphous molecular materials and poly(vinyl acetate) (PVAc) exhibit phase separation to produce dissipative patterns and that deformation of the resulting circular domains could be induced by irradiation with polarized laser beams.

2. EXPERIMENTAL SECTION

Azobenzene-based photochromic amorphous molecular materials using in the present study were BMAB, PBAB, and BFIAB (Figure 1). They were prepared by the methods reported in our previous papers [18,25]. PVAc was purchased commercially. The sample films were prepared onto transparent glass substrates by spin-coating method from 1,2-dichloroethane solutions of the azobenzene-based materials (20 wt%) and PVAc (80 wt%). Phase separation behaviors were observed by using optical microscope (Optiphot X2, Nikon) fitted with a hot stage (TH-600PM, Linkam). Deformation of the domain structure was observed using the microscope upon irradiation with a polarized

laser beam (488 nm, CYAN-488-100 CDRH, SpectraPhysics Inc.) from the bottom of the sample through the glass substrate.

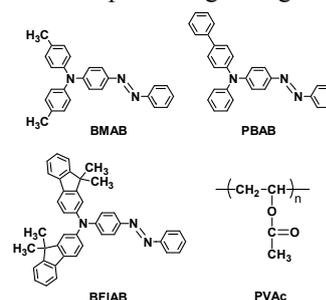


Figure 1. Chemical structures of the materials used in the present study.

3. RESULTS SECTION

It was found that the hybrid films of azobenzene-based photochromic amorphous molecular materials, BMAB, PBAB, and BFIAB, with PVAc exhibited phase separation and dissolution behaviors. For example, optical microphotographs of the BFIAB–PVAc film were shown in Figure 2.

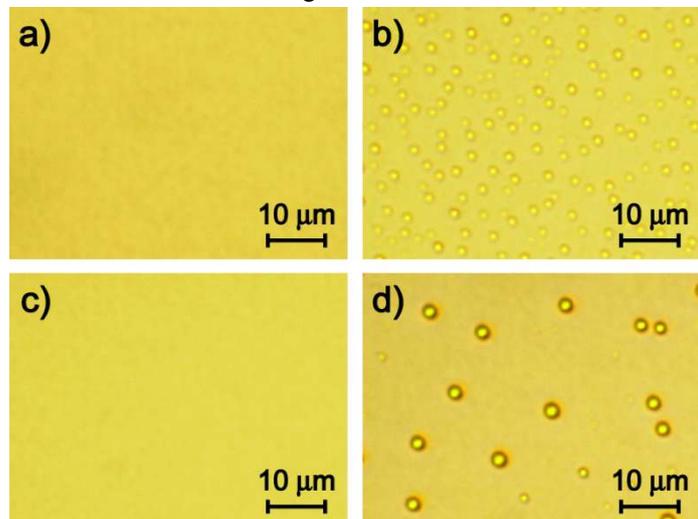


Figure 2. Optical microphotographs of BFIAB–PVAc film: a) room temperature; b) 227° C; c) 250 °C; d) room temperature after annealing.

The film obtained by spin-coating method seemed to be homogeneous (Figure 2a). When the film was heated, phase separation began to take place around 150–160 °C and dissipative pattern with circular domains was clearly observed around 230 °C (Figure 2b). The number of circular domains produced by heating was found to increase with the increase in concentration of BFIAB whereas the size of the domains was almost similar irrespective of the concentration, suggesting that the circular domains were mainly composed of BFIAB. Interestingly, phase dissolution was found to take place around 240–250 °C to become homogeneous again on further heating (Figure 2c). When the resulting homogeneous film was cooled on standing, phase separation took place below the dissolution temperature and the resulting dissipative pattern was maintained at room temperature (Figure 2d). The number and size of the circular domains obtained by the annealing procedure seemed to be depend on the cooling condition. Detailed studies for elucidating the mechanism of the formation of dissipative pattern due to phase separation are in progress. When the resulting phase-separated film obtained by annealing was heated, phase dissolution was again observed. Thus, the BFIAB–PVAc film was found to exhibit thermally reversible phase-separation behavior.

Such thermally reversible phase separation behaviors were also observed for BMAB–PVAc and PBAB–PVAc systems. Temperatures of phase separation (T_p) and dissolution (T_d) for these systems observed on heating of the spin-coated films were summarized in Table 1 together with those of glass-transition (T_g) and melting (T_m) for the corresponding azobenzene-based materials. It was found that T_p and T_d became higher in the order, BMAB < PBAB < BFIAB, suggesting that T_g of the azobenzene-based materials play a role for determining the T_p and T_d . Since

T_p and T_d for these systems were enough higher than the T_g of PVAc (32 °C determined by DSC), the micro-Brownian motion of PVAc might help their phase separation and phase dissolution behaviors.

Table 1. T_p and T_d for azobenzene-based materials (20 wt%)–PVAc systems together with T_g and T_m of the corresponding azobenzene-based materials.

	$T_p / ^\circ\text{C}$	$T_d / ^\circ\text{C}$	$T_g / ^\circ\text{C}$	$T_m / ^\circ\text{C}$
BMAB	110–120	150–160	27 ^a	124 ^a
PBAB	120–130	180–190	46 ^b	180 ^c
BFIAB	150–160	240–250	97 ^a	167 ^a

^areference [22], ^bunpublished data, ^creference [25]

Since the present phase-separated films composed of azobenzene-based photochromic amorphous molecular materials and PVAc were thought to act as new systems for investigation of photomechanical effects, deformation of the resulting circular domain structures upon irradiation with laser beam was investigated. When the phase-separated films of BMAB–PVAc and PBAB–PVAc were irradiated with polarized laser beam (488 nm, 10 mW) for several hours at room temperature, no significant structural change of the circular domains could be observed. On the other hand, the circular domain structures of BFIAB–PVAc film were found to be deformed upon irradiation with the laser beam. As shown in Figure 3, 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 upon irradiation at room temperature. The rate of such photo-induced deformation of domain structures were accelerated by heating. The division of the domain was observed within ca. 1 h upon irradiation at 80 °C.

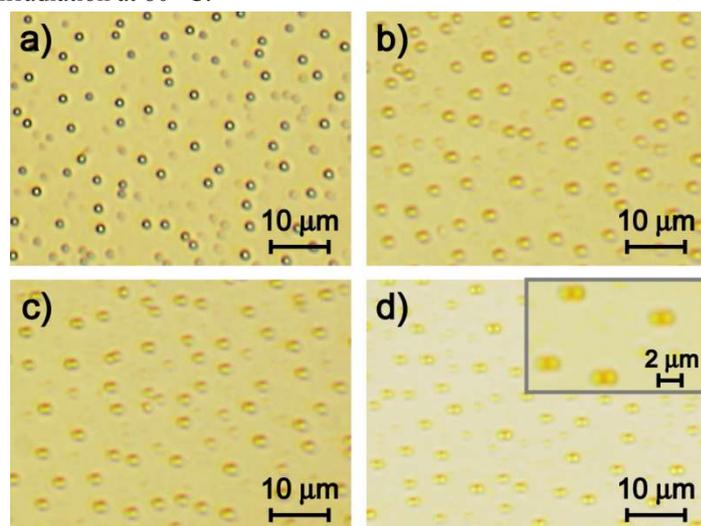


Figure 3. Optical microphotographs of phase-separated BFIAB–PVAc film upon laser irradiation. Polarization direction of the laser was parallel to the horizontal direction of these photographs. Irradiation time: a) 0 h, b) 3 h, c) 6 h, d) 9 h.

We have reported that mass flow at surface level of films of azobenzene-based photochromic amorphous molecular materials could be induced by angled irradiation of the film using a p-polarized laser beam and that the movement of the fragments of

these molecular glasses could be induced by angled irradiation from their bottom [32]. These phenomena can be understood by the vibration of the molecules parallel to the polarization direction of the laser beam. Based on the similar consideration, the present photoinduced deformation of the circular domains were explained as follows. Upon irradiation of the phase separated film with polarized laser beam, the azobenzene-based molecules existing near the interface of the domains vibrated parallel to the polarization direction of the incident laser beam and hence the circular domains extended in the same direction pushing the surrounding polymer away. Since such deformation increased the

4. CONCLUSIONS

Hybrid films of azobenzene-based photochromic amorphous molecular materials and PVAc were found to exhibit thermally reversible phase separation to produce dissipative patterns with circular domains. Whereas no significant structural change of these circular domains was observed for BMAB–PVAc and PBAB–PVAc films upon irradiation with the laser beam, photoinduced deformation of circular domain structures was found to take place for BFIAB–PVAc film, that is, the circular

5. REFERENCES

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area of the interface, the deformed domains were finally divided into two domains in order to reduce the interfacial energy. When the film was heated, the rate of deformation was increased due to softening of the surrounding polymer. On the other hand, the BMAB and PBAB molecules could not push the surrounding polymers away maybe because of their relatively low viscosity attributable to their low T_g. Thus, the photo-induced force to push the surrounding away was conceivable to become larger with the increase in the T_g of the azobenzene-based amorphous molecular materials.

domains 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. The present photomechanical effect could be explained by the vibration of the molecules existing near the interface of the domains parallel to the polarization direction of the incident laser beam, producing the photo-induced force to push the surrounding away.

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