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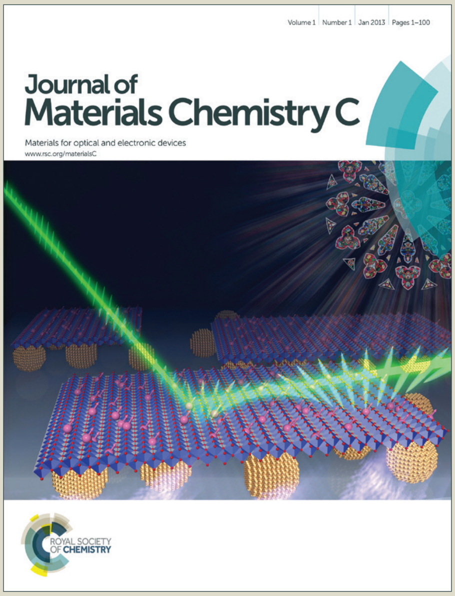

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COMMUNICATION

Photomobile materials with interpenetrating polymer network composed of liquid-crystalline and amorphous polymers

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We developed interpenetrating polymer networks (IPNs) composed of a crosslinked azobenzene liquid-crystalline polymer (PAzo) and poly(alkyl methacrylate)s (PAMAs). When irradiated with UV and visible light, the IPN films showed reversible bending. The photoresponsive and mechanical properties of PAzo films were significantly enhanced by incorporation of the PAMA components.

Photomobile polymer material is a novel class of liquid-crystalline (LC) polymers, which macroscopically deforms upon irradiation with light. This fascinating material enables the direct conversion of light energy into mechanical work, and therefore the creation of small, lightweight and remote-controllable actuators. The motion of photomobile polymer materials is based on the deformation of LC polymer chains.[1-3] In LC polymers, the alignment of mesogens is coupled with the conformation of polymer chains. Furthermore, the deformation of polymer chains leads to the macroscopic deformation of the materials in crosslinked systems. Thus, crosslinked LC polymer films deform when the alignment of mesogens is altered by stimuli such as heat, electricity and light. In LC systems containing photochromic molecules, the alignment change of mesogens can be induced by light. Azobenzene derivatives, especially those with LC properties, are mostly used photochromic components for photomobile polymer materials. Rod-like *trans*-azobenzenes stabilize LC phases, whereas *cis*–azobenzenes disturb them. When a crosslinked azobenzene LC polymer (PAzo) film is irradiated with UV light, which induces *trans*–*cis* isomerization of azobenzene moieties, the alignment of mesogens is disturbed by *cis* isomers.[4,5] When irradiated with visible light, the initial alignment of mesogens is recovered through *cis*–*trans* isomerization. This isothermal order–disorder transition leads to the macroscopic deformation of the polymer film.[6-8]

Although various motions such as bending, twisting and rotation have been successfully achieved with photomobile polymer materials,[9-16] there still remain several issues to be challenged for practical use in their response time and mechanical toughness. It is essential to develop methods to control the optical and mechanical properties of photomobile materials. In the previous studies, bilayer films consisting of PAzo and polyethylene layers were developed to enhance mechanical toughness.[12,13] However, they still show a drawback that PAzo layers tend to be peeled off from polyethylene substrates when driven repeatedly. In addition to toughness, elastic modulus is also an important mechanical property that governs deformation behavior such as contraction and bending. Controlling elastic modulus of photomobile materials would lead to an enhancement of their optical responses.

Mechanical properties of polymer materials can be controlled by using multiple polymer components. Interpenetrating polymer network (IPN) is a combination of two or more polymer networks synthesized in juxtaposition.[17] The properties of IPN films depend on the characteristics of constituent polymers and their composition. IPN has been applied to elastomers[18-20] and hydrogels[21-23] to improve mechanical properties. This approach would also enhance the performance of LC polymer systems. In this study, we developed photomobile materials with IPN structures by incorporating amorphous poly(alkyl methacrylate)s (PAMAs) into PAzo networks. The optical and mechanical properties of IPN films were investigated in relation to the characteristics of PAMA components.

One of the most important factors in preparing photomobile polymer materials is the alignment control of mesogens. The initial alignment of mesogens, which is fixed by crosslinking, strongly affects the deformation behavior of the materials. In order to obtain IPN films with highly-ordered azobenzene moieties, we applied sequential formation of PAzo and PAMA networks. Fig. 1 shows the chemical structures of the compounds used in this study. First, PAzo network was formed by photopolymerization of a monofunctional monomer (A6AB6) and a bifunctional crosslinker (DA6AB) in the presence of LC solvent (1BZ6) at a LC temperature in a glass cell coated with alignment layers. After the formation of PAzo network, 1BZ6 was removed to obtain a PAzo template film (PAzoTP), which contains numerous pores. Then PAzoTP was immersed in a mixture of

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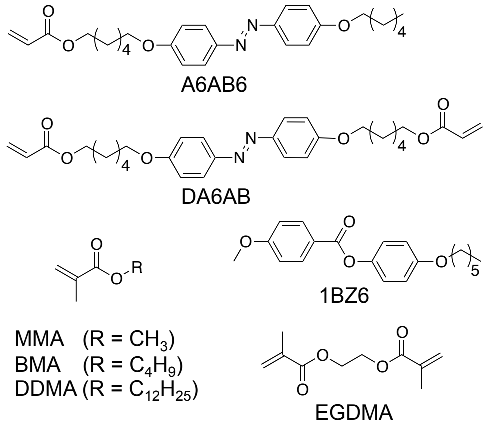

Fig. 1 Chemical structures of compounds used in this study.

an alkyl methacrylate monomer (MMA, BMA or DDMA), a crosslinker (EGDMA) and an initiator, followed by thermal polymerization to give IPN films (PAzo/PMMA, PAzo/PBMA and PAzo/PDDMA). For comparison, pristine PAzo films were prepared by photopolymerization of A6AB6 and DA6AB without LC solvent. The formation of IPN structures was confirmed by atomic force microscopy (AFM). Fig. S1 (supplementary information) shows AFM phase images of a pristine PAzo film and PAzo/PMMA. In contrast with a uniform structure of the pristine PAzo film, PAzo/PMMA showed phase-separated domains with sizes of 10–100 nm, which are typical for IPN structures.[17]

The alignment of azobenzene moieties in films was evaluated by polarizing optical microscopy (POM) and polarized UV-Vis absorption spectroscopy. POM images of PAzo and IPN films are shown in Fig. S2. Upon rotating the sample with respect to the polarizer, all films showed contrast inversion every 45˚, indicating uniaxial alignment of azobenzene moieties. Order parameter, S, was evaluated from polarized absorption spectra (Fig. S3): $S = (A_{/\!/} - A_{\perp})/(A_{/\!/} + 2\,A_{\perp})$, where $A_{/\!/}$ and $A_{\perp}$ denote absorbance obtained with light polarized parallel and perpendicular to the director, respectively. The values of S for PAzoTP and IPN films were almost the same as that of a pristine PAzo film. This result implies that the homogeneous alignment of azobenzene moieties is preserved even after incorporation of amorphous components. The value of S for PAzo/PBMA was somewhat lower than the others. The PAzo and PBMA components may be mixed well at a polymer chain level.

Fig. 2 shows the macroscopic bending behavior of freestanding IPN films upon irradiation with UV and visible light. When irradiated with UV light, the films bent toward a light source. This behavior is essentially the same as that of a pristine PAzo film. *Trans–cis* photoisomerization of azobenzene moieties leads to a decrease in the alignment order of mesogens and then contraction of polymer chains. Due to the high absorption coefficient and high concentration of azobenzene moieties, light is absorbed only at the surface region of the film. As a result, the films macroscopically bend toward an actinic light source. When irradiated with visible light, the films reverted to the initial flat state by *cis–trans* isomerization of azobenzene moieties.

The bending behavior of the films upon irradiation with UV light was analyzed in detail. We defined the bending angle as an angle between two straight lines connecting both ends of the sample film: one is before bending and the other after bending.

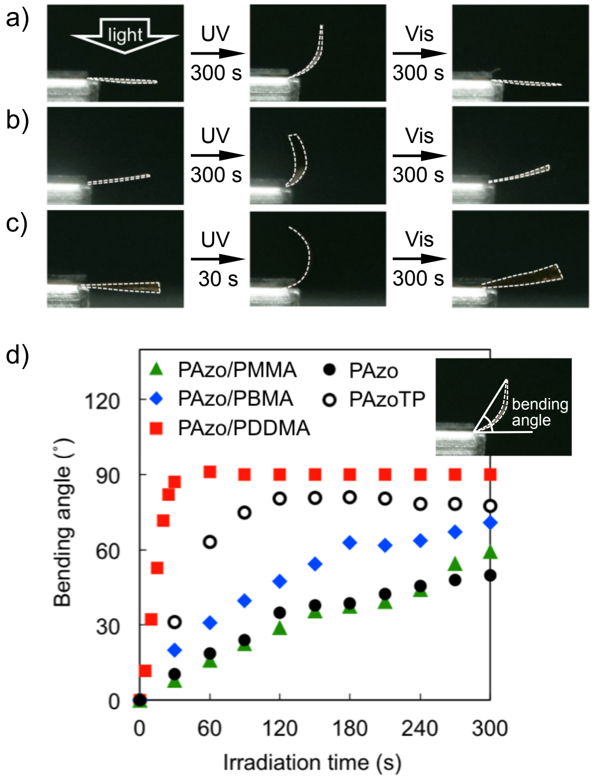

Fig. 2 Bending behavior of films upon irradiation with UV (10 mW cm^{-2}) and visible (40 mW cm^{-2}) light. a) PAzo/PMMA, b) PAzo/PBMA, c) PAzo/PDDMA, d) bending angle as a function of irradiation time of UV light. Size of the films: 3 mm × 1 mm × 16 μm. The white dashed lines in the photographs represent the edges of the films.

Fig. 2d shows the bending angle of the films as a function of irradiation time of UV light. When compared with a pristine PAzo film, PAzoTP bent faster. This result reflects the fact that PAzoTP contains numerous pores, which reduce elastic modulus of the film. The bending motion of PAzo/PMMA and PAzo/PBMA was slower than that of PAzoTP. On the other hand, PAzo/PDDMA showed higher bending speed than PAzoTP. The bending speed of IPN films strongly depends on the photoinert PAMA components.

To clarify the origin of the difference in bending behavior among the films, we evaluated the alignment change of azobenzene moieties upon exposure to UV light. The films were set between crossed polarizers and the intensity of transmitted probe light was measured. The angle between the polarizers and the director axis of azobenzene moieties was set at 45˚. Fig. 3 shows transmittance of the probe light as a function of irradiation time of UV light. A decrease in transmittance with irradiation time indicates a decrease in the alignment order of azobenzene moieties. The alignment change in PAzo/PMMA and PAzo/PBMA was slower than that of PAzoTP. This result implies that the free volume of azobenzene moieties decreases by incorporation of PMMA and PBMA components. The alignment change in PAzo/PDDMA was almost the same as that in PAzoTP. As the glass transition temperature, T_g, of PDDMA is much lower than room temperature ($T_g \approx -65$ ˚C for linear polymer),[24] PDDMA chains do not prevent the isomerization and change in alignment of azobenzene moieties.

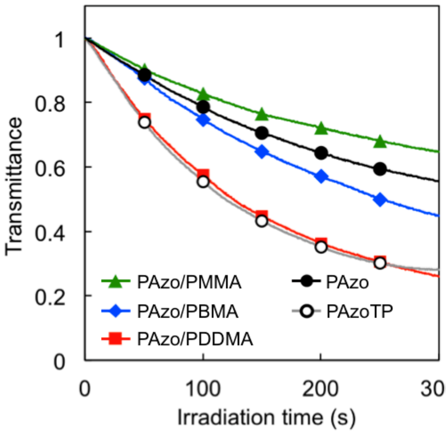

Fig. 3 Change in transmittance of probe light upon irradiation of the films between crossed polarizers with UV light (5 mW cm^{-2}). Thickness of the films: 1.5 μm.

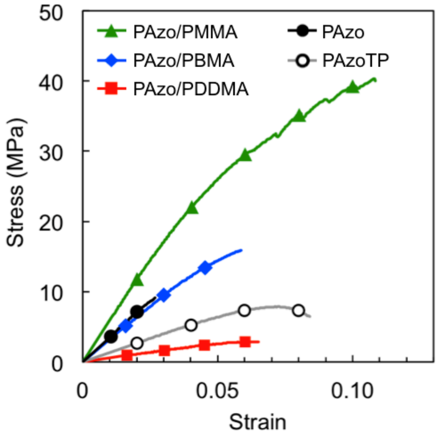

Fig. 4 Stress–strain curves of films upon stretching along the director axis of azobenzene moieties. Thickness of the films: 20 μm.

We next examined mechanical properties of the films. Fig. 4 shows stress–strain curves of the films upon uniaxial stretching along the director axis of azobenzene moieties. Young's modulus of the films was evaluated as a ratio of stress to strain in a small strain limit. PAzo/PMMA showed higher Young's modulus than PAzoTP. This is consistent with the fact that the IPN films are prepared by incorporation of PAMA components into pores of PAzoTP. On the other hand, PAzo/PDDMA showed lower Young's modulus than PAzoTP even after the addition of the second network. This anomalous behavior can be explained by an increase in mobility of PAzo chains upon incorporation of a low-T_g component, PDDMA, which reduces elastic modulus of the PAzo component.

The difference in the alignment change of azobenzene moieties and Young's modulus are related to the bending speed of IPN films. PAzo/PMMA and PAzo/PBMA show a slower alignment change of azobenzene moieties and a higher Young's modulus than PAzoTP, resulting in a slow bending motion. On the other hand, the rapid motion of PAzo/PDDMA results from its low Young's modulus. Interaction between different components plays significant roles in determining performance of IPN films.

Mechanical toughness is also an important factor for the practical use of photomobile polymer materials. As shown in Fig. 4, the pristine PAzo film is brittle due to the high crosslinking density. PAzo/PMMA showed much higher fracture stress than pristine PAzo and PAzoTP. Furthermore, the brittleness of a pristine PAzo film upon stretching along a direction perpendicular to the director axis was overcome by the formation of IPN structure with amorphous polymer components (Fig. S4).

In conclusion, we developed novel photomobile materials with IPN structures containing PAzo and PAMA components. By incorporating PDDMA, which shows a low T_g, the bending speed upon irradiation with UV light was much enhanced than pristine PAzo and PAzoTP. The mechanical toughness was significantly improved by the formation of IPN structures, especially by incorporation of PMMA. It was revealed that the optical and mechanical properties of photomobile polymer materials can successfully be controlled by forming IPN structures with adequate amorphous components.

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