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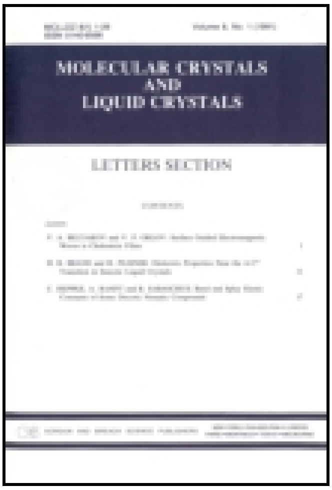

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Photomobile Properties of Interpenetrating Polymer Network Films Composed of Azobenzene Liquid Crystalline Polymer and Polymethacrylates

Toru Ube[a], Kiyohide Takado[b] & Tomiki Ikeda[a]
[a] Research & Development Initiative, Chuo University, Tokyo, Japan
[b] Graduate School of Science and Engineering, Chuo University, Tokyo, Japan

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Photomobile Properties of Interpenetrating Polymer Network Films Composed of Azobenzene Liquid Crystalline Polymer and Polymethacrylates

TORU UBE,[1] KIYOHIDE TAKADO,[2] AND TOMIKI IKEDA[1,*]

[1]Research & Development Initiative, Chuo University, Tokyo, Japan
[2]Graduate School of Science and Engineering, Chuo University, Tokyo, Japan

Various fabrication methods of photomobile polymer materials containing photochromic moieties have been developed to improve their photoresponsive and mechanical properties. Here, we newly prepared photomobile polymer materials with interpenetrating polymer network (IPN) structures. The IPN films, which are composed of azobenzene liquid crystalline polymer (LCP) and polymethacrylates, showed reversible bending behavior upon exposure to UV and visible light. Bending speed of the IPN films became higher with decreasing glass-transition temperature of polymethacrylate components. The IPN film containing poly(dodecyl methacrylate) showed faster bending than the pristine azobenzene LCP film.

Keywords Interpenetrating polymer network; liquid crystalline polymer; azobenzene; polymathacrylate; stimuli responsive material; actuator

Introduction

Stimuli responsive materials have attracted much attention due to their potential application to various devices such as actuators and sensors. Crosslinked liquid crystalline polymers (LCPs), which possess hybrid character of LCs and flexible polymers, are good candidates of soft actuator materials [1–5]. In crosslinked LCPs, orientation of mesogens is strongly correlated with the macroscopic shape. Therefore, crosslinked LCP materials can be deformed by stimuli such as heat, electric field and light, which can change the alignment of LC molecules. Since the initial alignment of molecules is memorized by the network, deformation of crosslinked LCPs is reversible. Incorporation of photochromic LC moieties into crosslinked LCP networks enables the photoinduced deformation [6–11]. Azobenzene is a photochromic molecule, which shows reversible *trans–cis* isomerization upon exposure to UV and visible light [12]. Rod-like *trans*-azobenzene stabilizes LC phases whereas bent *cis*-azobenzene disturbs them. When a crosslinked azobenzene LCP is exposed to light, molecular order is changed by the isomerization of azobenzene moieties, resulting in the macroscopic deformation. It has been shown that various three-dimensional movements such as bending, twisting, oscillation and rotation can be achieved by proper fabrication of LCP samples [13–18].

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[*] Address correspondence to Tomiki Ikeda, Research & Development Initiative, Chuo University, Tokyo 112-8551, Japan. E-mail: tikeda@tamacc.chuo-u.ac.jp

Although photomobile polymer materials are expected to be applicable for various applications such as microactuators and microfluidics devices, they still have some problems to be solved for the practical use. For example, highly crosslinked polymers are stiff and brittle, and are not easily processed. Various fabrication methods have been proposed to improve photoresponsive and mechanical properties of LCPs. We previously developed bilayer films of crosslinked azobenzene LCPs and flexible polyethylenes [13, 14]. This method improved mechanical properties of the material and enabled various three-dimensional motions resembling a robotic arm and a motor. It has been recently reported that incorporation of carbon nanotube to crosslinked LCP films improves mechanical properties of photomobile polymer materials [19, 20]. Absorption of light over a wide range of wavelength by carbon nanotube is also advantageous to the use of sunlight as an actinic light source. Development of composite structures has a potential to drastically improve performance of photomobile materials [21, 22].

Blending of multiple polymer components is a frequently used method to modulate the physical properties of materials such as glass transition temperature (*T*g) and Young's modulus. In case of crosslinked polymer materials, incorporation of multiple components results in the formation of interpenetrating polymer network (IPN) structures [23]. The formation of IPN or double network structures has been revealed to improve the performance of functional crosslinked polymers such as hydrogels and electroelastomers [24–28]. In this paper, we report fabrication of IPN films consisting of azobenzene LCPs and polymethacrylates. The bending behavior of IPN films was compared with those of the pristine azobenzene LCP film.

Experiments

Chemical structures of compounds used in this study are shown in Figure 1. The azobenzene LC monomer (A6AB6) and the azobenzene crosslinker (DA6AB) were synthesized according to the previously reported method [29]. The nonreactive LC solvent (1BZ6) was synthesized through the esterification of *p*-anisic acid and 4-hexyloxyphenol in dichloromethane catalyzed by *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). A mixture of A6AB6, DA6AB and 1BZ6 with a ratio of 35/15/50 (mol%) containing 2 mol% of a photoinitiator (Irgacure784) was melted and injected into a glass cell coated with rubbed polyimides at 90°C. Then it was cooled down to an LC temperature (72°C) and photoirradiation was carried out at >540 nm (2 mW cm^{-2}) with a 500 W high-pressure mercury lamp (USHIO, OPM2-502HQ) through glass filters (Tokina, Y52 and HA50) for 2 h.

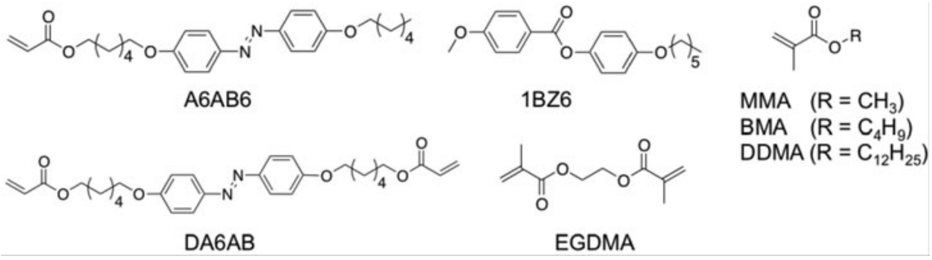

Figure 1. Chemical structures of compounds used in this study.

After the formation of crosslinked LCP, the cell was immersed in acetone to remove 1BZ6 and dried under reduced pressure. The resultant film is referred to as PA35D15. For the preparation of IPN films, the cell containing PA35D15 was immersed in a mixture of methacrylate monomer (MMA, BMA or DMMA, 90 mol%), crosslinker (EGDMA, 10 mol%) and 2,2′-azobisisobutyronitrile (1 mol% of the polymerizable molecules). Then the cell was set on a hot plate and thermally polymerized at 60°C for 3 h under argon atmosphere. After polymerization, the IPN film (referred to as PA35D15/PMMA, PA35D15/PBMA and PA35D15/PDDMA) was dried under reduced pressure.

The mesomorphic properties of films were examined with a polarizing optical microscope (POM) at room temperature. Photoinduced deformation of the films was brought about upon irradiation with UV light at 366 nm (10 mW cm^{-2}) and visible light at >540 nm (50 mW cm^{-2}) from a 500 W high-pressure mercury lamp through glass filters at 30°C.

Results and Discussion

The alignment of azobenzene moieties in the films was evaluated at room temperature using POM. Figure 2 shows POM images of pristine PA35D15 and IPN films. The IPN film showed contrast inversion every 45° upon rotating the sample with respect to the analyzer as in PA35D15. This indicates that a monodomain structure was maintained by the LCP network during the process of introducing the methacrylate component.

We explored the photoresponsive behavior of the films under the experimental setup shown in Fig. 3a. Part of a film was sandwiched between an aluminum plate and a glass plate. When the films were irradiated with UV light at 366 nm, they bent toward the light source (Figs. 3b–e). Upon exposure to UV light, the *trans*–*cis* photoisomerization of azobenzene moieties occurs in the surface region of the film, which decreases the orientational order of azobenzene moieties and leads to contraction of the surface of the film. The photoisomerization occurs only in the surface region of the film and azobenzene

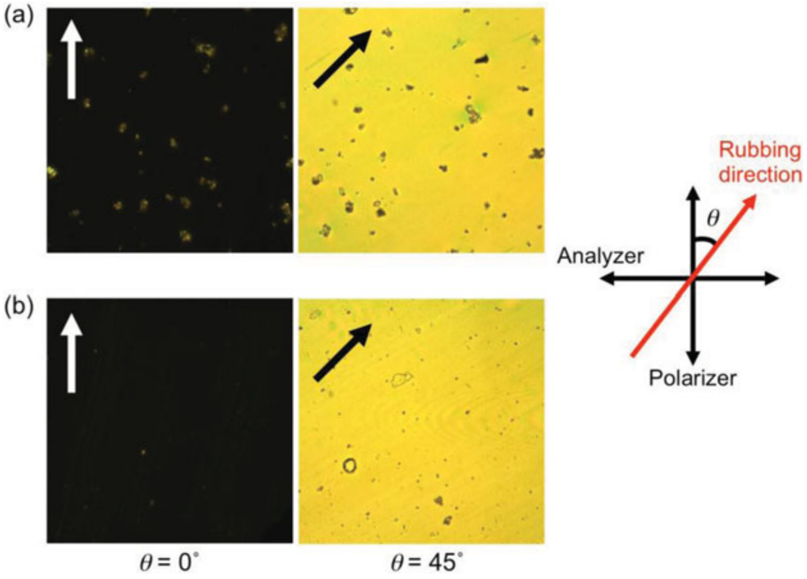

Figure 2. POM images of (a) PA35D15 and (b) PA35D15/PDDMA.

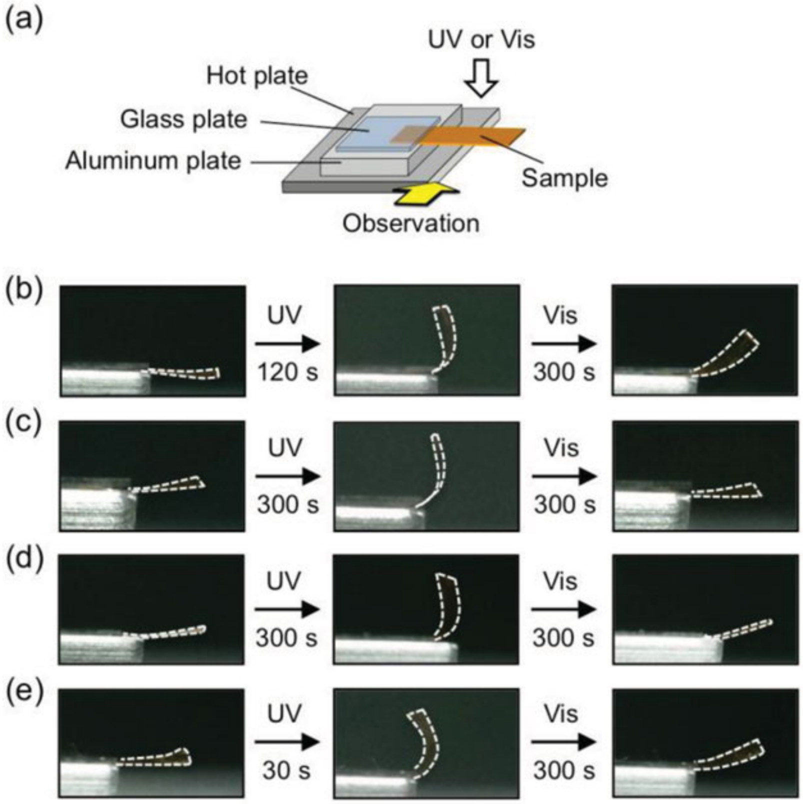

Figure 3. Photoresponsive behavior of films. (a) Schematic illustration of the experimental setup, and photographs of (b) PA35D15, (c) PA35D15/PMMA, (d) PA35D15/PBMA and (e) PA35D15/PDDMA. Size of the films: 3 mm × 1 mm × 16 μm.

moieties in the bulk of the film keep *trans* form due to the high extinction coefficient of azobenzene moieties, resulting in the bending toward the light source [10]. The bent films reverted to the initial states when irradiated with visible light at >540 nm. The bending behavior of the IPN films was similar to that of pristine PA35D15. This indicates that the second components (PMMA, PBMA, or PDDMA) do not significantly disturb the photomobile property of the films.

The time evolution of the bending behavior of the IPN films was compared with that of the pristine azobenzene LCP film (Fig. 4). We evaluated the bending angle from slopes of the lines connecting both ends of the specimen as shown in Fig. 4a. PA35D15/PMMA and PA35D15/PBMA showed slower bending and unbending motions than pristine PA35D15. This is caused by incorporation of polymers to the cavity of PA35D15, which increases elastic modulus of the films. On the other hand, PA35D15/PDDMA showed faster bending and unbending behavior than the pristine film. This may be attributed to the fact that incorporation of low-Tg component accelerates the photoactuation processes such as photoisomerization of azobenzene moieties, reorientation of mesogens and deformation of polymer chains. Bending speed of IPN films became higher with decreasing Tg of the second components [30]. This result indicates that one can control photoresponsive properties of crosslinked LCPs by incorporating second polymer components.

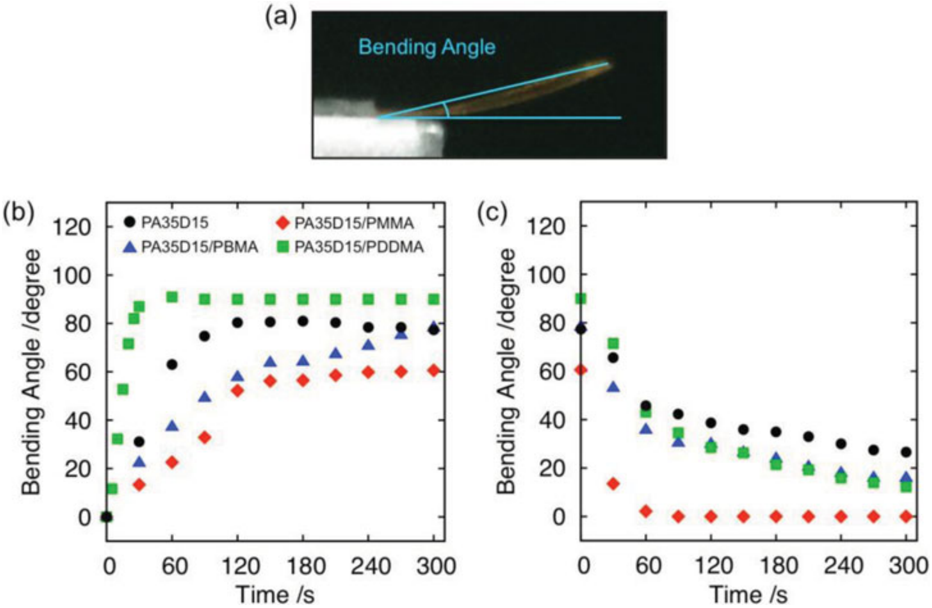

Figure 4. Analysis of the photoresponsive behavior. (a) Definition of the bending angle, (b) bending behavior of the films upon exposure to UV light, and (c) unbending behavior of the films upon exposure to visible light.

Conclusion

We prepared photomobile polymer materials composed of crosslinked azobenzene LCPs and polymethacrylates with IPN structures. IPN films exhibited reversible bending and unbending upon photoirradiation. The bending behavior of the IPN films reflected Tg of polymethacrylate components. The IPN film with a low-Tg component (PA35D15/PDDMA) showed faster bending than the pristine azobenzene LCP film. We have successfully developed a method to fabricate novel photomobile IPN films, which can be potentially applied to introduce various kinds of polymer components into photomobile materials and control their physical properties.

References

[1] de Gennes, P. G. (1975). *C. R. Acad. Sci. B*, *281*, 101.
[2] Finkelmann, H., Kock, H., & Rehage, G. (1981). *Makromol. Chem. Rapid Commun.*, *2*, 317.
[3] Küpfer, J., & Finkelmann, H. (1994). *Macromol. Chem. Phys.*, *195*, 1353.
[4] de Gennes, P. G., Hébert, M., & Kant, R. (1997). *Macromol. Symp.*, *113*, 39.
[5] Warner, M., & Terentjev, E. M. (2003). *Liquid Crystal Elastomers*, Oxford University Press: Oxford, UK.
[6] Finkelmann, H., Nishikawa, E., Pereira, G. G., & Warner, M. (2001). *Phys. Rev. Lett.*, *87*, 015501.
[7] Yu, Y., Nakano, M., & Ikeda, T. (2003). *Nature*, *425*, 145.
[8] Ikeda, T., & Ube, T. (2011). *Mater. Today*, *14*, 480.
[9] Yu, H. &, Ikeda, T. (2011). *Adv. Mater.*, *23*, 2149.
[10] Ikeda, T., Mamiya, J., & Yu, Y. (2007). *Angew. Chem. Int. Ed.*, *46*, 506.
[11] Yu, Y., Nakano, M., Shishido, A., Shiono, T., & Ikeda, T. (2004). *Chem. Mater.*, *16*, 1637.

[12] Ikeda, T., & Tsutsumi, O. (1995). *Science*, *268*, 1873.

[13] Tabiryan, N., Serak, S., Dai, X. M., & Bunning, T. (2005). *Opt. Express*, *13*, 7442.

[14] White, T. J., Tabiryan, N. V., Serak, S. V., Hrozhyk, U. A., Tondiglia, V. P., Koerner, H., Vaia, R. A., & Bunning, T. J. (2008). *Soft Matter*, *4*, 1796.

[15] van Oosten, C. L., Bastiaansen, C. W. M., & Broer, D. J. (2009). *Nat. Mater.*, *8*, 677.

[16] Yamada, M., Kondo, M., Miyasato, R., Naka, Y., Mamiya, J., Kinoshita, M., Shishido, A., Yu, Y., Barrett, C. J., & Ikeda, T. (2009). *J. Mater. Chem.*, *19*, 60.

[17] Kondo, M., Sugimoto, M., Yamada, M., Naka, Y., Mamiya, J., Kinoshita, M., Shishido, A., Yu, Y., & Ikeda, T. (2010). *J. Mater. Chem.*, *20*, 117.

[18] Serak, S., Tabiryan, N., Vergara, R., White, T. J., Vaia, R. A., & Bunning, T. J. (2010). *Soft Matter*, *6*, 779.

[19] Wang, W., Sun, X., Wu, W., Peng, H., & Yu, Y. (2012). *Angew. Chem. Int. Ed.*, *51*, 4644.

[20] Sun, X., Wang, W., Qiu, L., Guo, W., Yu, Y., & Peng, H. (2012). *Angew. Chem. Int. Ed.*, *51*, 8520.

[21] Marshall, J. E., Ji, Y., Torras, N., Zinoviev, K., & Terentjev, E. M. (2012). *Soft Matter*, *8*, 1570.

[22] Li, C., Liu, Y., Huang, X., & Jiang, H. (2012). *Adv. Funct. Mater.*, *22*, 5166.

[23] Sperling, L. H. (1994). In: *Interpenetrating Polymer Networks*, Klempner, D., Sperling, L. H., & Utracki, L. A., (Eds.), (Chapter 1, American Chemical Society: Washington, 3.

[24] Gong, J. P., Katsuyama, Y., Kurokawa, T., & Osada, Y. (2003). *Adv. Mater.*, *15*, 1155.

[25] Gong, J. P. (2010). *Soft Matter*, *6*, 2583.

[26] Wu, Z. L., Kurokawa, T., & Gong, J. P. (2011). *Bull. Chem. Soc. Jpn.*, *84*, 1295.

[27] Ha, S. M., Yuan, W., Pei, Q., Pelrine, R., & Stanford, S. (2006). *Adv. Mater.*, *18*, 887.

[28] Brochu, P., & Pei, Q. (2010). *Macromol. Rapid Commun.*, *31*, 10.

[29] Angeloni, A. S., Caretti, D., Carlini, C., Chiellini, E., Galli, G., Altomare, A., Solaro, R., & Laus, M. (1989). *Liq. Cryst.*, *4*, 513.

[30] Brandrup, J., Immergut, E. H., & Grulke, E. A. (Eds.) (1999). *Polymer Handbook*, 4th ed., Wiley: New York.