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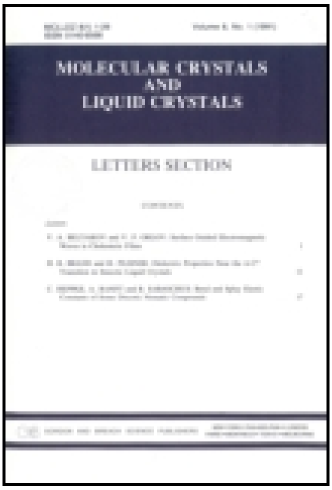

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Photomobile Polymer Materials with Double Network Structures: Crosslinked Azobenzene Liquid-Crystalline Polymer/Methacrylate Composites

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Published online: 06 Dec 2014.

To cite this article: Kiyohide Takado, Toru Ube & Tomiki Ikeda (2014) Photomobile Polymer Materials with Double Network Structures: Crosslinked Azobenzene Liquid-Crystalline Polymer/Methacrylate Composites, Molecular Crystals and Liquid Crystals, 601:1, 43-48, DOI: 10.1080/15421406.2014.940491

To link to this article: http://dx.doi.org/10.1080/15421406.2014.940491

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*Mol. Cryst. Liq. Cryst*, Vol. 601: pp. 43–48, 2014

ISSN: 1542-1406 print/1563-5287 online
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# Photomobile Polymer Materials with Double Network Structures: Crosslinked Azobenzene Liquid-Crystalline Polymer/ Methacrylate Composites

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*We prepared photomobile polymer materials composed of crosslinked azobenzene liquid-crystalline polymers (LCPs) and methacrylates with interpenetrating polymer network (IPN) structures, and explored their photoresponsive behavior. The IPN films exhibited reversible bending upon photoirradiation. In addition, the durability of the IPN films was much higher than that of the pristine crosslinked azobenzene LCP films.*

**Keywords** Photomobile polymer; azobenzene; photoisomerization; crosslinked liquid-crystalline polymer; interpenetrating polymer network; photoinduced bending

## Introduction

Many studies on actuators for the construction of artificial muscles have been performed recently. Various types of materials have been developed as artificial muscle-like materials such as carbon nanotube sheets [1] and polymers [2]. It is desirable to use soft materials with high mechanical flexibility and durability. Soft actuators that respond to external stimuli such as pH [3], solvent composition [4], heat [5] and light [6, 7] have been developed. Crosslinked LCPs exhibit a spontaneous deformation along the director axis when the molecular alignments of mesogens are changed by external stimuli such as heat [5] and electricity [8]. By incorporating photochromic molecules into crosslinked LCPs, large motions can be induced by photochemical reactions of these chromophores.

Azobenzene is a widely used photochromic molecule that shows reversible photoisomerization between a rod-like *trans* and a bent *cis* isomer upon irradiation of light. Azobenzenes stabilize LC states in a *trans* form, while a *cis* form works as an impurity. Irradiation with UV light induces *trans-cis* isomerization of azobenzene moieties, resulting in an isothermal reduction of molecular order [9]. The extinction coefficient of azobenzene moieties at around 360 nm is so large (larger than $2 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) that when a

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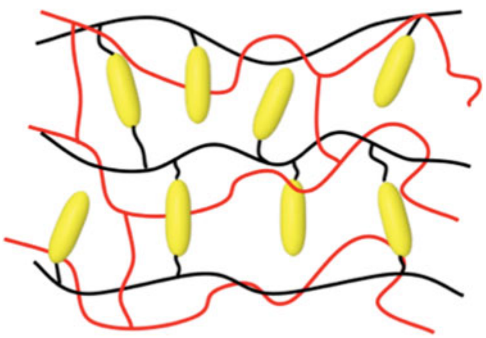

**Figure 1.** Schematic illustration of IPN structures.

crosslinked azobenzene LCP film is irradiated at 366 nm, *trans*-*cis* isomerization of azobenzene moieties takes place only at the surface region, giving rise to contraction of a surface layer of the film [10]. As a result, the film bends toward the actinic light source. When the bent film is irradiated with visible light to cause *cis*-*trans* back-isomerization, the film returns to its initial flat shape.

Furthermore, various three-dimensional movements such as translational and rotational motions have been achieved with laminated films of a crosslinked photochromic LCP film and a flexible polymer film [11]. In the laminated films, good mechanical properties can be provided, while an adhesive layer between the two layers prevents efficient translation of deformation generated in the photoactive layer to a flexible plastic sheet.

IPNs have received much attention as they can significantly improve mechanical properties of polymers through their unique topological entanglement and interpenetration between networks. IPNs are composed of two or more polymer components that are mixed at a molecular level in network forms [12]. Gong *et al.* improved the toughness and strength of hydrogels by preparing a double-network structure for various combinations of hydrophilic polymers [13]. In this work, we prepared photomobile polymer materials composed of crosslinked azobenzene LCPs and methacrylates (Fig. 1), and explored their photoresponsive behavior.

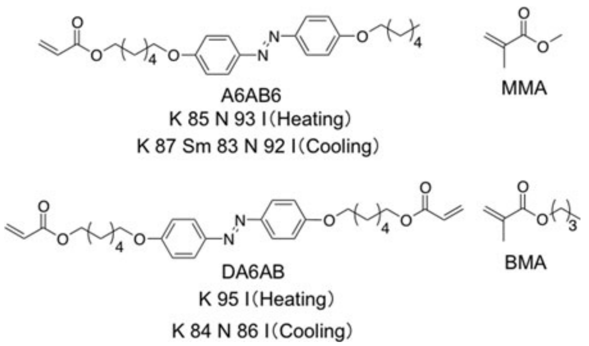

**Figure 2.** Chemical structures of compounds used in this study.

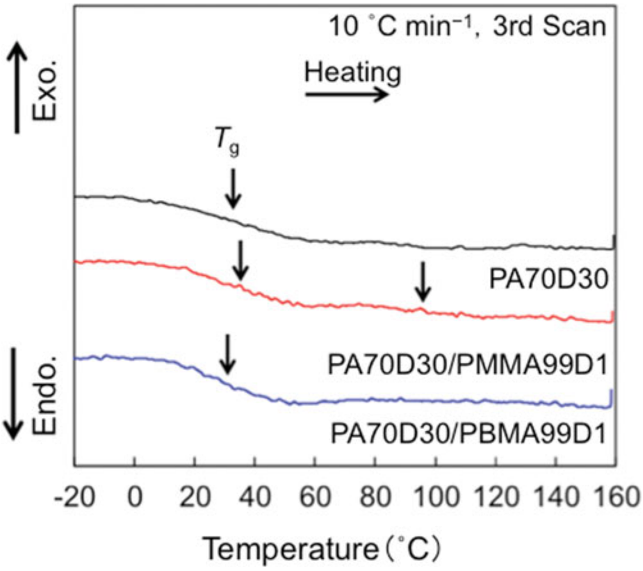

**Figure 3.** DSC thermograms: PA70D30, PA70D30/PMMA99D1 and PA70D30/PBMA99D1. Arrows show $T_g$s.

## Experimental

Chemical structures of compounds used in this study are shown in Fig. 2. LC monomers (A6AB6 and DA6AB) were prepared according to a previously reported method [14]. Methyl methacrylate (MMA) and butyl methacrylate (BMA) were purified by washing with base and distillation under reduced pressure before used. Crosslinked LCP films were prepared by *in situ* photopolymerization. The mixture of A6AB6 and DA6AB with a ratio of 70/30 (mol%) containing 2 mol% of a photoinitiator (Irgacure784) was melted and injected into a glass cell (cell gap: 16 $\mu$m) coated with rubbed polyimides at 110°C. Then it was cooled down to an LC temperature (88°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. The film is referred to as PA70D30. After polymerization, PA70D30 was swollen with anisole containing MMA or BMA, DA6AB with a ratio of 99/1 (mol%) and 1 mol% of 2,2′-azobisisobutyronitrile. Then the mixtures were thermally polymerized at 80°C to obtain IPN films, PA70D30/PMMA99D1 and PA70D30/PBMA99D1. After polymerization, the IPN films were dried under reduced pressure.

Thermal properties of pristine PA70D30 and IPN films were investigated by differential scanning calorimetry (DSC; SHIMADZU, DSC-60) at a heating rate of 10°C min$^{-1}$. Photoinduced bending and unbending of the films were brought about by irradiation with UV light (366 nm, 10 mW cm$^{-2}$) and visible light (>540 nm, 50 mW cm$^{-2}$) from the high-pressure mercury lamp. The durability of the films was explored by scratching with graphite.

## Results and Discussion

Thermal properties of pristine PA70D30 and IPN films were investigated by DSC. Figure 3 shows DSC thermograms of the films. PA70D30 and PA70D30/PBMA99D1 exhibited only

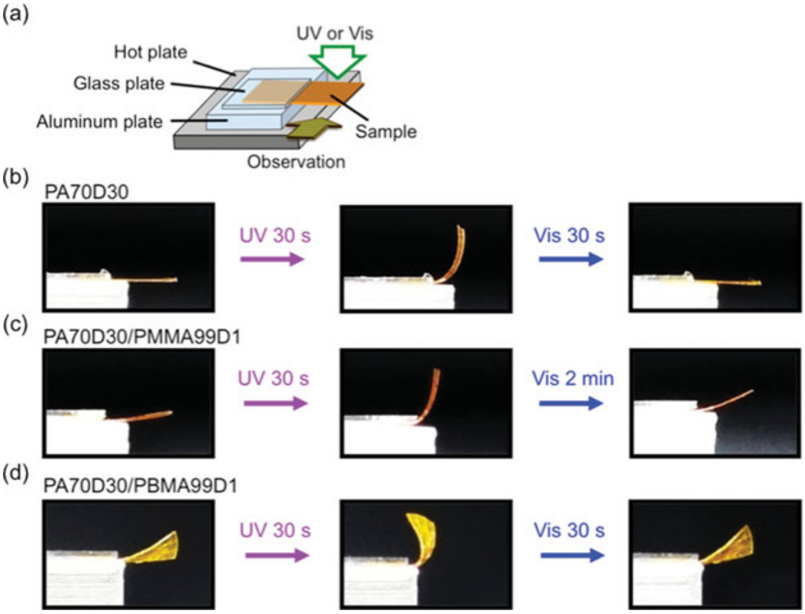

**Figure 4.** The photoresponsive behavior of PA70D30 and IPN films at 65°C. (a) Schematic illustration of the experimental setup; (b) Photographs of PA70D30, (c) PA70D30/PMMA99D1 and (d) PA70D30/PBMA99D1. Size of the films: 3 mm × 1 mm × 16 $\mu$m.

one glass transition temperature ($T_g$) at ~30°C, whereas PA70D30/PMMA99D1 showed two $T_g$s at ~30°C and ~95°C. The glass transition at ~30°C can be assigned to $T_g$ of PA70D30 component. $T_g$ at ~95°C in PA70D30/PMMA99D1 derives from the PMMA component. This result indicates that the PA70D30/PMMA99D1 film is composed of partially mixed double network structures. PA70D30/PBMA99D1 shows only one inflection point because $T_g$ of PBMA is close to that of PA70D30 [15].

We explored the photoresponsive behavior of pristine PA70D30 and IPN films at 65°C and room temperature. As shown in Fig. 4a, part of a film was sandwiched between an aluminum plate and a glass plate and heated with a hot plate.

When pristine PA70D30 and IPN films were irradiated with UV light (366 nm, 10 mW cm$^{-2}$) at 65°C, all films bent toward the light source (Figure 4b, c and d). The bent films reverted to the initial states when irradiated with visible light (>540 nm, 50 mW cm$^{-2}$). The bending angle of PA70D30 and IPN films as a function of irradiation time is shown in Fig. 5. The photoinduced bending and unbending behavior of PA70D30/PBMA99D1 was similar to that of the pristine PA70D30 film at 65°C (Figure 5a and b). However, the bending speed of the PA70D30/PMMA99D1 film was lower than the others. These results indicate that bending behavior of IPN films depends on $T_g$ of methacrylate components. When PA70D30 and IPN films were exposed to light at room temperature, the films showed the reversible bending as shown in Fig. 5c and d. Bending and unbending of the PA70D30/PBMA99D1 film was similar to that of the pristine PA70D30 films also at room temperature.

Next, the durability of films was investigated by the scratching test using graphite with various hardnesses. The pristine PA70D30 film was fragile and broken easily by scratching with graphite at 10 B. In contrast, the PA70D30/PMMA99D1 film was not broken with the graphite at 6 B and the PA70D30/PBMA99D1 film survived at 8 B (Fig. 6). These

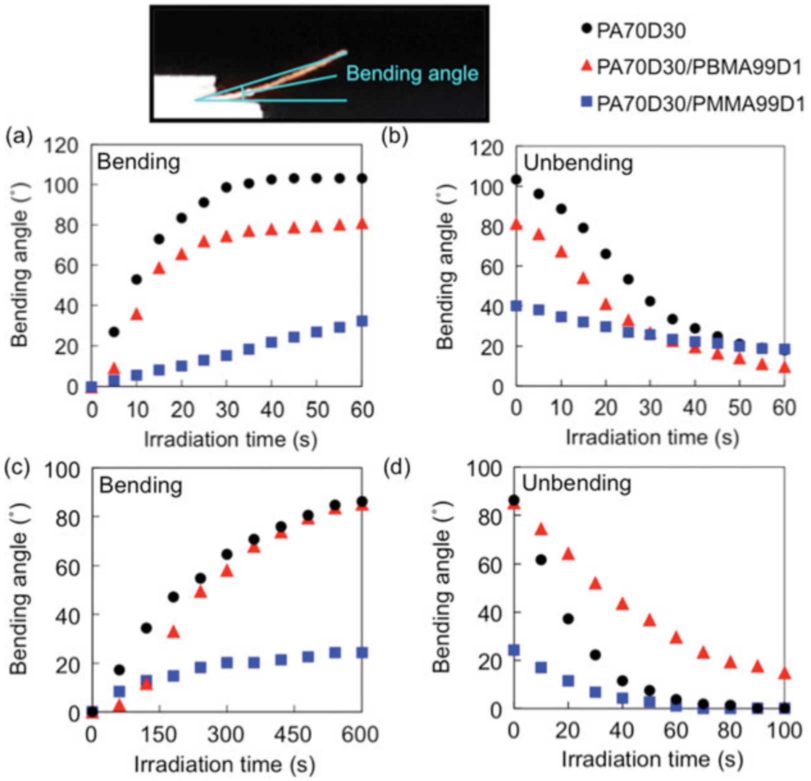

**Figure 5.** (a) Bending angle as a function of irradiation time with UV light (366 nm, 10 mW cm$^{-2}$) and (b) visible light (>540 nm, 50 mW cm$^{-2}$) at 65°C; (c) Bending behavior of the films on irradiation with UV light and (d) visible light at room temperature. Size of the films: 3 mm × 1 mm × 16 $\mu$m.

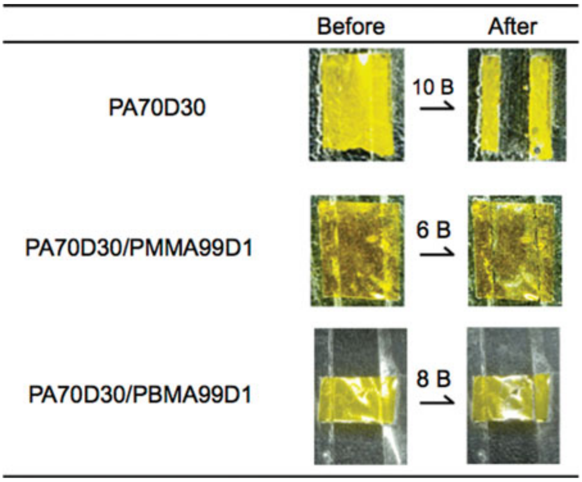

**Figure 6.** Hardness test of the PA70D30 and IPN films.

results suggest that the toughness of the films was drastically enhanced by introducing the methacrylate components.

## Conclusion

We prepared photomobile polymer materials composed of crosslinked azobenzene LCPs and methacrylates with IPN structures. Upon exposure to UV light, the films exhibited photoinduced bending and the bent films reverted to the initial states when irradiated with visible light. Bending behavior of IPN films depends on $T_g$ of methacrylate components. Moreover, the durability of the IPN films was drastically improved as compared with the pristine PA70D30 film.

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