A rapid photomechanical switching polymer blend system composed of azobenzene-carrying poly(vinylether) and poly(carbonate)

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Abstract

A new material with photomechanical switching ability was developed. The material is a binary polymer blend composed of a poly(vinylether) having azobenzene moiety in the side chain and a polycarbonate as a matrix. Upon switching UV-irradiation on and off, the developed polymer blend showed deformation that was both rapid and reversible. This observed photomechanical effect is attributed to a reversible modulus change in the polymer blend, arising from an UV-controlled isomerization of the azobenzene moiety, causing a switching behavior between its highly aggregated and dissociated states. These two states are the physical crosslinking and decrosslinking of the polymer chains.
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1. Introduction

Photo-responsive materials containing photochromic moieties have been widely studied over the past couple of decades because of their unique optical properties [1–4]. Among these materials, the polymers containing azobenzene moiety and having photomechanical properties have been the subject of intense interest in recent years owing to their potential applications to nano- and micro-scale devices such as sensors and actuators [5–12]. Recently, a large degree of deformation has been attained by employing various materials with highly sophisticated molecular designs and combinations. For example, Finkelmann et al. have reported on liquid crystal (LC) networks containing

azobenzene groups [8]. Cviklinski et al. theoretically predicted the possibility of a large deformation of LC elastomers, promoting several experimental investigations in this area [9]. Ikeda et al. have reported on cross-linked LC gels showing photo-stimulated actuation behavior that results from a photoselective volume contraction [10–12].

Our research interest is in clarifying the photo-responsive behavior of azobenzene-related molecules in polymer matrices with the aim of applying this fundamental knowledge to the development of photo-responsive materials with simpler designs. In this way, such materials could then be obtained without the need for cumbersome and complicated synthesis and fabrication processes. Herein, we wish to report on a new binary polymer blend system composed of a polycarbonate matrix and a linear azobenzene-carrying polymer (Scheme 1). The polymer is a poly(vinylether), which has received little attention despite its poly(acrylate) counterparts having been extensively studied [8,11]. The key feature of the present polymer blend system is its rapid mechanical response to switching UV-irradiation on and off at ambient temperatures.

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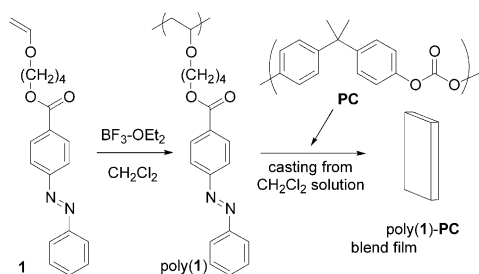
Scheme 1. Preparation of the blend film of poly(vinylether) having azobenzene pendant and polycarbonate.

2. Experimental

2.1. Materials

The vinyl ether monomer and polymer were synthesized according to the procedures described below. Polycarbonate was purchased from Scientific Polymer Products, Inc. Dehydrated tetrahydrofuran (THF) was purchased from Kanto Chemicals Co., Ltd. The other regents and solvents were purchased from Tokyo Kasei Co., Ltd, and were used as received.

2.2. Measurements

Fourier transform infrared (FT-IR) spectrum was recorded with Perkin–Elmer spectrum one. ^{1}H and ^{13}C NMR spectra were recorded with JEOL Lambda-300 with tetramethylsilane as an internal standard; the δ and J values were given in parts ppm and Hz, respectively. *Trans-* and *cis-*forms of the azobenzene group in the monomer and polymer were investigated using an UV–vis spectrophotometer (JASCO, V-570). Differential scanning calorimetry (DSC) measurements were carried out under a nitrogen flow of 20 mL min^{-1} at a 10 °C min^{-1} heating rate using a Seiko DSC-6200. High-resolution electron ionization mass spectrometry (HR-EIMS) was recorded on a JEOL LMS-HX-100. The molecular weight of polymer was measured on a gel permeation chromatography (GPC) system with refractive index (RI) and ultraviolet detectors using polystyrene standards with low polydispersity values, and using chloroform as an eluent. The photomechanical switching behavior was examined by using a 200 mercury–xenon lamp (MORITEX Co., MUV-202-U) equipped with a cut filter (Edmund, model no. 43103-F) for UV irradiation (365 nm) and a heat cut filter (Schott, KG-1). The strain change and Young's modulus for each film were measured using a Seiko TMA/SS6100.

2.3. Synthesis and characterization of the monomer 1

To a solution of 4-vinyloxybutanol (0.59 g, 5.1 mmol), triethylamine (1.03 g, 10.2 mmol), and 4-(dimethylamino) pyridine (50 mg, 0.40 mmol) in THF (30 mL), a solution of azobenzene-4-carbonyl chloride (1.0 g, 4.1 mmol) in THF

(20 mL) was added dropwise at 0 °C for 1 h. After stirring for 24 h at room temperature, the resulting mixture was filtered to remove triethylamine hydrochloride, concentrated under reduced pressure, and fractionated by column chromatography (silica gel; eluent, hexane:ethylacetate = 1:4 (v/v)) to obtain monomer **1** as an orange solid (1.06 g, 3.3 mmol, 80% yield). Melting point: 60 °C; FT-IR (KBr) :(cm^{-1}) 3060, 3050 (ν_{CH}, aromatic ring), 2956, 2874 (ν_{CH}, CH$_2$), 1720 ($\nu_{C=O}$, carboxylic group), 1615 ($\nu_{C=C}$, O–CH=CH$_2$), 1601 ($\nu_{C=C}$, aromatic ring), 1497 ($\nu_{N=N}$, azo group), 1279 ($\nu_{as\ C-O}$, C(=O)–O), 1210, 1196 ($\nu_{as\ C-O-C}$, C–O–C=C), 1121, 1080 ($\nu_{sy\ C-O-C}$, C–O–C=C), 777, and 697 (δ_{CH}, mono-substituted aromatic ring); ^{1}H NMR (CDCl$_3$): δ (ppm) 1.8–2.0 (4H, m, –CH$_2$CH$_2$–), 3.77 (2H, t, ^{3}J=5.96 Hz, –CH$_2$–O–C=C), 4.01 (1H, d-d, $^{2}J_{gem}$=2.02 and $^{3}J_{cis}$=6.79 Hz, CHH=), 4.20 (1H, d-d, $^{2}J_{gem}$=1.84 and $^{3}J_{trans}$=14.31 Hz, CHH=), 4.40 (2H, t, ^{3}J=6.15 Hz, –CH$_2$–O(C=O)), 6.49 (1H, d-d, $^{3}J_{cis}$=6.88 and $^{3}J_{trans}$=14.40 Hz, –O–CH=), 7.51–7.58 (3H, m, aromatic H *meta* and *para* to C–N=N), 7.94–7.97 (4H, aromatic H *ortho* to C–N=N), 8.18–8.21 (2H, aromatic H *ortho* to C(=O)–O); UV: $\lambda_{max,trans}$=326 nm, $\lambda_{max,cis}$=457 nm; ^{13}C NMR (CDCl$_3$): δ (ppm) 25.45, 25.75, 64.89, 67.23, 86.48, 122.61, 123.12, 129.15, 130.56, 131.68, 131.94, 151.75, 152.50, 155.07, 165.98; HR-EIMS: C$_{19}$H$_{20}$O$_3$N$_2$ (M/Z=324.3794).

2.4. Synthesis and characterization of poly (1)

To a solution of monomer **1** (1.01 g, 3.1 mmol) in dichloromethane (10 mL), boron trifluoride diethyl ether complex (64 μL, 70 μmol, 20.68 mol% to the monomer) was added at −45 °C under a nitrogen atmosphere, and the resulting solution was stirred at the same temperature for 60 min. The reaction was quenched by the addition of cold pyridine (2 mL) and the mixture was then poured into 100 mL of cold ether. The formed precipitate was collected by filtration with suction, washed with ether, and dried overnight under vacuum to obtain the homopolymer of **1** (0.71 g, 70% yield) as a red solid. FT-IR (KBr): (cm^{-1}) 3063 (ν_{CH}, aromatic ring), 2944, 2869 (ν_{CH}, CH$_2$), 1717 ($\nu_{C=O}$, carboxylic group), 1603 ($\nu_{C=C}$, aromatic ring), 1497 ($\nu_{N=N}$, azo group), 1273 ($\nu_{as\ C-O}$, C(=O)–O), 1219 ($\nu_{as\ C-O-C}$, C–O–C=C), 1109, 1095 ($\nu_{sy\ C-O-C}$, C–O–C=C), 777, and 697 (δ_{CH}, aromatic ring); ^{1}H NMR (CDCl$_3$): δ (ppm) 1.6–1.9 (6H, >CH–CH$_2$–, –CH$_2$–CH$_2$–), 3.46 (3H, –CH$_2$–O–CH<), 4.28 (2H, –CH$_2$–OC(=O)–), 7.39 (3H, aromatic H *meta* and *para* to C–N=N), 7.77 (4H, aromatic H *ortho* to C–N=N), 8.01 (2H, aromatic H *ortho* to C(=O)–O); UV: $\lambda_{max,trans}$=326 nm, $\lambda_{max,cis}$=457 nm.

3. Results and discussion

Scheme 1 shows the preparation of a film of the blend polymer. The poly(vinylether), having an azobenzene pendant, was synthesized by a conventional cationic
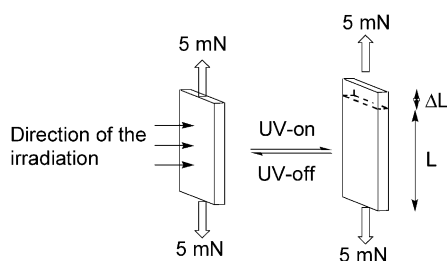
Scheme 2. Schematic of the TMA experimental setup.

polymerization of a new azobenzene-containing monomer **1**, which was readily obtained by the condensation reaction of azobenzene-4-carbonyl chloride and 4-vinyloxybutanol. The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the poly(**1**) were estimated by size exclusion chromatography (SEC) to be 11,500 and 36,000, respectively. The obtained poly(**1**) and

polycarbonate (PC; $M_w = 60,000$) were dissolved in dichloromethane, and the resulting solution containing these two polymers in a 90:10 weight ratio with 1 wt% concentration was applied to a glass surface to obtain the corresponding cast film. The morphology of the homogeneously blended film was confirmed by DSC analysis: poly(**1**) inherited the intrinsic flexible structure of the poly(vinylether)s and exhibited a low glass transition temperature (T_g) at 16 °C, whereas PC exhibited it at 146 °C. On the other hand, in the DSC profile of the blend system, these glass transitions for the original two polymers disappeared, and a single transition was observed at 101 °C, indicating the successful formation of a homogeneous blend without segregation of the polymers.

The photo-response behavior of the obtained blend film was investigated using a thermal mechanical analyzer (TMA). During the TMA measurement, the film was subject to a constant tensile stress of 150 mN mm^{-2} (Scheme 2).
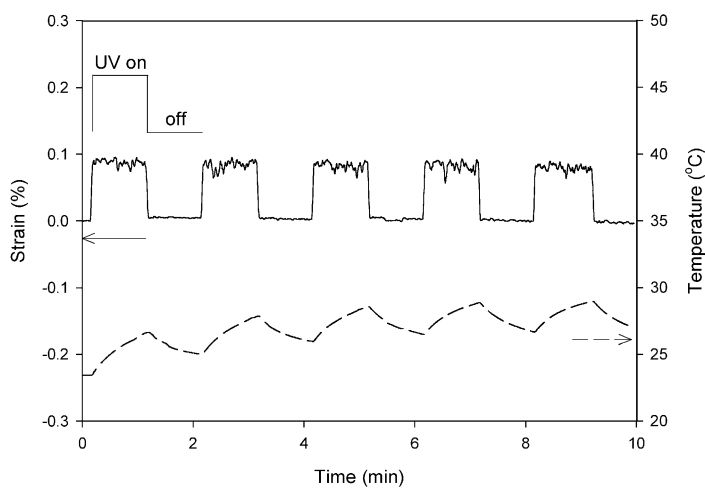
(a)
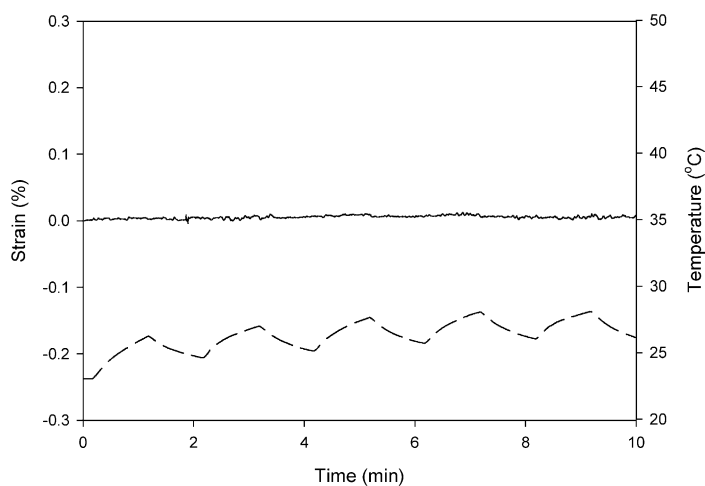
(b)

Fig. 1. Strain for (a) blend film and (b) PC film under switching of UV light.
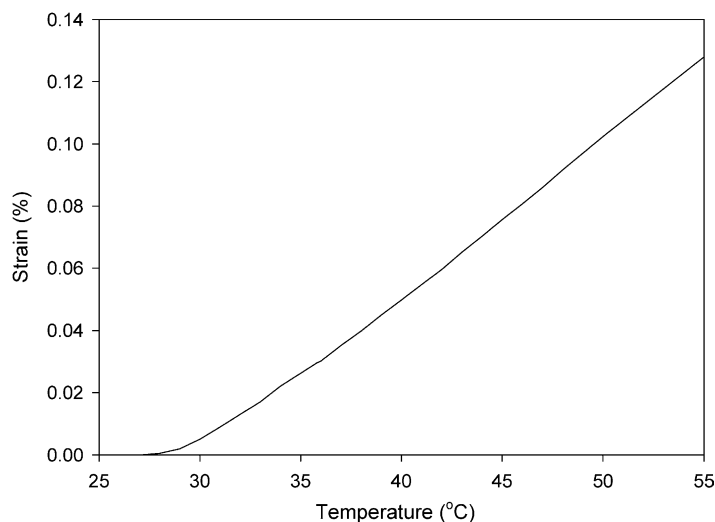
Fig. 2. Strain as a function of temperature for blend film.

This load is in a force range sufficient to cause elastic deformation of the film. The film was irradiated normal to its surface with filtered UV (365 nm) at an intensity of 50 mW cm^{-2} generated by a 200 W mercury–xenon lamp. During the experiment, the film temperature was maintained in a range of 25–29 °C by placing a heat absorption filter between the film and the lamp. By this means, the change in length of the film (size: 15×3 mm^2, thickness: 11 µm) induced by UV-irradiation was accurately measured.

When the polymer film was irradiated with UV, its elongation in the direction of the tensile load was observed. The degree of strain ($\Delta L/L_0$) reached a maximum at 0.1% when the UV-absorption of film reached saturation point (Fig. 1(a)). Upon turning off the irradiation, the film rapidly returned to its original length. The surprising feature was the rapid response displayed in the reversible deformation of the film. The time taken to reach saturation with UV-irradiation turned on and the time to recover with the irradiation turned off were both approximately 2 s. This corresponds to a rate of more than 3 µm s^{-1}; reversible changes of unprecedented rapidity. The reversible deformation of the film could be repeated by switching the UV-irradiation on and off (in Fig. 1(a), only five cycles of the reversible and rapid photo-response of the film were demonstrated, but actually more cycles could be successfully performed). As shown in Fig. 1(b), the PC matrix itself did not show any mechanical response to the UV switching, suggesting that the reversible E–Z isomerization of the azobenzene moiety was responsible for the reversible deformation. Any significant thermal effect on the deformation was excluded by studying the time–temperature relationship (shown as a dotted line): when UV was turned on, the temperature around the film became high, but its response to the UV-switching was quite sluggish, nothing like the rapid deformation, suggesting that the change in the temperature in Fig. 1(a) had no significant effect on the deformation. In addition, the slow cooling process after turning the UV off could not explain the rapid

recovery of the film to its original size. We further studied the temperature–strain relationship, loading a constant tensile stress (150 mN mm^{-2}) by TMA. As shown in Fig. 2, to achieve a 0.1% elongation of the film length required heating the film to 50 °C. This temperature is rather higher than that observed in the UV-switching experiment, and it is hard to believe that the UV-irradiation could effectively heat the film to 50 °C so quickly.

The reversible deformation of the film under a constant tensile load can be correlated with the photo-response change in the modulus of the film: Fig. 3 shows the stress–strain profile of the film, which was measured by TMA under a controlled tensile stress so that the strain of the film constantly increased (100 µm min^{-1}). During the experiment, UV-irradiation was switched on and off several times, producing a significant change in the modulus, and, throughout the whole process, the modulus values under irradiation were smaller than those obtained in darkness. In other words, UV-irradiation induced a decrease in Young's modulus of the film, allowing the film to be elongated by the
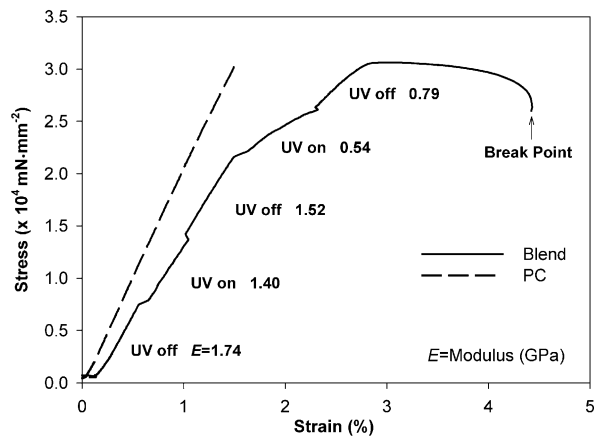

Fig. 3. Stress vs strain profiles for the blend film and the PC-matrix under switching of UV light.
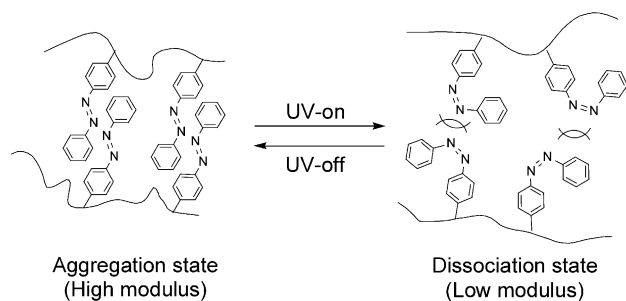
Fig. 4. Schematic model for the UV-induced change in the modulus.

applied load, which supplied a constant external tension. Turning off the irradiation led to the film recovering its original elasticity and thus returning to its original length. To provide a control for the experiment, the stress–strain relationship for the PC matrix itself was studied. As shown by the dotted line in Fig. 3, the matrix did not show any response when the UV-irradiation was turned on and off with the same switching interval. This also suggests that variables such as the unavoidable change in temperature during the experiment could be disregarded.

The mechanism for the UV-induced change in the modulus can, with the assistance of the model described in Fig. 4, be tentatively explained as follows: Generally, the *trans*-form of the azobenzene group is almost planar with relatively extended conformation, and this feature is considered to be the origin of the strong intermolecular π–π attractive interaction for the self-aggregation tendency of *trans*-azobenzene [13]. The resulting aggregation is destroyed by the photo-induced isomerization to produce *cis*-azobenzene that has a folded molecular shape, and no longer allows the efficient aggregation through the π–π attractive interaction. This reversible aggregation-dissociation behavior was inherited by the azobenezene-containing polymer, resulting in the switching of a physical crosslink of the polymer through the non-covalent bond. This reversible physical crosslinking-decrosslinking of the polymer must have a strong influence on the physical properties of the whole blend system, because poly(**1**) and the PC-matrix are blended at a molecular level. This hypothetical mechanism is consistent with the fact that turning off the UV-irradiation triggered the recovery of the modulus, suggesting the recovery of the physical crosslink occurred by regeneration of the *E*-azobenzene moiety, which has an aggregation tendency.

4. Conclusions

In conclusion, the present material, obtained as a polymer blend of the azobenzene-carrying poly(vinylether) and polycarbonate, has several favorable features that have been difficult to achieve in previous systems: (1) It shows photo-responsive deformation without needing an external heat supply. (2) The deformation that occurs is reversible and can be repeatedly switched by turning on and off UV-irradiation. The system, therefore, does not require a UV-visible dual photo-apparatus used for the conventional photo-responsive systems. (3) The deformation responds rapidly to the photo-switching with a response rate of the order of a few seconds.

Besides these physical aspects, the ease of preparation of the material is another feature that makes the present system highly attractive. Optimization of the present system and its application to new photo-actuator systems that have an amplified mechanical motion is currently proceeding.

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