Photoreaction and molecular reorientation studies of ultra-violet light irradiated azobenzene containing polymer films using two-dimensional correlation infrared spectroscopy

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Abstract

A photosensitive polymer with azobenzene side groups was synthesized from free radical polymerization and characterized. Photoreaction and photoinduced molecular reorientation was investigated in films of poly(4-methacryloyloxyazobenzene) (PMAAz) through ultraviolet (UV) absorption spectra and two-dimensional (2D) correlation analyses of their infrared (IR) spectra. The PMAAz polymer molecules were found to undergo trans–cis photoisomerization upon UV irradiation. The fraction of the cis-isomer of azobenzene increased with an increasing UV light exposure dose. The analysis of the 2D IR correlation spectra revealed that the isomerization of azobenzene chromophores induced molecular movement of azobenzene moiety as well as alkyl main chains in PMAAz films. The mono-substituted benzene ring changed sooner than the para-substituted benzene ring for trans–cis isomerization. The azobenzene chromophores in the PMAAz film induced the molecular reorientation by photoreaction in the following sequence: mono-substituted benzene ring → N→Φ bond → cis-N=N→ → para-substituted benzene ring.

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1. Introduction

Polymers containing the azobenzene moiety have attracted interest in both the academic and industrial communities, because of their special photochemical properties and potential applications. It is well known that the azobenzene group has two configurations, the trans-isomeric form and cis-isomeric form. The trans–cis isomerization occurs when azobenzene moieties are exposed to light and treated by heat. The trans–form of azobenzene derivatives is rod-like, whereas the cis–form is bent. These changes in the chemical structure of azobenzene groups via photoisomerization in polymer films are accompanied by changes in the polymer properties, such as the phase, conformation and optical properties [1–3]. Therefore, polymers bearing azobenzene derivatives reveal liquid crystalline [4–6] and nonlinear optical properties [7,8], photochromism and photoinduced optical dichroism [9,10]. These properties are also of great interest due to the potential application of azobenzene bearing polymers. Therefore, these polymers have been extensively studied in an attempt to apply them in different technological fields, such as optical information storage, waveguides, chemical photo receptors, and special devices based on molecular switches and photo-responsive materials [1–10].

Recently, the control of azobenzene derivatives has been studied in an attempt to understand the nature of the azobenzene moieties in the bulk and at the surface [11–15]. Several different methods can be applied to prepare an azobenzene surface layer. One of the approaches is based on the use of self-assembled monolayers (SAM) attached to the substrate surface [16,17]. A second approach utilizes the Langmuir–Blodgett (LB) film method [18,19]. This approach has been intensively studied because the LB technique allows for the possibility of producing molecularly tailored azobenzene layers. A third approach is the conventional spin coating method using polymers containing azobenzene derivatives [20,21]. The spin coating method has also been studied intensively, because it provides a simple way to obtain polymer films. However, the sequence of reorientation for the azobenzene moieties and its photoproducts during photoreaction has not been investigated yet.
Two-dimensional (2D) correlation spectroscopy has been generalized through rigorous research over the past decade and applied extensively to the analysis of spectral data obtained during the observation of a system under some external perturbation [22–25]. Moreover, 2D correlation spectroscopy can analyze systematic patterns of subtle spectral changes induced by an external perturbation that are not readily noticeable in conventional one-dimensional spectra. The details of this technique were described previously [22–25].

In this study, 2D correlation spectroscopic analysis was extended to the photochemistry of poly(4-methacryloyloxyazobenzene) (PMAAz) (see the chemical structure shown in Fig. 1). The photochemistry of PMAAz in films was examined using ultraviolet–visible (UV–visible) spectroscopy and 2D correlation analyses of the Fourier transform infrared (FTIR) spectroscopy. And the reorientation sequence of the chromophore and the main chain in the films was determined.

2. Experimental

2.1. Materials

All of the chemicals, including methacrylic acid, N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDAC), 4-hydroxyazobenzene, 4-dimethylaminopyridine (DMAP) and azobisisobutyronitrile (AIBN), were purchased from the Aldrich Chemical Company and used without further purification. Tetrahydrofuran (THF) and dichloromethane (MC) were distilled over calcium hydride under a nitrogen atmosphere.

2.2. Synthesis of polymer

4-Hydroxyazobenzene (2.44 g, 12.3 mmol), methacrylic acid (1.06 g, 12.3 mmol) and EDAC (2.36 g, 12.3 mmol) were dissolved with a DMAP catalyst (0.15 g, 1.23 mmol) in dry MC, and the reactant mixture was stirred at ambient temperature for 12 h. After stirring, the reaction solution was filtered, and the solvent was removed by rotary evaporation. The residue was purified using column chromatography [SiO2, MC/ethylacetate (45:1 in volume)] to yield 4-methacryloyloxyazobenzene (yield: 74%). The product was determined to be 4-methacryloyloxyazobenzene using a proton nuclear magnetic resonance (1H NMR) spectrometer (Bruker Aspec 300 MHz) with deuterated chloroform (CDCl3). 1H NMR (300 MHz, CDCl3): δ = 7.88 (m, 4H, ArH), 7.43 (m, 3H, ArH), 7.20 (m, 2H, ArH), 6.31 (s, 1H, Ar—CH=), 5.72 (s, 1H, CH=CH—Ar), 2.01 (s, 3H, CH3).

A solution of 4-methacryloyloxyazobenzene (1.62 g, 6.11 mmol) and AIBN (0.05 g, 0.3 mmol) in dried THF was heated at 60 °C overnight. After cooling to room temperature, the reaction mixture was poured into 300 mL of hot methanol. The precipitate was filtered, washed with methanol, and dried under vacuum to produce a 71% yield of poly(4-methacryloyloxyazobenzene) (PMAAz) (see Fig. 1). The molecular weight of the polymer product was determined by a gel permeation chromatography (GPC) system (Polymer Labs Model PL-GPC 210) equipped with a set of four columns (Alltech Jordi 100A, 1000A, 10,000A, and 100,000A), which was calibrated free radical polymerization using a series of polystyrene standards free radical polymerization with Mn(weight averaged molecular weight) in the range of 2800 to 1,260,000 g/mol. The GPC measurements were carried out with a THF eluent at a flow rate of 1.0 mL/min. The polymer product had a Mn of 37,000 g/mol and a polydispersity of 2.13. The glass transition temperature, Tmax, was determined using a differential calorimeter (DSC) (Seiko DSC 220CU) with a 10.0 K/min ramping rate under a nitrogen atmosphere. The glass transition temperature of PMAAz free radical polymerization was 120.1 °C. The polymer product was determined to be PMAAz by 1H NMR spectroscopy in CDCl3. 1H NMR (δ, CDCl3): δ = 7.71 (m, 4H, ArH), 7.32 (m, 3H, ArH), 7.18 (m, 2H, ArH), 2.33 (s, 3H, CH3), 1.46 (m, 2H, C—CH).

2.3. Film preparation

For the FTIR spectral measurements, the polymer films were obtained by spin casting a 1.0 wt.% solution in chloroform onto sodium chloride (NaCl) windows (25 mm diameter × 2 mm thick). The films were then dried at room temperature for 12 h under vacuum.

2.4. Measurements

The polymer films were irradiated with UV light with a wavelength in the range of 260–380 nm using a high pressure 1.0 kW Hg lamp system (Altech Inc.) with an optical filter (Miles Griot Company). UV–visible absorption spectra were obtained as a function of the exposure dose using a Sinco UV–visible spectrophotometer. The FTIR spectroscopic measurements were carried out in transmission on a Bomem DA8 FTIR spectrometer with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector under vacuum. The film planes of the samples were installed perpendicular to the incident beam direction for all of the transmission FTIR spectra. The 2D correlation spectra were obtained using an algorithm based on a numerical method developed by Noda [22,26,28–30]. The 2D correlation analyses were carried out after the baseline of the FTIR spectra was corrected. A subroutine named KG2D, written in Array Basic language (GRAMS/386; Galactic Inc., NH), was employed in the 2D correlation analyses [27].

3. Results and discussion

The photoactive polymer containing the azobenzene side groups, PMAAz, was prepared from free radical polymerization of 4-methacryloyloxyazobenzene. In the 1H NMR spectrum of the polymer, the protons of the ethylene groups (CH2=C—) in 4-methacryloyloxyazobenzene appeared at 6.31 and 5.72 ppm. However, this chemical shift was not detected for the PMAAz product, indicating that the ethylene group reacted to form the vinyl backbone of the polymer. The molecular weight of the polymer product was determined using GPC. A number average molecular weight (Mn) of 37,000 g/mol and a polydispersity of 2.13 were found for the polymer product. The glass transition temperature (Tg) of 120.1 °C for PMAAz was measured using DSC.

Fig. 2 shows the UV–vis absorption spectra of the PMAAz film irradiated with unpolarized UV light at various exposure doses.
The UV absorption spectra exhibited an absorption maximum at 325 nm, which corresponded to the $\pi-\pi^*$ transition of the trans-azobenzene moiety. The absorption peak at $\lambda_{\text{max}} = 325$ nm decreased drastically with increasing exposure dose. This change was due to the trans–cis isomerization of the azobenzene moiety. The fraction of the cis-isomers in the film were determined using the equation:

$$f_{\text{cis}} = (1 - A_c/A_0)/(1 - e_0/e_1)$$

$A_0$ and $A_c$ are the absorbance at $\lambda_{\text{max}} = 325$ nm measured before and after the exposure to unpolarized UV light [31,32]. The ratio of the molar absorption coefficient ($e_0/e_1$) of the cis and trans-isomers is equal to 0.05 at 325 nm [31,32]. The fractions of the trans- and cis-isomers as a function of the dose of unpolarized UV light are illustrated in the inset of Fig. 2. The fraction of the cis-isomer of azobenzene increased with increasing UV light exposure dose with 21% of the cis-isomer being produced at a dose of 20 J/cm$^2$.

Fig. 3 shows the FTIR spectra of the PMAAz film irradiated with unpolarized UV light for various exposure energies. All of the vibrational bands observed in the spectra were assigned in accordance with previous results [33–36].

The asymmetric CH$_3$ stretching vibrations, asymmetric and symmetric CH$_2$ stretching vibrations, and C=O stretching vibration of ester linkages corresponded to the bands at 2960, 2922, 2850, and 1750 cm$^{-1}$, respectively. All of these vibrations were associated with the polymer’s main chains.

The bands due to the phenyl ring vibrations in azobenzene units were detected in the region of 1400–1600 cm$^{-1}$. Previous works showed that the semicircle stretching of benzene ring appears between 1430–1465 cm$^{-1}$ for mono, ortho, and meta substituted benzene rings and between 1400–1420 cm$^{-1}$ for the para-substituted benzene ring [33–36]. The mono- and para-substituted phenyl ring stretching modes were detected at 1450 and 1415 cm$^{-1}$, respectively. Additionally, the $-\text{N}=\text{N}-$ stretching vibration of the trans-isomer was observed at 1444 cm$^{-1}$ as a shoulder. The band at 1515 cm$^{-1}$ can be assigned to $-\text{N}=\text{N}-$ stretching vibration of the cis-isomer in the azobenzene units [33–36]. As shown in Fig. 3, the new band at 1515 cm$^{-1}$ increased with increasing exposure dose. This observation coincided with UV–vis spectroscopic spectra. This result also confirmed that the PMAAz film underwent trans–cis photoisomerization of the azobenzene side groups.

Fig. 4 displays the synchronous and asynchronous 2D correlation IR spectra of the PMAAz film irradiated with various exposure doses, measured in the range of 2700–3200 cm$^{-1}$. A power spectrum extracted along the diagonal line of the synchronous 2D correlation spectrum is shown at Fig. 4. In the power spectra, the band at 3046 cm$^{-1}$, due to the aromatic C–H stretching vibration in azobenzene moiety, was strongly influenced by the photoisomerization. To investigate the segmental motion of azobenzene moiety by photoisomerization, the sequence of the spectral peaks of the azobenzene chromophores was determined using the synchronous and asynchronous 2D correlation IR spectra of the PMAAz film irradiated with various exposure doses, measured in the range 1100–1700 cm$^{-1}$.

Fig. 5 represents the synchronous and asynchronous 2D correlation IR spectra of the PMAAz film irradiated with various exposure doses. The cross peak at (1450, 1415) cm$^{-1}$ for the mono- and para-substituted phenyl ring stretching in the azobenzene chromophores indicated that the mono-substituted phenyl ring changed more rapidly than the para-substituted phenyl ring. The cross peaks at (1450, 1144) and (1415, 1144) cm$^{-1}$ of the N–$\Phi$ stretching vibration in the azobenzene chromophores at 1144 cm$^{-1}$ with the phenyl ring in the azobenzene groups indicated that mono-substituted benzene ring changed more rapidly than the N–$\Phi$ bond, and the N–$\Phi$ bond changed more rapidly than para-substituted benzene ring. The cross peak at (1515, 1415) cm$^{-1}$ for the cis-N=N- stretching vibration of the photoproduct and para-substituted phenyl ring stretching in the azobenzene chromophores indicated that the cis-N=N- stretching vibration of the photoproduct changed more rapidly than the para-substituted phenyl ring. In addition, the cross peak of cis-N=N- stretching vibration of the photoproduct with mono- substituted phenyl ring stretching in the azobenzene chromophores (1515, 1450) and with the N–$\Phi$ stretching vibration in the azobenzene chromophores (1515, 1144) indicated that the N–$\Phi$ bond and mono-substituted benzene ring changed before the cis-N=N- stretching vibration of the photoproduct.

Collectively, the azobenzene chromophores in the PMAAz film induced molecular reorientation by photoreaction in the following sequence: mono-substituted benzene ring $\rightarrow$ N–$\Phi$ bond $\rightarrow$ cis-N=N$\rightarrow$ para-substituted benzene ring. The isomerization of the azobenzene units induced the movement of phenyl ring. The trans–cis isomerization induced the segmental motions of the mono-substituted benzene ring, N–$\Phi$ bond, cis-N=N$\rightarrow$ and para-substituted benzene ring sequentially. The photoproduct, cis-azobenzene, was produced after the mono-substituted benzene ring and N–$\Phi$ bond were changed. Isomerization via inversion corresponded to the in-plane inversion, whereas isomerization via rotation corresponded to the out-of-plane rotation around the N=N-...
bonds. Furthermore, previous works have reported that trans–cis photo-isomerization is induced by rotation and cis–trans thermal isomerization occurs via inversion [37–39]. These results suggested that trans–cis isomerization occurred via rotation assuming that the out-of-plane rotation of the phenyl ring was accompanied by a phenyl ring change. Then the rearrangement of the N=Φ and N=N bonds free radical polymerization occurred during photoreaction.

4. Conclusions

A photosensitive polymer with photoreactive azobenzene side groups was synthesized. The chemical structure, molecular weight, and thermal properties of the polymer were determined. The PMAAz polymer molecules underwent trans–cis photoisomerization upon UV irradiation. The fraction of cis-isomers in the film increased with increasing UV exposure dose.

Moreover, the molecular motion of the azobenzene chromophores was investigated in the PMAAz film by 2D correlation analysis. The analysis of the 2D correlation IR spectra revealed that the isomerization of the azobenzene chromophores induced molecular movement of the azobenzene moiety as well as the alkyl main chains. The mono-substituted benzene ring changed faster than the para-substituted benzene ring for trans–cis isomerization. The mono-substituted benzene ring also changed sooner than the N=Φ bond for trans–cis isomerization. The azobenzene chromophores in the PMAAz film induced molecular reorientation by photo-reaction in the following sequence: mono-substituted benzene ring → N=Φ bond → cis-N=N → para-substituted benzene ring.

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References
