

Isomerization Behavior of Aromatic Azo Chromophores Bound to Semicrystalline Polymer Films

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ABSTRACT: The *cis*–*trans* isomerization of azo chromophores covalently bound to semicrystalline polymer films was investigated. Various azo chromophores were introduced onto the functionalized semicrystalline polymer films by a chemical transformation reaction and their isomerization behavior was investigated by UV-visible spectroscopy and a contact-angle goniometer. The thermal *Z* → *E* isomerization rate of the azo moiety covalently bound to low-density polyethylene (LDPE) and polypropylene (PP) films was determined. The rate of thermal isomerization was also compared between amorphous and semicrystalline polymer films bearing azo chromophores. The effect of the intramolecular steric factor and the nature of chromophores was studied on the thermal isomerization rate of the polymer films. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2923–2928, 2001

Key words: functionalization; polymer; azobenzene; *cis*–*trans* isomerization

INTRODUCTION

Photoresponsive polymers have great potential for applications in a wide variety of areas, including optical information storage and optical switching systems.¹ For use in a photomemory system, materials containing azobenzene units are promising because these have dipole moments and optical parameters that are highly susceptible to change due to their reversible photoisomerization. The geometrical configuration of the azo bond in azobenzene can be changed reversibly from *trans* (*E*) to *cis* (*Z*) by irradiation with light of an appropriate wavelength. The two states have distinct absorption spectra which allows reversible storage of data on the basis of *cis* and *trans* states.

The real interest in this subject started with liquid-crystalline (LC) polymer films. LC polymers containing azo aromatic mesogenic groups in the side chain or in the main chain offer the possibility to modify the order state by external fields and/or light.^{2–4} The nematic-to-isotropic phase transition and reverse process was successfully induced by the photoisomerization of the azo groups in the polymer. Besides LC polymers, a number of studies have been reported on the *E* ⇌ *Z* isomerization of azobenzene moieties doped in or covalently incorporated into both amorphous polymers and sol–gel glasses.^{5–9} These studies indicate that the isomerization of the azobenzene moiety depends on various factors such as the polarity, viscosity of the local environment, and free-volume distribution around the moiety. It is also observed that the kinetics of the thermal *cis*–*trans* back relaxation of a chromophore embedded in a polymer matrix differs from the behavior in solution.

However, the photoisomerization of the azobenzene moiety covalently bound to the semicrys-

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talline polymer system has not been paid much attention. We, therefore, developed a simple method of attaching various azo moieties onto semicrystalline polyolefin [e.g., low-density polyethylene (LDPE) and polypropylene (PP)] films. We also undertook a study of the influence of different matrices (LDPE, PP), different substituents on the azobenzene moiety, and intramolecular steric effects of chromophores on the thermal isomerization of the azobenzene group covalently bound to semicrystalline polyolefin films.

EXPERIMENTAL

Materials

Commercial samples of LDPE (Indothene 16 MA 400) and isotactic PP (i-PP, Koylene S3030) were obtained from the Indian Petrochemical Corp. Ltd. (Vadodara, India). Maleic anhydride (E. Merck, Mumbai, India) was recrystallized from chloroform and stored under a dry condition. Benzophenone (Aldrich Chemicals, Milwaukee, WI) was recrystallized from ethanol. 4-Aminoazobenzene (E. Merck), 4-(4-nitrophenyl azo)aniline (Aldrich Chemicals), and PCl_5 (S.D. Fine Chemicals, Mumbai, India) were all reagent grade and used as received. Acetone, chloroform, and diethyl ether were obtained from S.D. Fine Chemicals and were distilled before use.

Preparation of Polyolefin Film Bearing Azo Compounds

We described the synthesis and characterization of polymer films bearing azo chromophores elsewhere^{10,11} (Scheme 1). The thickness of the film and concentration of the azo chromophores were adjusted to such a level that the absorbance did not exceed the value of 1 in order to obey the law of Lambert and Beer. The thickness of the film was 60 μm and the concentration of the azo moieties was found to be $\sim 2 \times 10^{-7}$ $\mu\text{mol}/\text{cm}^2$. The concentration of the azo moieties was determined by UV and gravimetric analysis and the depth of the modification of these films was found to be beyond the XPS level as described in our earlier report.^{10,11} The azo moieties are not only present on the surface but also penetrate the bulk (beyond the XPS level) in this reaction condition.

Polyolefin Film Bearing Mono-4-(4-nitrophenyl azo)aniline (3,4)

Film 1 (Scheme 1) was immersed in 3 mL of a 0.01M 4-(4-nitrophenyl azo)aniline solution in

chloroform. The film was allowed to react with 4-(4-nitrophenyl azo)aniline at 30°C for 6 days with occasional stirring. The film was thoroughly extracted using hot chloroform and dried under a vacuum at 30°C for 4 h.

Polyolefin Film Bearing Bis-4-(4-nitrophenyl azo)aniline (5,6)

Film 2 (Scheme 1) was placed in 10 mL of dry diethyl ether containing 2 g of PCl_5 at 30°C for 3 h. The film was removed and immersed immediately in a 0.01M solution of 4-(4-nitrophenyl azo)aniline in chloroform for 2 h at 30°C. The film was rinsed with chloroform and Soxhlet-extracted with acetone for 4 h and dried under a vacuum at 30°C for 4 h.

Preparation of Poly(4-azophenyl *N*-phenyl methacryamide) (7)

Synthesis of Monomer [*p*-(*N*-methacrylyl)aminoazobenzene]

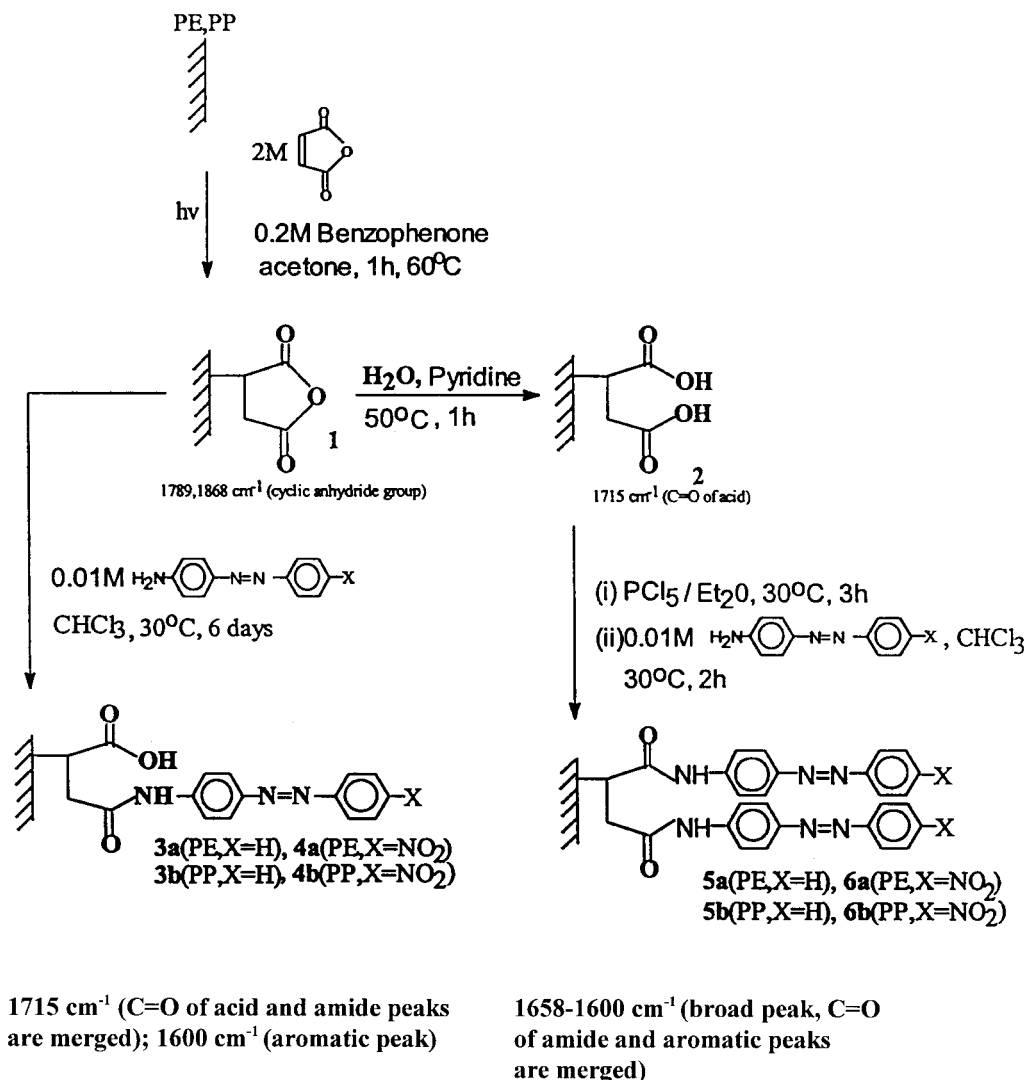
Methacryloyl chloride (8 mL, 0.064 mol) was dissolved in THF (15 mL) and the solution was kept in an ice bath for 10 min. A solution of 4-aminoazobenzene (12 g, 0.064 mol) was added slowly to the above mixture. After the addition of methacryloyl chloride, the resulting mixture was stirred at room temperature overnight. The solvent was removed by applying a vacuum and the residue was dissolved in chloroform, extracted with water, and dried over anhydrous Na_2SO_4 . The solution was filtered and the solvent removed using a rotavapor. The solid product was purified by column chromatography and recrystallized from methanol/water. Yield 60%. ¹H-NMR(δ , CDCl_3): 2.20 (— CH_3), 5.50–5.85 ($\text{CH}_2=$), 6.85 (amide proton), 7.20–8.00 (aromatic proton), mp 151–153°C (literature¹² mp 150–152°C).

Synthesis of Polymer

Polymerization was performed in dry toluene (10 mL) with 10% by weight AIBN as the initiator at 60°C for 4 days. The polymer was precipitated in *n*-hexane and purified by reprecipitation in a THF/*n*-hexane system. The yield was 90%. The polymer had an M_w (GPC) = 7250 (determined relative to PMMA standards) and a T_g of 152°C.

Preparation of Film

Thin film of poly(4-azophenyl-*N*-phenyl methacrylamide) was obtained by dissolving the polymer



Scheme 1 Synthetic methods for modification of polyolefin films with azo chromophores.

in THF and casting onto a clean glass slide as a substrate. The film was allowed to dry initially at room temperature and subsequently at $70^{\circ}C$ for 4 h under a vacuum.

Analysis

FTIR measurements were carried out with a Perkin-Elmer 16PC spectrometer. The polymers (LDPE, PP) were purified to be free of additives and stabilizers and the films were prepared by melt pressing. The methods of purification and sample preparation (60- μm -thick film) were reported.¹⁰ Advancing contact angles were determined on an NRL contact angle goniometer 100-00230. The reported contact-angle values are the

average of at least 10 readings and are accurate to within $\pm 2^{\circ}$. Samples were weighed on a Mettler-M5 microbalance for gravimetric analysis, which has a weighing accuracy of $\pm 0.005\text{ mg}$.

For determination of slow $E \rightleftharpoons Z$ isomerization rates, the films bearing azo chromophores were exposed for 30 min in a 400-W, high-pressure mercury lamp with a Pyrex cooler and a glass filter (Toshiba UV-D33S) to cut off the wavelength below 300 nm and the visible region, long enough to reach a photostationary state. After irradiation, the film was quickly ($< 20\text{ s}$) introduced into a Hewlett-Packard 8452 A diode array UV-visible spectrophotometer and the thermal reversion was monitored by measuring the

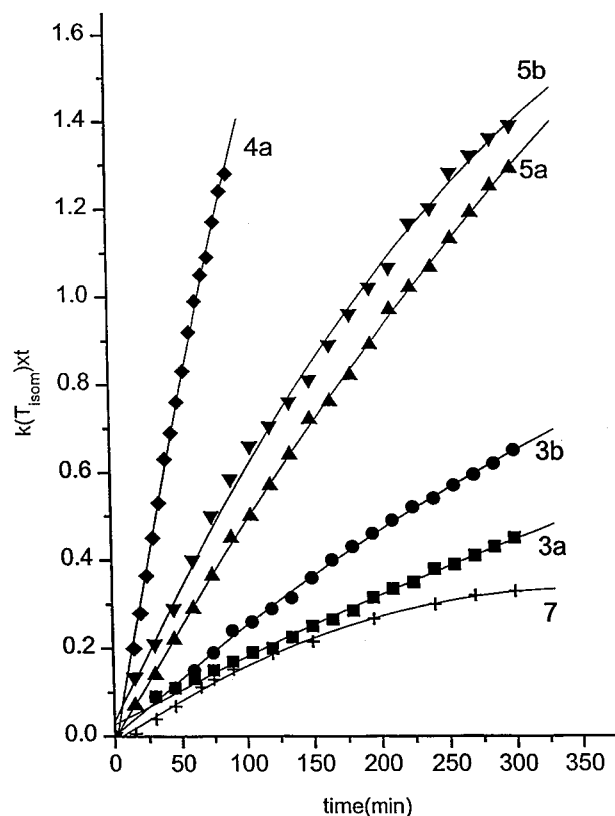


Figure 1 Plots of $K(T_{\text{isom}}) \times t$ versus time t for the polymer (3a–b, 4a, 5a–b) and amorphous azo polymer 7.

change in absorbance of the film at their λ_{max} . The film was exposed to visible light to increase the rate of $Z \rightarrow E$ isomerization for switching experiments using a 25-W light bulb placed at a distance of 5 cm from the film. The thermal isomerization rate constant $K(T_{\text{isom}})$ was determined by performing UV measurements as a function of time. The amount of the E azobenzene group is assumed to be linearly related to its absorbance at $\lambda_{\text{max}}(t)$, since, during the whole process, the absorbance was less than 1. Furthermore, the thermal $Z \rightarrow E$ back-isomerization is an irreversible process.

Kinetic of $E:Z$ Isomerization

By applying eq. (1), $K(T_{\text{isom}})t$ can be computed. Plotting $K(T_{\text{isom}})t$ versus time (t) gives a curve with slope $K(T_{\text{isom}})$ (Fig. 1):

$$K(T_{\text{isom}})t = \ln \frac{A_E - A_Z}{A_E - A_t} \quad (1)$$

A_E is the absorbance reached at infinite time, which is (normally) also the starting situation after storage in the dark before irradiation with UV light. A_Z is the absorbance measured directly after irradiation, and A_t , the absorbance at time “ t ” after irradiation. Values for the absorbance were taken at $\lambda_{\text{max}}(t)$. The half-life times $t_{1/2}$ of the Z state were derived from absorption at

$$t_{1/2} = A_Z + (A_E - A_Z)/2 \quad (2)$$

$$t_{1/2} = \ln 2/K(T_{\text{isom}}) \quad (3)$$

Since eq. (3) assumes a first-order process and $K(T_{\text{isom}})$ was not found to be constant during the process of thermal back-isomerization, $t_{1/2}$ was determined from eq. (2) (Table I). By applying this equation, plotting $K(T_{\text{isom}}) \times t$ versus time (t) presents the nature of thermal relaxation curve (Fig. 1).

RESULTS AND DISCUSSION

Proof of Functionalization

A mild photochemical technique was used to introduce the succinic anhydride moiety onto the polyolefin films (LDPE, PP) (Scheme 1). In this experimental condition, functional groups are not only bound to the surface but also are present in the bulk of the films (beyond the XPS level). In our previous report,¹⁰ we described in detail the

Table I Half-life of Thermal Isomerization of Polyolefin-bound Azo Chromophore and Amorphous Azo Polymer

Polymer Code	λ_{max} (nm)	$t_{1/2}$ (min) ^{a,b}
3a	342	510
4a	380	50
3b	342	300
4b	380	45
5a	342	150
6a	380	40
5b	342	105
6b	380	35
7	344	1080

^a Polymer films were irradiated by UV light for 30 min and thermal relaxation was measured at 25°C.

^b Five samples of each polymer were examined for $t_{1/2}$ measurements; $t_{1/2}$ is the average value with standard deviation ± 2 .

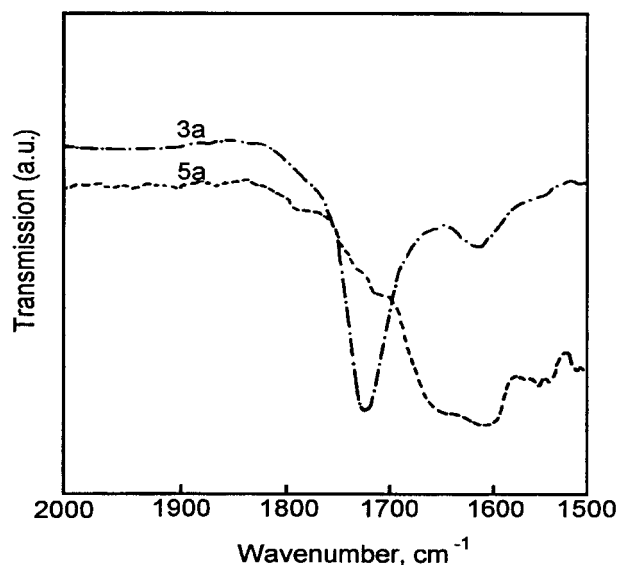


Figure 2 FTIR spectra of samples **3a** and **5a**.

photochemically attachment of the succinic anhydride moiety bound to polyolefin films and its characterization. Thereafter, the azobenzene moiety with different substituents was successfully attached to the functionalized polyolefin films by a chemical transformation reaction (samples **3a-b**, **4a-b**, **5a-b**, **6a-b**) (Scheme 1). The FTIR spectra of the films (**3a-b** and **4a-b**) showed peaks at 1715 cm^{-1} due to acid and amide and an aromatic peak at 1600 cm^{-1} , whereas films **5a-b** and **6a-b** showed amide and an aromatic peak in the range of $1658\text{--}1600\text{ cm}^{-1}$ but no peak due to carboxylic acid (Fig. 2).

Photoisomerization and Wettability

The azobenzene group can be isomerized by irradiation with light of an appropriate wavelength. Isomerization alters the molecular shape and polarity of the azobenzene group. Sample **3a** (Scheme 1) shows the main absorption band ($\pi \rightarrow \pi^*$ transition) at 342 nm , which decreased upon UV light irradiation, indicating that the azobenzene group bound to the polyolefin film could be isomerized from the *E* to the *Z* conformation by irradiation (Fig. 3). However, the *Z* state is thermodynamically unstable with respect to the *E* state, but the complete thermal relaxation process occurs after several hours at an ambient condition. This thermal back reaction can be enhanced by light, temperature, and solvents.^{5,13,14} Transformation from *Z* to *E* was enhanced using visible light on sample **3a**. From Figure 4, it was

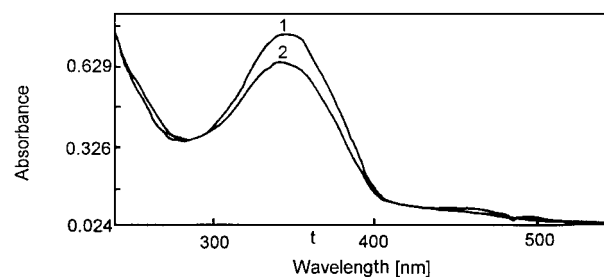


Figure 3 Absorption spectra of **3a** before and after 30 min. UV light irradiation (1 and 2, respectively).

revealed that sample **3a** changed its advancing contact angle from 98° to 90° (*E* to *Z*) after 15-min UV irradiation and thermal relaxation occurred within 15 min when visible light irradiation had been used. At the same time, the absorbance decreased with the UV light irradiation, while it increased with the visible light irradiation.

Kinetics of Thermal *cis* to *trans* Isomerization

To examine the isomerization behavior, azo chromophores were chemically bound to semicrystalline polymer films and various environmental effects were studied. All the films (**3-6**, Scheme 1, and sample **7**) were irradiated by UV light for 30 min. Then, the half-lifetime of the thermal back-isomerization was determined by a kinetic study.

Effect of Structure of Chromophore on Isomerization

The easy availability of an azobenzene group chemically bound to a polyolefin (Scheme 1) af-

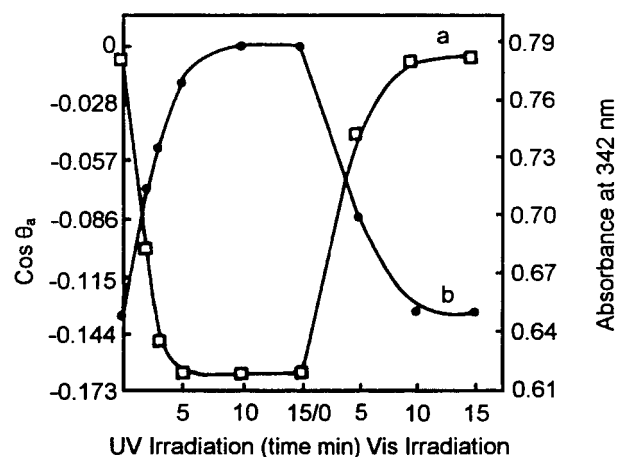


Figure 4 Photoinduced changes in (a) absorbance and (b) wettability (sample **3a**).

forded an opportunity to examine the $E \rightleftharpoons Z$ isomerization of the azo linkage bound to a polymer film. The thermal back-isomerization rate was found to depend on the type of the chromophore.^{5,6} The azobenzene groups without any substituents (electron-donor or electron-acceptor groups) showed relatively slower thermal $Z \rightarrow E$ isomerization.⁶ Similar results were observed in the case of polyolefin film bearing azobenzene and the substituted azobenzene group. Comparison of thermal isomerization rates of **3a** and **4a** (Scheme 1) indicated that the rate of isomerization of **3a** is 10 times slower than that of **4a**, possibly due to the substituent effect of the nitro group (Table I and Fig. 1).

Effect of Nature of Attachment of Chromophore on Isomerization

The rate of thermal isomerization also appears to be enhanced by steric factors.⁵ It was observed that substituting both the carboxylic group with an azobenzene moiety has the effect of accelerating the rate of thermal isomerization of $Z \rightarrow E$. Films **5a–b** and **6a–b**, showed a higher rate of thermal back-isomerization than that of films **3a–b** and **4a–b**, respectively (Table I). This could be due to the intramolecular steric effect of azo chromophores when both the chromophores are present as the Z form.

Effect of Polymer Matrix on Isomerization

We compared the results of $t_{1/2}$ of two semicrystalline polymer films bearing azo chromophores. It was revealed that the PP films **3b**, **4b**, **5b**, and **6b** relaxed faster than did the PE films **3a**, **4a**, **5a**, and **6a**. This observation could be understood in terms of the effect of free-volume distribution in a polymer matrix. Depending on the crystallinity of the polymer, it can be assumed that the effective free volume per azo group is relatively more in LDPE than in PP due to lower crystallinity in the former. Thus, an azobenzene group attached to a PP film relaxed faster than did the one attached to the LDPE film. To understand this well, we synthesized an amorphous azo polymer (**7**) and the kinetic study showed that the amorphous azo polymer film **7** relaxed significantly slow as compared to the semicrystalline polymers films (Table I and Fig. 1). Therefore, the structural compactness of the semicrystalline polymer makes the isomer more unstable, resulting in faster conversion to the stable E state.

CONCLUSIONS

Azobenzene chromophores isomerizes from a thermally stable *trans* form to less stable *cis* form by the irradiation of UV light and the reverse process takes place thermally and/or by visible light irradiation. Thus, surface wettability of the semicrystalline polymer films bearing azobenzene chromophores can be switched on or off by the irradiation of these polymer films with light of an appropriate wavelength. The thermal rate of relaxation depends mostly on nature of the chromophore, intramolecular interaction, as well as the polymer matrix. It was revealed that the azo chromophore containing an electron-acceptor group showed a faster thermal $Z \rightarrow E$ isomerization rate. The steric factor also accelerates the rate of thermal isomerization. It was also observed that the azo chromophore attached to a more crystalline PP film relaxed faster than did the one attached to the LDPE film.

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