

# Synthesis and Photoisomerization Behavior of a Novel Thiazolylazo Polyimide

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Received 12 December 2005; accepted 19 March 2006

DOI 10.1002/app.24545

Published online 9 May 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Polyimide (PI) with thiazolylazo side chain was prepared via a post azocoupling reaction scheme. The PI film could easily be obtained by spin coating and consequent imidization from the precursor polymer, which was soluble in several polar organic solvents such as *N*-methyl-2-pyrrolidine and *N,N*-dimethylformamide. The polymer showed a reverse trans–cis photoisomerization when irradiated by the

lights of 365 nm and 440 nm. The glass-transition temperature ( $T_g$ ) and temperature at 10% of weight loss under  $N_2$  of the polymer are 138.9°C and 510.6°C, respectively, which confirm that the thermal stability of the polymer is quite good. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2460–2464, 2008

**Key words:** polyimide; thiazolylazo; dye; photoisomerization

## INTRODUCTION

In recent years, azo-containing polymers have been widely studied because of their unique photochromic behavior and their potential applications in high-density optical memory and nonlinear optical materials.<sup>1–5</sup>

Side chains were normally used to prevent the relaxation of chromophores in a polymer; therefore, to graft the chromophores-containing side chains to the main chains of various polymers is considered to be one of the best methods for stabilizing chromophores in the polymeric backbones.<sup>6–9</sup> Among all the side chain polymers, polyimide (PI) has attracted much attention because of its excellent thermal stability. In the present work, a novel PI with thiazolylazo side-chains was prepared via a post azocoupling reaction scheme. Since the photoisomerizable azogroups in the novel polymer are very sensitive to UV light, it is interesting to observe the variation of the properties of the polymers irradiated by UV light. The investigation of the present work is emphasized on the photoisomerization of the novel polymer, the microstructure and the thermal properties of the novel polymer were also studied according to the measurements of <sup>1</sup>H NMR, FT-IR, DSC, XRD, TG, and UV–vis.

## EXPERIMENTAL

### Chemical reagents

Aniline (A.R.) was distilled twice under a reduced pressure before use. *N*-Methyl-2-pyrrolidine (NMP)

(A.R.) was distilled under a reduced pressure over  $P_2O_5$  before use. *N,N*-Dimethylformamide (DMF) (A.R.) was dried over 4A molecular sieves. All of the other chemicals were obtained commercially and were used as received. The diazo salt was prepared before use according to that described in Ref. 10.

### Synthesis of monomers and polymers

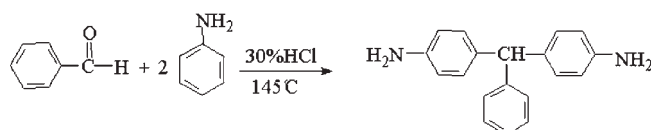
#### 4,4'-Diaminotriphenylmethane

A mixture of benzaldehyde (5.78 mmol) aniline hydrochloride (0.289 mmol) and aniline (57.98 mmol) was stirred for 2 h at 110°C under nitrogen atmosphere and then stirred at 145°C for 1.5 h. The excess aniline was removed by reduced pressure distillation after the mixture was cooled down to 60°C. Then 2 mol/L of HCl was added to the residue and the filtrate was neutralized to pH 7~8 by NaOH of 2 mol/L to obtain a gray deposition. The deposition was then washed by deionized water for several times and recrystallized by ethanol/water twice. Finally, it was dried in vacuum at 60°C for 24 h. The yield was 53% (0.84 g). IR (KBr pellets): 3059, 3090 (C–H, str), 1598.5, 1507.2, 1617.8, 836 (benz ring), 1308 (Cph–N, str)  $cm^{-1}$ . The synthetic route was shown in Scheme 1.

#### 5-Aldehyde-2-amino-4-chlorothiazole

Ethyl chloroacetate (0.1 mol) was added to a mixture of 0.1 mol thiourea and 100 mL acetone with stirring, and refluxed for an hour. The deposit matter obtained by refluxing was dissolved into 300 mL of deionized water, the solution was neutralized to pH = 8 by a saturation solution of sodium carbonate. A white, needle-like crystal was obtained when the neutralized solu-

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**Scheme 1** Synthetic route for DTM.

tion was cooled to below 5°C. The crystal was then filtered, washed, and dried for further synthesis.

$\text{POCl}_3$  (0.25 mol) was dropped slowly to DMF (1 mol) below 5°C, and then 0.125 mol of the needle-like crystal mentioned above was added to the solution. The resultant mixture was stirred for 14 h at 70°C and then was cooled down to room temperature to add in another mixture of sodium acetate (1 mol) and ice water (120 mL). Then, it was stirred at 50°C for 2 h and cooled down to room temperature again. The yellow powders of 5-aldehyde-2-amino-4-chlorothiazole were obtained after the deposit was filtered, washed, and dried. IR (KBr pellets): 3413.3, 3022.23 ( $N-H$ , str), 1703.2 ( $C=O$ ), 1130.68 ( $C-Cl$ )  $\text{cm}^{-1}$ .

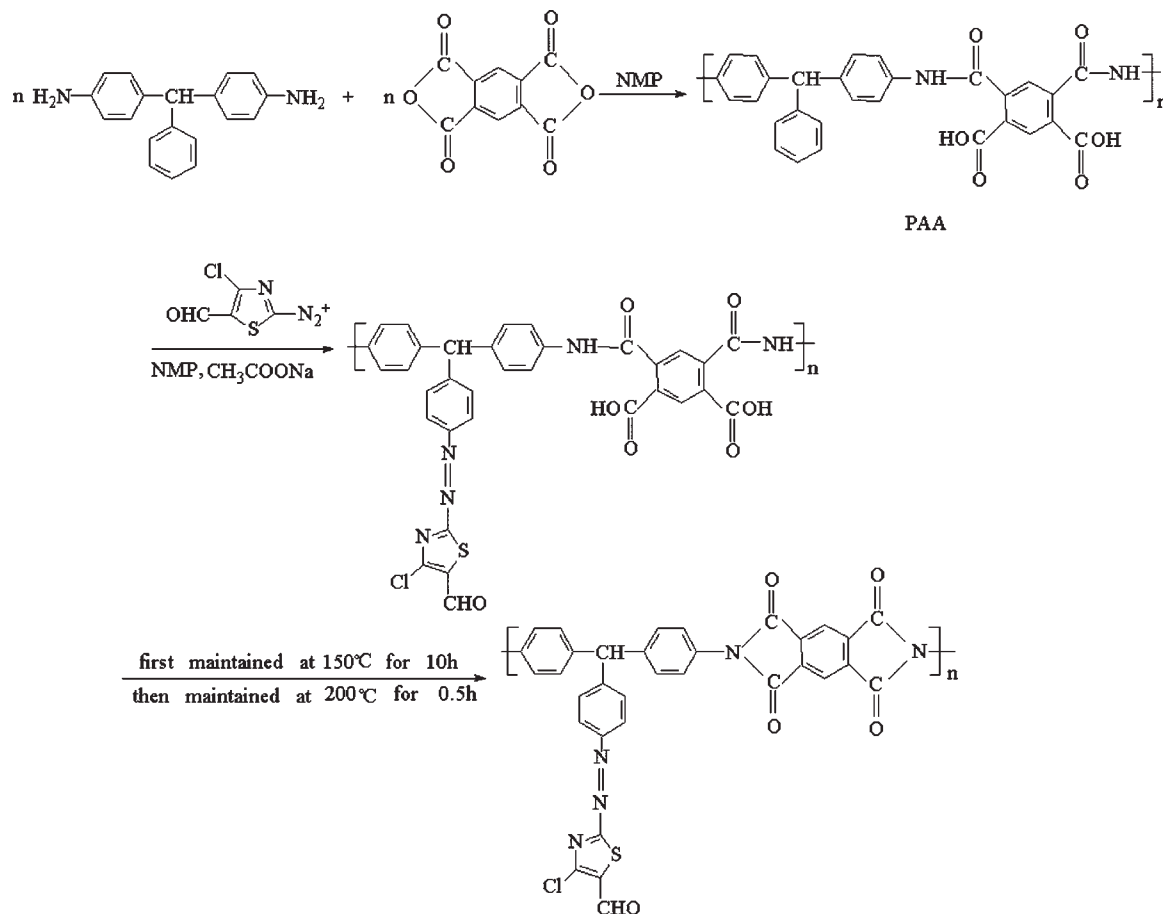
Synthesis of poly(amic acid) attached with azodye chromophore side chain

A 250 mL flask was charged with 200 mmol of DTM and 40 mL of freshly distilled NMP. The mixture was

stirred until complete dissolution of DTM was achieved, followed by addition of PMDA (200 mmol) under the protection of  $\text{N}_2$ . The mixture solution was maintained at 0°C for 2 h and at room temperature for 48 h, respectively. Then 250 mmol diazonium salt and 400 mmol sodium acetate were simultaneously added to the mixture solution. The color of the reaction mixture turned red immediately. The reaction was stopped after 24 h. The resulting poly(amic acid) (PAA) attached with azodye chromophore was then precipitated in deionized water, washed with water, and dried in vacuum at room temperature for 48 h. The red-brown powder polyamide with azodye chromophore side chain was obtained.

Synthesis of polyimide attached with azodye chromophore side chain

A small amount of the polyamide was dissolved in *N*-methyl-2-pyrrolidone (NMP). The solution was filtered before the preparation of its thin film. A polyamide thin film was deposited on a glass substrate from the filtered solution by spin-coating. The spin-coating process was carried out at low speed of 100 r/min with time of 10 s and high speed of 1000 r/min with time of 30 s, respectively. The obtained sample was dried in



**Scheme 2** Synthetic route of the thiazolylazo PI.

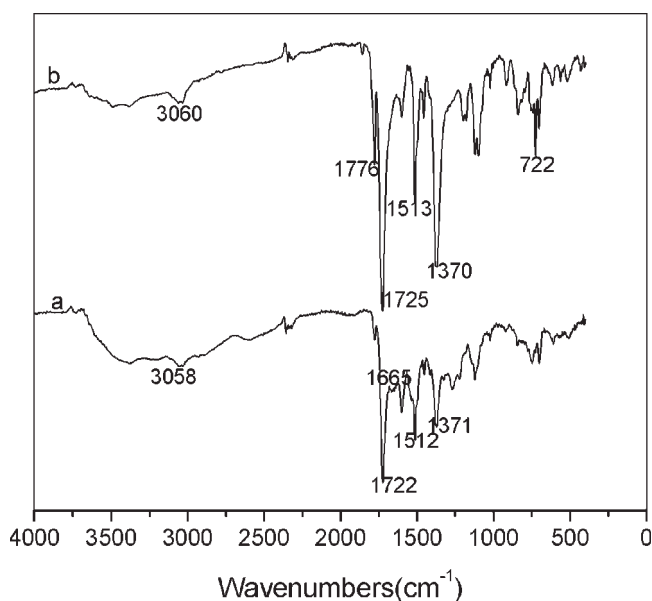


Figure 1 FT-IR spectra of PAA (a) and PI (b).

vacuum first at 150°C for 10 h and then heated to 200°C in 15 min. After being kept at this temperature for half an hour, the sample was cooled to room temperature, thus a polyimide (PI) film was obtained.

The synthetic route of the thiazolyazo PI was shown in Scheme 2.

### Measurements

Photoisomerization experiments were carried out by an ultraviolet lamp with a wavelength of  $365 \pm 5$  nm. Both the UV-vis spectra of the samples before and after the UV irradiation were measured by a UNICO UV-2102 PC spectrophotometer.

The  $^1\text{H}$  NMR spectrum was taken on an Avance DRX500. The FT-IR spectra were taken on a Nicolet-Magna-IR 550 FT-IR spectrophotometer with KBr pellets. The DSC curve was obtained by a DSC 2910

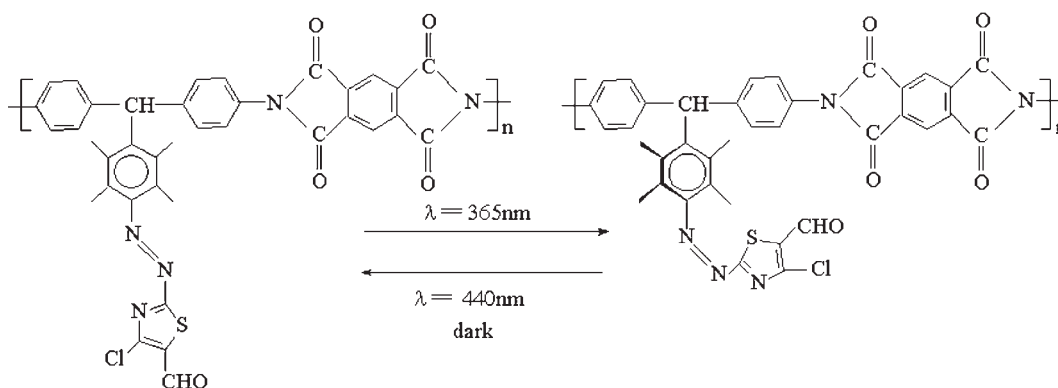


Figure 2 Conformational variations associated with the trans-cis photoisomerization of the azo units.

TABLE I  
 $^1\text{H}$  NMR Spectrum Data of Polyamic Acid (PAA)

Chemical shift $\delta$ (DMSO- $d_6$ )	
—phCH—	6.65
—CHO	10.5
—COOH	13.3
—NHCO—	10.49
ph—H	7.06~8.37

Modulated differential scanning calorimetry. The thermogravimetry analysis (TG) was measured by using the WRT-2 microthermal balance at a heating rate of 10°C/min under nitrogen atmosphere range from 10~900°C by a reference compound of  $\alpha\text{-Al}_2\text{O}_3$ . The sample was dried in vacuum at 50°C for 20 min before all the measurements.

## RESULTS AND DISCUSSION

### FT-IR spectra

Figure 1 shows the infrared spectra of PAA and PI. In curve (a), the absorption bands at  $1722\text{ cm}^{-1}$  and  $1665\text{ cm}^{-1}$  represent the stretching vibration absorption of carbonyl groups in acylamide and carboxylic groups, respectively. The absorption peak at  $1371\text{ cm}^{-1}$  attributes to the stretching vibration of C—N absorption in the main chain. Also the curve (a) shows a strong absorption peak at  $1512\text{ cm}^{-1}$  because of the antisymmetrical stretching vibration of azo chromophore in the side-chain.

In curve (b), the absorption peak appeared at  $1776\text{ cm}^{-1}$  represents the carbonyl asymmetric stretching of the imide ring formed after imidization reaction. The absorption peaks at  $1370\text{ cm}^{-1}$  and  $722\text{ cm}^{-1}$  attribute to the C—N stretching and bend vibration in imide ring, respectively. On the other hand, the absorption peak at  $1665\text{ cm}^{-1}$  due to C=O stretching vibration of carboxylic groups shown in curve (a) disappeared in curve (b). There is no obvious change for the absorp-

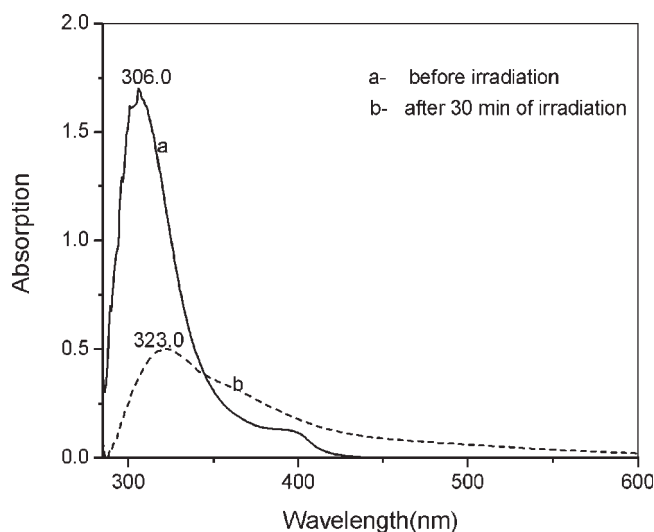
tion peak of azo chromophore between curve (a) and (b), which means that there is no significant effect for the imidization process to the azo chromophore.

### $^1\text{H}$ NMR spectrum

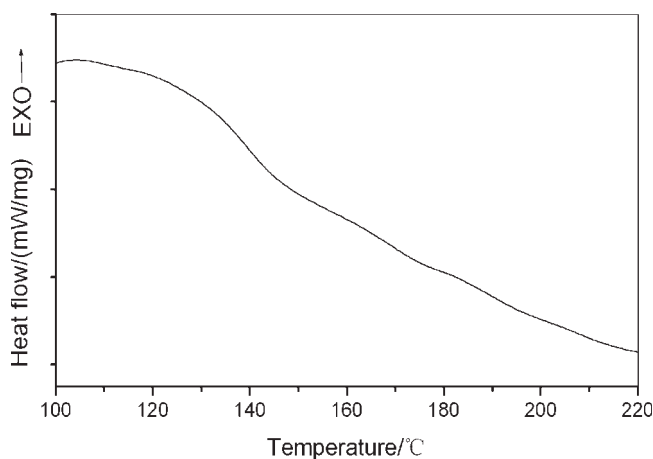
The structure of the polyamic acid was also characterized by  $^1\text{H}$  NMR spectrometer. The figures of  $^1\text{H}$  NMR spectrum were shown in Table I. The chemical shift due to acidic protons appeared at 13.3 ppm. The peak at 10.49 ppm can be ascribed to the amide protons. Such spectral assignments clearly support that the novel polymer has a structure as shown in Scheme 2.

### UV-vis spectra

The photoresponsive behavior is associated with photoisomerization of azogroup moieties. At room temperature in the dark, azogroup is in the trans-configuration, which is planar and fully conjugated (Fig. 2). Irradiation results in an isomerization reaction to make the molecule structure change from trans- to a cis-configuration, which is not planar for steric reasons. The two isomers are characterized by different absorptions because of the difference in the electronic situations. The absorption spectrum of the trans configuration shows an intense band at 306 nm assigned to  $\pi-\pi^*$  transition. The photoisomerization is accompanied by strong variations in the UV-vis absorption spectra. In particular, the trans-to-cis-isomerization is revealed by a strong decrease in the intense band at about 306 nm. Figure 3 is the UV-vis absorption spectra of PI film measured after irradiation at about 365 nm. The sample irradiation was performed in a time period of 30 min. Longer expositions did not produce further variations in the absorption spectra.



**Figure 3** Variation in the UV absorption of the PI before and after irradiation at 365 nm.

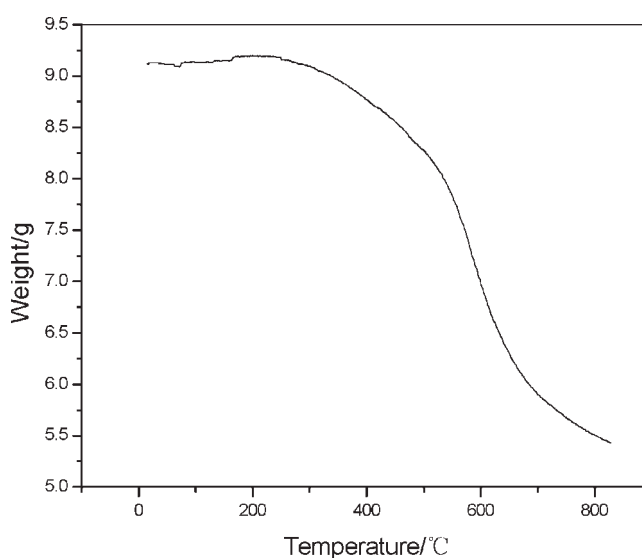


**Figure 4** DSC curve of the polymer PI.

### Thermal properties

Thermal properties of side-chain PI are shown in Figures 4 and 5. The  $T_g$  value of 138.9°C determined by DSC in air is pretty high. We believe that the high  $T_g$  is due to the grafting of the robust chromophores to the PI backbone.

The TG curve indicates that no weight loss occurs for the sample below 290°C. There is an initial decomposition at 290.2°C because of thermal breaking of the azodye group from polymer backbone. After that, a steady decrease in mass occurs in the range of 290~510°C. The decrease of mass is only 5% at 427.4°C and 10% at 510.6°C, respectively. After 510.6°C, the decomposition accelerates. Even so, residual mass of the polymer is still more than 60% at 800°C because of the high rigidity and thermal stability of the PI structure.



**Figure 5** TG curve of the PI.

## CONCLUSIONS

PI with thiazolylazo side chain can be prepared via a post azocoupling reaction scheme. The polymer will behave a reverse trans–cis transition when irradiated by the lights with the wavelengths of 365 nm and 440 nm. The glass-transition temperature ( $T_g$ ) and temperature at 10% of weight loss under  $N_2$  of the polymer are 138.9°C and 510.6°C, respectively, which confirm that the thermal stability of the polymer is quite good. All the above good properties show that, such a PI film might be developed as a new rewritable optical recording material for high density optical data storage.

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