

# Rapid Bending of a Nonliquid Crystal Azobenzene Polymer Film and Characteristics of Surface Relief Grating

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**ABSTRACT:** A nonliquid crystal polymer was prepared by introducing the azobenzene group into the main chain of the poly(amic acid). The polymer film can be easily prepared by a general method. The obtained film exhibits a high bending intensity and shows fast bending response and a very large bending angle (reach of 90°) at room temperature without temperature heating, which can improve the efficiency of the transformation of energy from light to

mechanical energy. The surface structure of the relief grating also was investigated by atomic force microscopy. The depth of typical surface relief was approximately 65 nm. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1330–1334, 2009

**Key words:** Azo polymer; photo response; surface relief gratings

## INTRODUCTION

It is well known that azo possesses *trans–cis* isomerization characteristics under ultraviolet (UV) and visible (Vis) irradiation. Its polymers have attracted more and more attention in recent years because of their potential application for optical elements and photonic devices.<sup>1–3</sup> One of the most interesting properties of Azo polymers is bending, which can be induced by exposure to light at modest intensities on Azo polymer films.<sup>4</sup> Light as a clean energy can be controlled rapidly, precisely, and remotely. Therefore, many works are reported. For example, Agolini and Gay<sup>5</sup> reported the synthesis of polyimide-containing Azo groups in the main chain in 1970. When the polymer film is heated or irradiated, part of the undefined area of Azo contracts from *trans* to *cis*. In 1980, Eisenback<sup>6</sup> reported light initiation of deformation at about 4,4-*bis* (dimethylacrylamide) Azo cross-linkage poly (propylene imide) and found a 0.15–0.25% rate of contraction. Pierre-Gilles de Gennes,<sup>7</sup> Nobel laureate in 1991, reported possible research about the obvious transmutation of the liquid crystal

gel. Later, several groups reported that the obvious transmutation of the liquid crystal network was excited by electric field or temperature in 1997. Finkelmann et al.<sup>8</sup> reported that obvious transmutation of the liquid crystal network containing Azo took place in 2001. Miguel Camacho-Lopez et al.<sup>9</sup> also reported liquid crystal elastomer swim by irradiation in 2004.

However, there are few reports concerning the introduction of the Azo groups into high-performance nonliquid crystal polymers, which possess many virtues, such as a high  $T_g$ , excellent mechanical performance, good resistance to chemical erosion, endurance of high temperatures, low electric performance, and resistance to irradiation. In our experiment, the Azo group was introduced into the main chain of the poly(amic acid) (PAA), and a novel nonliquid crystal polymer was obtained. The obtained film exhibits a high  $T_g$  and a high bending intensity and shows fast bending responses at room temperature, which can improve the efficiency of the transformation of energy from light to mechanical energy.

## EXPERIMENTAL SECTION

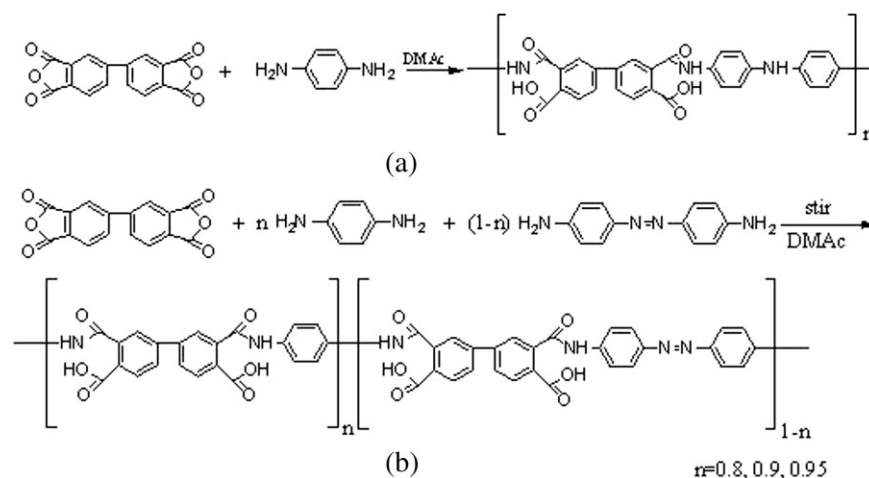
### Materials

All chemicals were purchased and used as received unless otherwise noted. *N,N*-Dimethylacetamide (DMAc) was purchased from Tianjin Tiantai Chemical (Tianjin, China); tetrahydrofuran (THF) was purchased from Tianjin Tiantai Chemical (Tianjin, China); 4,4'-Azodianiline was purchased from Acros

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**Figure 1** Outline of synthesis of PAA (a) and PAAA (b).

Organics; 1,4-diaminobenzene was purchased from Aladdin Reagent; and 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) was purchased from Guangdong Triway Chemical (Guangdong, China).

#### Synthesis of PAA and PAA containing azo

The synthesis of PAA is classical, and the procedure was the same as that reported in the literature.<sup>10</sup> The schematic diagram is shown in Figure 1(a).

IR: 1440, 1500, 1600 ( $\nu_{C=C}$ ), 1648 ( $\nu_{C=O}$ ) 3440 ( $\nu_{N=H}$ )  $\text{cm}^{-1}$ .

<sup>1</sup>H-NMR spectrum (500 MHz, DMSO)  $\delta = 13.20$  (s, COOH), 10.47 (s, N—H).

PAA:  $M_w$ : 65,800,  $M_n$ : 49,600, PDI: 1.33

The process of synthesis of PAA containing Azo (PAAA) is shown in Figure 1(b). The typical process was as follows: 0.973 g (0.009 mol) of 1,4-diaminobenzene was added into a three-necked bottle under  $N_2$  conditions, and then 20 mL DMAc was poured into the bottle and stirred until the 1,4-diaminobenzene was dissolved. Then, 0.212 g (0.001 mol) of azobenzene was put into the bottle. The solution turned red. Then, 2.942 g (0.01 mol) of s-BPDA was added into the above solution, followed by adding 19.6 mL of DMAc into the bottle. After stirring for 5 h at room temperature, the poly(amic acid) containing 10% azobenzene group was formed. The polymer with a concentration of Azo groups at 5% and 20% also was prepared by using the same procedure.

IR: 1445, 1500, 1600 ( $\nu_{C=C}$ ), 1648 ( $\nu_{C=O}$ ), 3440 ( $\nu_{N=H}$ )  $\text{cm}^{-1}$  (example 10% PAAA).

<sup>1</sup>H-NMR spectrum (500 MHz, DMSO)  $\delta = 13.21$  (s, COOH), 10.45 (s, N—H), 8.05 (d, —N=N—Ar—H), 7.64 (d, —N=N—Ar—H) (example 10% PAAA).

5% PAAA:  $M_w$ : 68,000,  $M_n$ : 50,000, PDI: 1.36

10% PAAA:  $M_w$ : 58,700,  $M_n$ : 40,600, PDI: 1.44

20% PAAA:  $M_w$ : 62,000,  $M_n$ : 40,000, PDI: 1.57

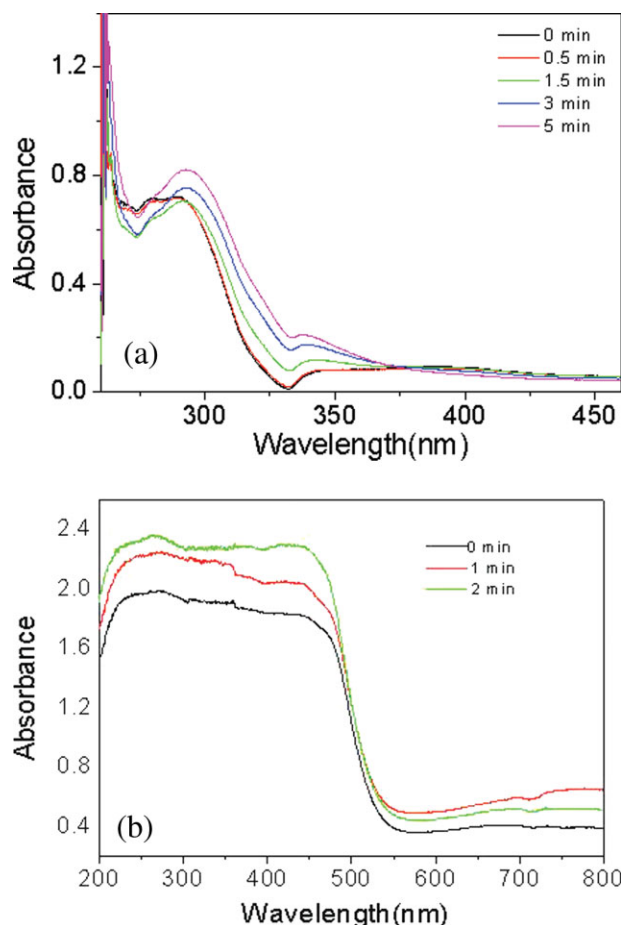
#### Preparation of polymer film

The polymer solution prepared above was added into THF by stirring to separate out PAAA and obtain orange powder after drying. Then PAAA was dissolved in DMAc by stirring; the solid content in the solution is 10 wt %.

The polymer film was prepared by casting polymer/DMAc solution onto the surface of the polyimide film. The film was then allowed to dry at room temperature for 4 h, followed by heating at, respectively, 80, 100, and 150°C for 1 h at atmosphere. To investigate the surface morphology of the film irradiated by laser, the film was also prepared by spin-coating polymer solution on a precleaned Si slide and drying as mentioned above.

#### Equipment

FTIR measurements were recorded on a BRUKER VECTOR 22 Spectrometer. The samples were mixed with KBr and pressed into a plate for measurement at 25°C. The <sup>1</sup>H-NMR spectra of poly(amic acid) containing Azo in deuterated dimethyl sulfoxide (DMSO) were run on a BRUKER-500 spectrometer to determine the chemical structure; tetramethylsilane was used as the internal standard. UV-vis spectra were performed on a UV-2501 PC Spectrometer (SHIMADZU) in DMAc. Tensile testing was performed under an AG-I electronic universal testing machine controlled by computer (SHIMADZU Corporation, Japan) at a crosshead speed of 10 mm/min under ambient conditions. The bending behavior of the film was observed under irradiation of UV light at 366 nm from a 500 W high-pressure mercury lamp through glass filters (Jiangsu Yaguang ZWB<sub>2</sub> and BG39). The bent film was exposed to unpolarized visible light at >540 nm (Jiangsu Yaguang JB450 and BG39). The photographs of the bending



**Figure 2** (a) UV-vis absorption spectra of 10% PAAA solution in DMAc; (b) UV-vis absorption spectra of 10% PAAA film. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

and unbending behavior were taken with a digital camera (Sony, DSC-F505). Holographic irradiation with the laser beam (Nd:YAG Lasers) at 355 nm was performed on the film. The physical morphologies of the films were examined by using atomic force microscopy (AFM) (Park Scientific Instrument) with tapping mode.

## RESULTS AND DISCUSSION

UV-vis spectra of the PAAA in the DMAc solution are shown in Figure 2(a). The changes of the UV absorption spectra of Azo solution were recorded. The UV absorption spectra were observed by a strong  $\pi$ - $\pi^*$  transition of the *trans* azobenzene at 300 nm and a weak absorption at 400 nm, which was related to the  $n$ - $\pi^*$  transition. Under UV light irradiation, the intensity of the  $\pi$ - $\pi^*$  transition band at 300 nm decreases, whereas the  $n$ - $\pi^*$  transition band at 400 nm increases, indicating that the transition of *trans* to *cis* takes place. This phenomenon indicates

that the Azo group has been introduced into the main chain of PAA. UV-vis spectra of the PAAA film are shown in Figure 2 (b), in which the same phenomenon was observed.

The introduction of the Azo groups into the main chain of PAA has little effect on the mechanical properties of the polymer films (Table I), and it does not significantly influence the maximum stress-and-break strain rise. This indicates that Azo polymers can obtain the quality of PAA to improve the performance of the film.

The photoinduced bending of the Azo polymers film was studied under irradiation of UV light ( $\lambda = 365$  nm). The thickness of the film is 10  $\mu\text{m}$  (with the sizes 2 cm  $\times$  6 cm). The film containing Azo groups does bend, whereas poly(amic acid) without Azo groups does not bend, which suggested that the Azo groups play an important role in the deformation of the polymer films [Fig. 3(a)]. Part of the polymer PAAA orientation takes place along one way when rubbed. When the film was irradiated by UV light, Azo isomerization deformed the polymer chain. However, light cannot penetrate the film completely.<sup>11</sup> Most of the energy was absorbed into the surface of the film. As a result, the polymer chain on the substrate deformed very little, which suggested that the bending of the film results from the deformation of the polymer chain on the top surface. The nonliquid crystal film shows a very large bending angle (90°) and fast bending responses at room temperature without temperature heating. However, the bend response for liquid crystal polymer film needs temperature heating to achieve nematic crystal state. The nonliquid crystal film can improve the efficiency of the transformation of energy from light to mechanical energy. Figure 3(b) shows the effect of irradiation time on bending of PAAA films containing different contents of Azo groups. At the beginning part of the Azo isomerization there was not enough energy for the film to bend. The amount of *cis* Azo increased with time prolonged. At a given time, the film changes qualitatively and can bend suddenly, which corresponds to a rapid inflexion in the chart. With the content of Azo increased, there would be

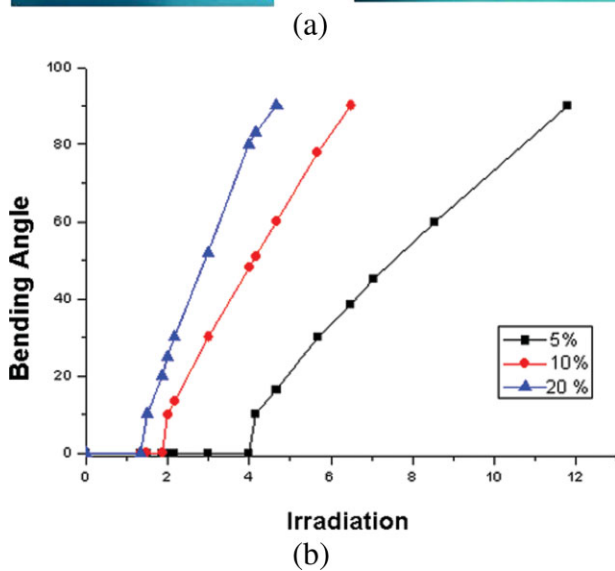
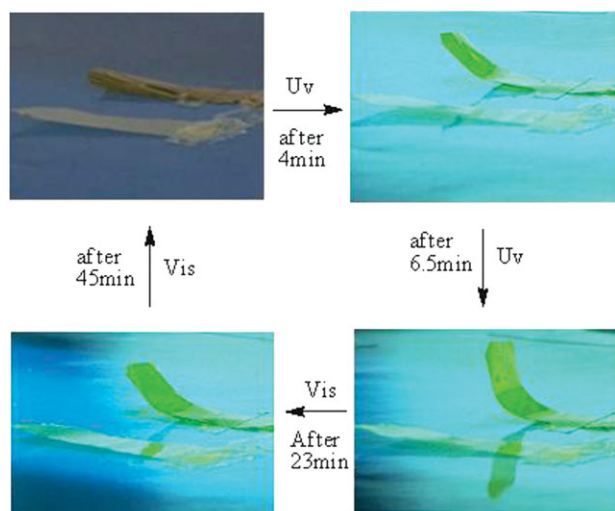
**TABLE I**  
Tensile Properties of Polymer Films with Different Azo Contents

	Elastic (MPa)	Max stress (MPa)	Break strain (%)
PAA	2328 $\pm$ 35	94.0 $\pm$ 5.4	11.1 $\pm$ 2.5
5% PAAA	2093 $\pm$ 18	88.9 $\pm$ 3.8	12.5 $\pm$ 1.1
10% PAAA	2062 $\pm$ 39	76.4 $\pm$ 2.5	12.7 $\pm$ 1.8
20% PAAA	1908 $\pm$ 27	67.5 $\pm$ 4.6	13.8 $\pm$ 1.6

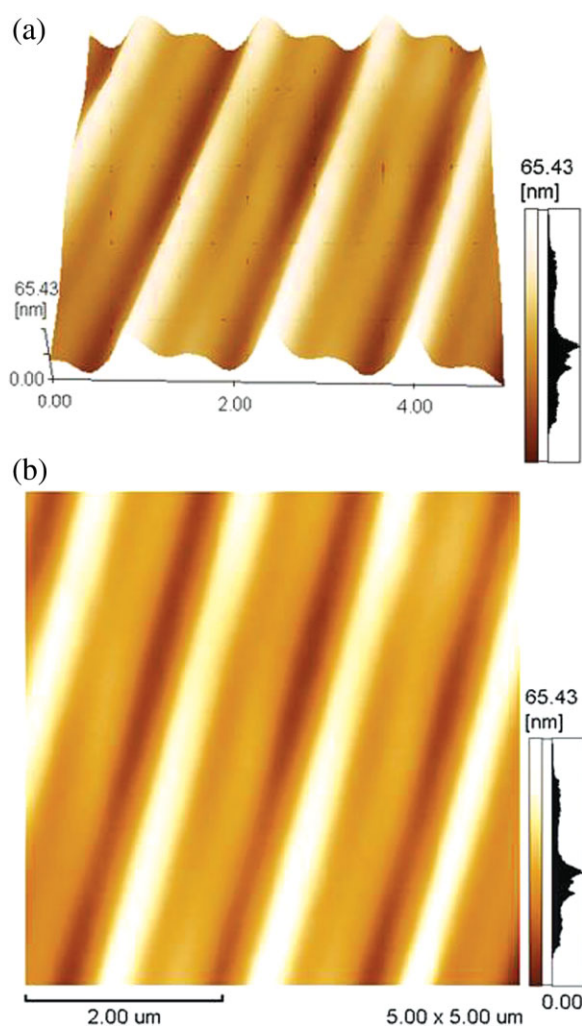


more Azo isomerization in the same area of irradiation, which was related to inflexion ahead.

A laser beam divided into two beams at 355 nm with an intensity of 22 mW/cm<sup>2</sup> was used as the light source in this research. The surface profiles were investigated by using an AFM in which the scans are made with a nanoscope on the recorded spot. Surface relief was observed in the AFM picture. As shown in Figure 4(a), the three-dimensional view of the surface gratings shows regularly spaced sinusoidal surface relief structures with a period of 1.8 μm. The grating period could be adjusted by changing the incident angle of the two writing beams. Figure 4(b) shows the two-dimensional view of the AFM picture for grating formation. A grating height of 65.43 nm was confirmed by AFM measure-



**Figure 3** (a) Bending of PAAA film with 10% content under the UV-vis spectra; (b) relationship between irradiation and bending angle. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** (a) Three-dimensional view of the AFM picture of the surface relief grating structure on polymer film; (b) two-dimensional view of the AFM picture of the surface relief grating structure on the polymer film. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ments. It was also found that the formation of surface relief gratings was dependent on the irradiation time.

### CONCLUSION

In summary, a kind of poly(amic acid) containing the Azo group in the main chain has been synthesized. This is a new nonliquid polymer that is different from liquid crystal reported before. The obtained polymer film exhibits a high  $T_g$  and a high bending intensity and shows fast bending responses at room temperature (without heating) and a very large bending angle, which can improve the efficiency of the transformation of energy from light to mechanical energy. The surface structure of the relief gratings has also been investigated by AFM. The depth of a typical surface relief is found to be ~ 65 nm.

Because of the unique properties of this Azo polymer, it is expected to be a promising candidate for cantilevers, micropumps, and many other micromechanical applications and information storage.

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