

# Synthesis and Photosensitive Properties of Poly(aryl imino) Containing Azobenzene Group (PAI-A)

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Using 4,4'-dibromobenzophenone and 4,4'-diaminoazobenzene as monomers, poly(aryl imino) containing azobenzene unit (PAI-A) was synthesized via palladium-catalyzed amination, and structurally characterized by means of FT-IR, <sup>1</sup>H NMR spectra and elemental analysis, the results of which show an agreement with the proposed structure. The UV absorption spectra were tested under different conditions. Additionally, differential scanning calorimetry (DSC) and thermogravimetric (TG) measurements show that PAI-A possesses high glass transition temperature ( $T_g > 176$  °C) and good thermal stability with high decomposition temperatures in nitrogen atmosphere ( $T_D > 410$  °C).

**Keywords** poly(aryl imino), azobenzene unit, palladium-catalyzed amination

## Introduction

Polymer syntheses using organotransition-metal complexes as catalysts are the subject of recent interest, and various bond formation processes involving the reaction of two kinds of functional groups catalyzed by organometallic complexes have been applied to the polycondensation reactions of bifunctional organic compounds to give novel poly(arylene)s, aromatic polyesters, polyamides, and the related polymers.<sup>1-5</sup>

Since the Pd-catalyzed amination reaction offers advantages over the classical methods, which require either activated substrates or severe reaction conditions. The Pd-catalyzed polycondensation could provide various regiodefined polyamines by changing the structure of the aryl dibromides and diamines.<sup>6</sup> In 2004, aromatic poly(imino ketone)s (PIK) as new high-performance polymers were reported by Müllen.<sup>7</sup> Then, Chang *et al.*<sup>8,9</sup> expanded the scope of poly(imino ketone)s in 2007, and a series of poly(arylene imino)s (PAI) were synthesized. In order to functionalize the PAIs, here we want to introduce azobenzene as the functional group into the polymer chain. Azobenzene group is a well-known photosensitive chromophore, which undergoes photo-induced *cis-trans* isomerization.<sup>10,11</sup> Owing to the photoactivities, a large number of polymers containing azobenzene groups have attracted interest because of their potential uses in various photonic applications.<sup>12,13</sup> Thus, the Pd-catalyzed polycondensation of 4,4'-dibromobenzophenone with 4,4'-diaminoazobenzene to afford polymers (PAI-A) were carried out. These polymers have an azobenzene structure in the main chain and are expected to show photochromic properties similar to those of the reported polymers containing

azobenzene groups.<sup>14,15</sup> Photoinduced *cis-trans* isomerization behavior of the polymers will be investigated.

## Experimental section

### Materials and measurements

Tris(dibenzylideneacetone)-dipalladium(0) [Pd<sub>2</sub>(dba)<sub>3</sub>] and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) were purchased from Alfa Aesar, a Johnson Matthey Company in USA; 4,4'-diaminoazobenzene was purchased from Daikin Finechemical Laboratory, LTD, Toshima, Kita-ku, Tokyo, Japan; 4,4'-dibromobenzophenone was synthesized in our laboratory; *N,N*-dimethylacetamide (DMAc) was distilled in our laboratory. The rest materials and reagents were obtained from different commercial sources and used without further purification.

FTIR spectra were recorded on a Nicolet 6700 FTIR spectrometer. Elemental analysis was performed on a Perkin-Elmer model 2400 CHN analyzer. <sup>1</sup>H NMR spectra were recorded using Bruker AMX 500 Hz NMR spectrometers in DMSO-*d*<sub>6</sub>. Gel permeation chromatography (GPC) measurements were used to determine molecular weights and molecular weight distributions by universal calibration generated with narrow molecular weight distribution polystyrene standards using dimethylformamide as eluent. The differential scanning calorimetry (DSC) curves obtained during the second heating scan were taken into consideration. The samples were heated at a rate of 10 °C/min under flowing nitrogen gas. Thermo-gravimetric analysis was performed on a Mettler TG 10A instrument at a heating rate of 10 °C/min under nitrogen atmosphere.

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### Synthesis of aromatic 4,4'-dibromobenzophenone

In a 50 mL three-necked, round-bottom flask equipped with a mechanical stirrer, 0.025 mol of *p*-bromobenzoic chloride and 0.25 mol of bromobenzene were placed, then 0.05 mol of anhydrous powdered aluminum chloride was added to the stirred solution. The solution was stirred for 12 h at room temperature, then heated at 90 °C for 3 h, cooled to room temperature, and poured into water. The cream solid was washed with water for five times and then dried at 50 °C in air. Finally the crude product was recrystallized from absolute alcohol, dried at 50 °C for 5 h to give product as colorless crystal.

### Synthesis of polymer

An oven-dried resealable Schlenk flask (50 mL) equipped with a magnetic stirrer, a nitrogen outlet, inlet and a water-cooled condenser, was added with 4,4'-diaminoazobenzene (5.0 mmol), 4,4'-dibromobenzophenone (5.0 mmol), sodium *tert*-butoxide (1.350 g, 14.0 mmol), tris(dibenzylideneacetone)dipalladium(0) Pd<sub>2</sub>(dba)<sub>3</sub> (45.75 mg, 0.05 mmol), 2,2'-bis-(diphenylphosphino)-1,1'-binaphthyl (BINAP) (62.0 mg, 0.10 mmol), and DMAc (10 mL). The reaction mixture was flushed with high purity argon atmosphere. This procedure was repeated four times. The flask was immersed in a 100 °C oil bath for 10 h, and then in a 150 °C oil bath for 5 h with continuous stirring. The resulting polymer solution was allowed to slowly cool to room temperature, filtered and subsequently poured into methanol, filtered, the solid washed with methanol several times, and then dried at 100 °C under vacuum. Yield 1.87 g, 96%. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ: 9.28 (s, NH), 7.70 (s, H-1), 7.26 (s, H-2), 6.62 (s, H-3); FT-IR (KBr) ν: 3381 (N—H), 1663 (C=O), 1310 (C—N) cm<sup>-1</sup>. Anal. calcd for C<sub>25</sub>H<sub>18</sub>N<sub>4</sub>O: C 76.91, H 4.65, N 14.35; found C 76.89, H 4.71, N 14.32.

## Results and discussion

### Polymer synthesis

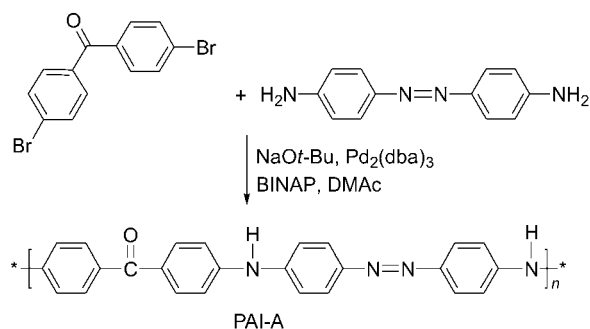
Using 4,4'-diaminoazobenzene and 4,4'-dibromobenzophenone as the monomers, poly(aryl imino) containing azobenzene unit in the main chain was synthesized via palladium-catalyzed polycondensation reaction. The catalytic system generated from the combination of tris(dibenzylideneacetone)dipalladium(0) [Pd<sub>2</sub>(dba)<sub>3</sub>] and BINAP as shown in Scheme 1.

The polymer synthesized was characterized by FT-IR, <sup>1</sup>H NMR and elemental analysis. The results showed good agreement with the proposed structure. The molecular weight of the reprecipitated polymer was measured by GPC (calibrated by polystyrene standards) with its *M*<sub>n</sub> = 43200 and *M*<sub>w</sub> = 98100.

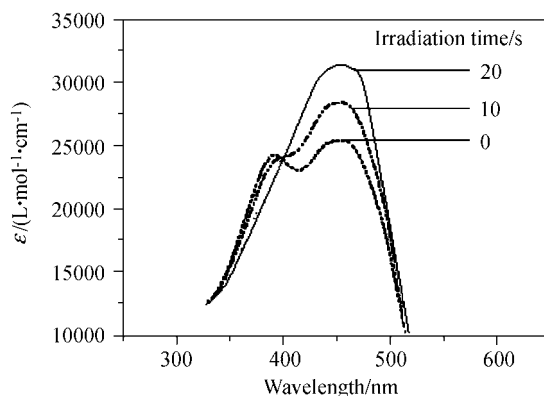
### UV spectra of PAI-A

The UV-Vis absorption spectrum of polymer PAI-A in DMF exhibits two absorption peaks at 386 and 457

**Scheme 1** Synthesis of PAI-A via Pd-catalyzed aryl amination



nm, presumably based on the  $\pi \rightarrow \pi^*$ - and  $n \rightarrow \pi^*$ -transitions of phenyl and aminoazobenzene units, respectively. Before irradiation, the polymer PAI-A exhibited the above two absorption bands at 386 and 457 nm<sup>-1</sup>. After irradiation of PAI-A by light at about 365 nm, the absorption peak at 386 nm gradually decreased while the absorption peak at 457 nm gradually increased by increasing the irradiation time (Figure 1), which can be attributed to the *trans-cis*-photoisomerization of the azobenzene moieties in the main chain of PAI-A backbone.



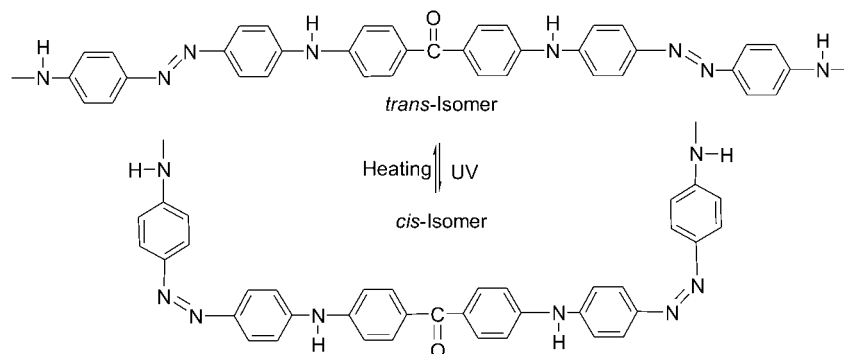
**Figure 1** Changes in the absorption spectra of PAI-A ( $2 \times 10^{-5}$  mol·L<sup>-1</sup> of the azobenzene unit in DMF).

In the thermal isomerization the polymer PAI-A, previously irradiated at about 365 nm, was annealed at 80 °C in the dark. The absorption peak at 386 nm steadily increased while the absorption peak at 457 nm steadily decreased to the starting value before irradiation. This indicates that the *cis-trans*-isomerization of the azobenzene groups occurred thermally. The photoinduced and thermal *cis-trans*-isomerization was induced repeatedly (Scheme 2). Both thermal and photoinduced-isomerization processes would occur by in-plane translation of the benzene ring further from the main chain rather than by rotation around the N=N bond.

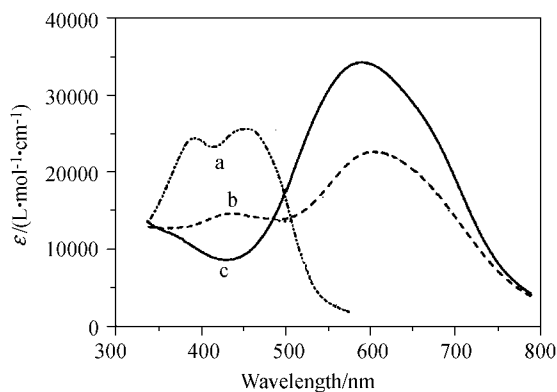
### Protonation of PAI-A

The absorption properties of the polymer synthesized are also dependent on the acidity of the media. Figure 2 shows the changes in the absorption spectra of

Scheme 2 Photoisomerisation of PAI-A



DMF solutions of PAI-A with increasing concentration of  $\text{CF}_3\text{COOH}$ . The addition of  $\text{CF}_3\text{COOH}$  leads to a decrease of the bands at 388 and 452 nm and an appearance of a new band at 600 nm with no isosbestic points. The absence of the isosbestic points indicates the formation of different reaction products or intermediates as shown in Scheme 3. The new band at 600 nm may be assigned to the protonated resonating form of aminoazobenzene group expressed by Scheme 3. Upon complete protonation, the color of the polymer solution was transferred from yellow to blue which differs significantly from other polymers containing azobenzene group where the color transferred from yellow to purple.<sup>12,13</sup> The blue color is due to the interaction of the positive charge with the extent of the  $\pi$ -electron system in the former.

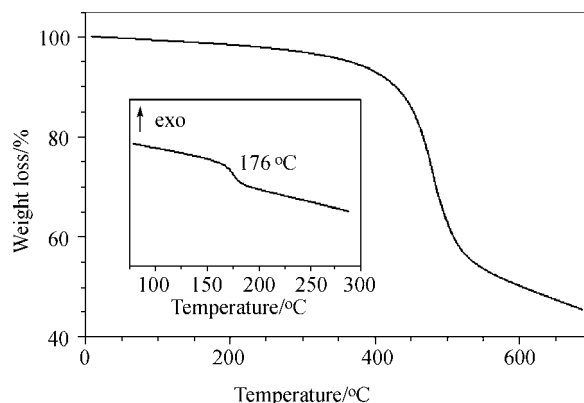
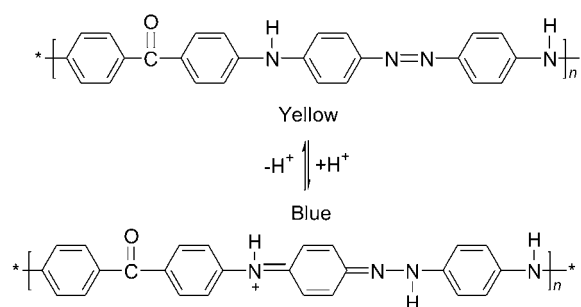


**Figure 2** Changes in the absorption spectra of PAI-A.  $2 \times 10^{-5}$  mol·L<sup>-1</sup> of the azobenzene unit in DMF. [TFA]: (a)  $1.0 \times 10^{-1}$ , (b)  $20 \times 10^{-1}$ , (c)  $50 \times 10^{-1}$  mol·L<sup>-1</sup>.

### Thermal behavior of PAI-A

One of the essential requirements of a new polymer material for high temperature applications is thermal stability, which makes polymers attractive for potential application. Hence, typical TG trace and DSC in nitrogen are demonstrated in Figure 3 for PAI-A. TG curves revealed that PAI-A was thermally stable at up to 400 °C. 50% weight loss took place at over 600 °C in nitrogen. DSC of PAI-A up to 176 °C showed a single  $T_g$  (the inset in Figure 3).

**Scheme 3** Protonated resonating form of aminoazobenzene group



**Figure 3** TG and DSC curve of PAI-A.

### Conclusion

Poly(aryl imino) containing azobenzene unit (PAIA) was synthesized via a palladium-catalyzed amination. Before irradiation, the UV-Vis absorption spectrum of PAI-A in DMF exhibited two absorption peaks at 388 and 452 nm, after irradiation of PAI-A by light at about 365 nm, the absorption peak at 388 nm gradually decreased while the absorption peak at 452 nm gradually increased by increasing the irradiation time. In the thermal isomerization the PAI-A, previously irradiated at about 365 nm, was annealed at 80 °C in the dark. The absorption peak at 388 nm steadily increased while the absorption peak at 452 nm steadily decreased to the starting value before irradiation. The addition of  $\text{CF}_3\text{COOH}$  led to a decrease of the bands at 388 and 452

nm and an appearance of a new band at 600 nm with no isosbestic points. Additionally, DSC and TG measurements show that the PAI-A possesses high glass transition temperature ( $T_g > 176$  °C) and good thermal stability with high decomposition temperatures in nitrogen atmosphere ( $T_D > 410$  °C).

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