

# Photoactive Polyamideimides Synthesized by the Polycondensation of Azo-dye Diamines and Rosin Derivative

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**ABSTRACT:** New rosin-based photoactive polyamideimides (**PAI-a** and **PAI-b**) with a large second-order nonlinear optical coefficient and photoinduced birefringence were synthesized by the polycondensation of rosin–maleic anhydride adduct (**RMA**) with azo-dye diamines, 2-(2-[ethyl-[4-(4-nitrophenylazo)phenyl]aminoethoxy]benzene-1,4-diamine (**4a**) or 2-(2-[ethyl-[4-(4-methylsulfonylphenylazo)phenyl]amino]ethoxy)benzene-1,4-diamine (**4b**). Due to the bulky alicyclic structure of the rosin, these polymers were highly soluble in organic solvents and could easily be processed by spin-coating into thin films of high optical quality. Fabricated polymer films were very smooth, tough, adhesive to the substrate, and optically clear. Second-order nonlinear optical coefficients ( $d_{33}$ ) of the corona-poled **PAI-a** and **PAI-b** films were 83 and 54 pm/V, respectively, at the fundamental wavelength of 1064 nm. Birefringences as high as 0.072 for **PAI-a** and 0.035 for **PAI-b** could be induced and erased repeatedly by the irradiation of linearly polarized and circularly polarized 532-nm light, respectively. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 687–695, 2001

**Key words:** rosin; nonlinear optical; photoinduced birefringence; azo; polyamideimide

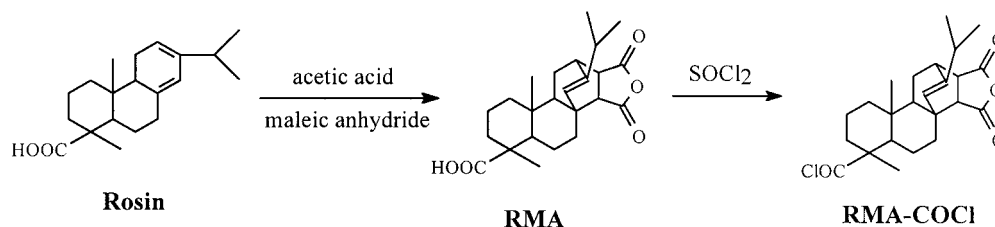
## INTRODUCTION

Azobenzene chromophores with push–pull substituents exhibit a large dipole moment, hyperpolarizability, and *trans*–*cis* isomerization. Therefore, polymers containing these chromophores are receiving great attention due to their interesting

photoactive properties such as second-order nonlinear optical properties, photoinduced birefringence, photo-assisted dipolar alignment, and all-optical poling.<sup>1–7</sup> Second-order nonlinear optical properties are revealed when the dipolar azobenzene chromophores are reoriented to align along the applied electric field and subsequently frozen to keep the polar ordering.<sup>1,2</sup> Photoinduced birefringence is observed when the azobenzene polymer film is exposed to the linearly polarized light. The mechanism of this process involves repeated *trans*-to-*cis* photoisomerization and thermal re-

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**Scheme 1** Synthesis of rosin derivative.

verse isomerization of azobenzene, resulting in the alignment of the azobenzene group perpendicular to the polarization direction of incident light.<sup>3–7</sup> Therefore, both the second-order nonlinear optical property and photoinduced birefringence, which are primarily related to the structure of the push–pull azobenzene chromophore, depend strongly on the structure of the polymer as well, since the molecular motion and realignment are required to show these photoactive properties.

Considering the transparency and stability as the fundamental properties needed for optical film, we have found and demonstrated for the first time that rosin-based polymers, particularly polyesterimide in our previous publication, are very promising for second-order nonlinear optical application as monitored by the thermally stable electrooptic coefficient.<sup>8</sup> Excellent optical quality, coherency, adhesion, and thermal stability of this polymer were attributed tentatively to the bulky alicyclic fused-ring structure of the rosin.<sup>8–10</sup>

To be further convinced of this idea and to observe various photoactive properties, we synthesized a different class of a rosin-based polymer in this work, that is, polyamideimide with a push–pull azobenzene chromophore. Two different azo-dye diamines with largely different optical absorption were synthesized and adopted for the polymer synthesis. We report and discuss the details of the polymers syntheses and the outstanding photoactive properties of them in terms of the second-harmonic generation (SHG) and photoinduced birefringence.

## EXPERIMENTAL

### Rosin–Maleic Anhydride Adduct (RMA)

Rosin (60.40 g, 200 mmol) was heated to 180°C under a nitrogen atmosphere. After cooling to 130°C, 240 mL of acetic acid was added and stirred into a homogeneous solution. After cooling

to 70°C, maleic anhydride (17.65 g, 180 mmol) and *p*-toluenesulfonic acid (0.76 g, 4.4 mmol) were added and stirred at reflux for 12 h. When the mixture was cooled, a white crystalline product was precipitated. The precipitates (**RMA**, see Scheme 1) were filtered and recrystallized from acetic acid to yield 28 g of a white solid (Y = 35%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 5.54 (s, 1H, —CH=C) 1.18 [d, 6H, —CH=C—(CH<sub>3</sub>)<sub>2</sub>] 0.71 (d, 3H, HOOC—C—CH<sub>3</sub>); IR (KBr pellet, cm<sup>-1</sup>): 3400–2600 (OH, carboxylic acid), 2959–2872 (CH, aliphatic), 1842–1778 (C=O, cyclic anhydride), 1695 (C=O, carboxylic acid).

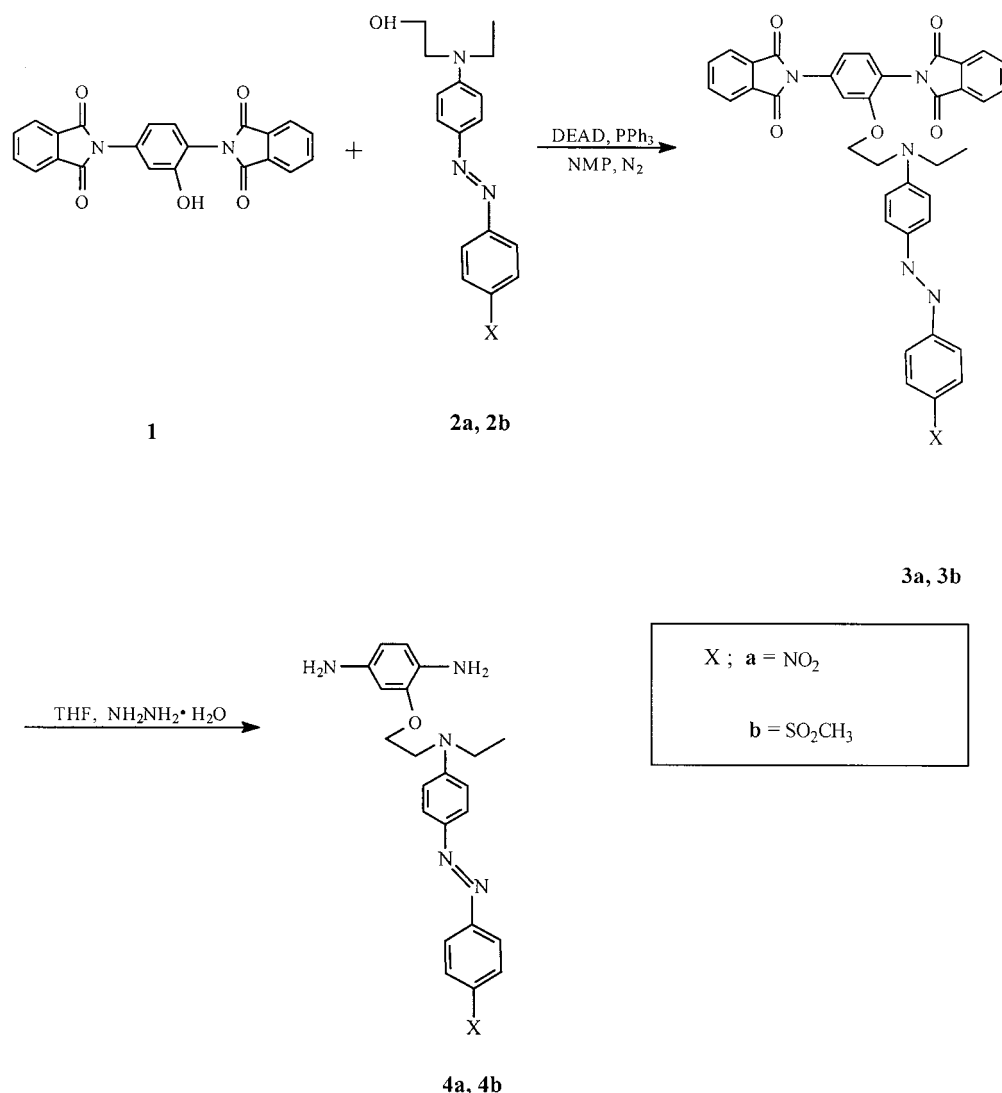
### 2-(2-Ethyl-[4-(4-nitrophenazo)phenyl]-aminoethoxy)benzene-1,4-diamine (**4a**)

Azo-dye diamine **4a** was synthesized from compound **1** and **2a** according to the literature method<sup>2</sup> as depicted in Scheme 2. Briefly, diimide compound **3a** was yielded by the Mitsunobu reaction of compound **1** and 2-[ethyl-[4-(4-nitrophenazo)phenyl]-amino]ethanol (**2a**) in a 90% yield. Subsequent hydrazinolysis of **3a** gave **4a** (65%, mp 185°C).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 8.25 (d, 2H, aromatic H's), 7.84 (m, 4H, aromatic H's), 6.77 (d, 2H, aromatic H's), 6.49 (d, 2H, aromatic H's), 6.16 (t, 2H, aromatic H's), 6.12 (d, 1H, aromatic H), 4.10 (t, 2H, —NCH<sub>2</sub>CH<sub>2</sub>O—), 3.81 (t, 2H, —NCH<sub>2</sub>CH<sub>2</sub>O—), 3.53 (q, 2H, —NCH<sub>2</sub>CH<sub>3</sub>), 3.27 (br, 4H, Ar NH<sub>2</sub>), 1.21 (t, 3H, —NCH<sub>2</sub>CH<sub>3</sub>); IR (KBr pellet, cm<sup>-1</sup>): 3425, 3325 (NH<sub>2</sub>), 1599 (amine NH bend), 1516, 1330 (nitro N=O); *m/z* (EI, low resolution). Calcd for C<sub>22</sub>H<sub>24</sub>N<sub>6</sub>O<sub>3</sub>: 420.47; found: 420.

### 2-(2-[Ethyl-[4-(4-methylsulfonylphenylazo)phenyl]-amino]ethoxy)benzene-1,4-diamine (**4b**)

This compound was synthesized similarly by the reaction of **1** and **2b**. Sulfone-containing azo-dye diamine **2b** was synthesized, in turn, from 4-(methylmercapto)aniline in four steps as shown in Scheme 3.



**Scheme 2** Synthesis of azo-dye diamine monomers.

**2-(4-Methylsulfonylphenyl)isoindole-1,3-dione (2b-1)**

To a solution of 4-(methylmercapto)aniline (2.5 mL, 2.78 g, 20 mmol) in 20 mL of DMF was added phthalic anhydride (4 g, 27 mmol) and then the mixture was stirred at room temperature for 1 h. After adding 16 mL of acetic anhydride and 8 mL of pyridine, the mixture was stirred at room temperature for 2 h and at 90°C for an additional 4 h. After cooling, a white solid was precipitated and collected by filtration and recrystallized from ethanol to yield 4.6 g of **2b-1** (Y = 87%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 7.93 (q, 2H, aromatic H's), 7.77 (q, 2H, aromatic H's), 7.34 (s, 4H, aromatic H's), 2.49 (s, 3H, —SCH<sub>3</sub>).

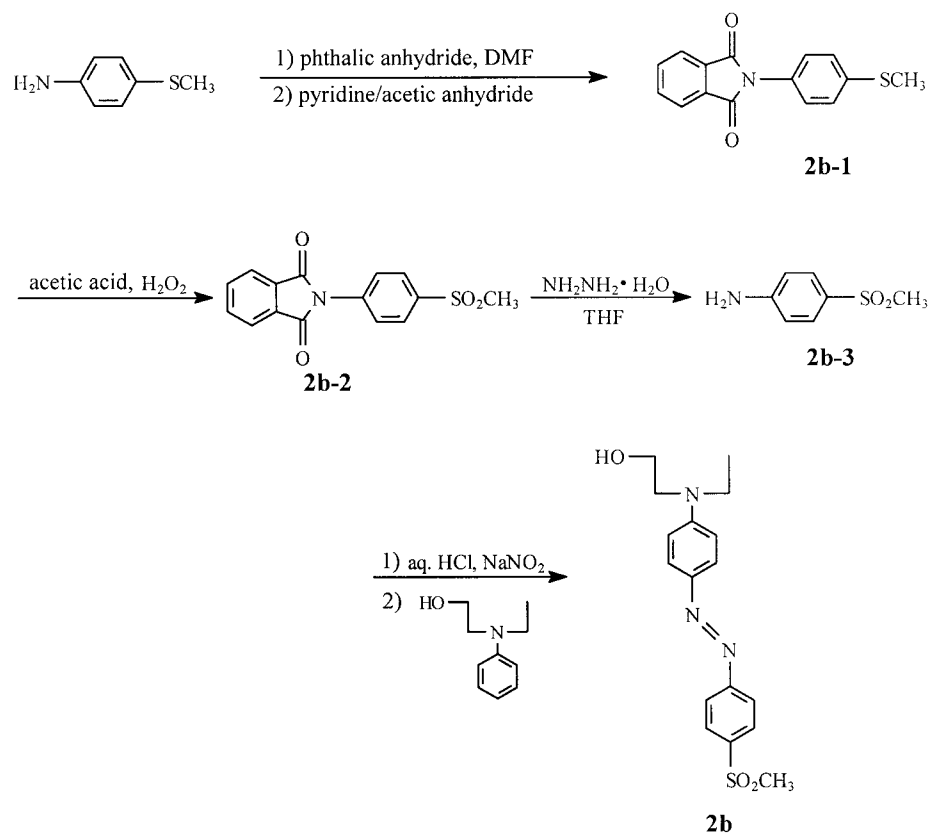
**2-(4-Methylsulfonylphenyl)isoindole-1,3-dione (2b-2)**

To a solution of **2b-1** (3.8 g, 14.1 mmol) in 250 mL of acetic acid was added hydrogen peroxide (25 mL, 35% in water, 258 mmol) and then the mixture was refluxed for 4 h. After cooling, the solution was poured into water, and the precipitate was filtered and recrystallized from ethanol to yield 3.7 g of **2b-2**. (Y = 86%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 8.03 (d, 2H, aromatic H's), 7.78 (q, 2H, aromatic H's), 7.69 (d, 2H, aromatic H's), 3.03 (s, 3H, —SO<sub>2</sub>CH<sub>3</sub>).

**4-Methylsulfonylphenylamine (2b-3)**

To the solution of **2b-2** (4.5 g, 12 mmol) in THF was added hydrazine monohydrate (10 mL,



**Scheme 3** Synthesis of sulfone-containing azo chromophore **2b**.

10.3 g, 200 mmol). The solution was refluxed for 3 h. After cooling, the organic layer was separated from the water layer. The organic solution was then concentrated to the minimum amount. The solution was poured into distilled water and extracted by ethyl acetate. The organic layer was washed twice with distilled water and dried over magnesium sulfate. The solvent was removed by evaporation and the resulting product was recrystallized from ethanol to yield 1.3 g of **2b-3** (Y = 63%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 7.61 (d, 2H, aromatic H's), 6.63 (d, 2H, aromatic H's), 4.17 (br, 2H, aromatic NH<sub>2</sub>), 2.93 (s, 3H, —SO<sub>2</sub>CH<sub>3</sub>).

**2-{Ethyl-[4-(4-methylsulfonylphenylazo)phenylazo]-phenyl}amino}ethanol (**2b**)**

To a mixture of **2b-3** (2.7 g, 16 mmol), concentrated hydrochloric acid (30 mL, 35%, 375 mmol), distilled water (10 mL), and sodium nitrite (3.45 g, 50 mmol) was added dropwise a solution of 2-(*N*-ethylanilino)ethanol (8.3 g, 50 mmol) in 20 mL of ethanol. The reaction mixture was stirred

at 0°C for 2 h and then at room temperature for additional 20 h. After the reaction was completed, the reaction mixture was poured into 100 mL of distilled water and neutralized with an aqueous NaOH solution. The orange solid precipitated out of the solution was collected by filtration and was recrystallized from ethanol to yield 2.4 g of **2b** (Y = 42%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 7.93 (d, 2H, aromatic H's), 7.86 (d, 2H, aromatic H's), 7.79 (d, 2H, aromatic H's), 6.72 (d, 2H, aromatic H's), 3.80 (t, 2H, —CH<sub>2</sub>OH), 3.50 [m, 4H, —N(CH<sub>2</sub>)<sub>2</sub>], 3.01 (s, 3H, —SO<sub>2</sub>CH<sub>3</sub>), 1.67 (br, 1H, —OH), 1.18 (t, 3H, —CH<sub>3</sub>).

**2-{4-(1,3-Dioxo-2,3-dihydro-1H-2-isoindolyl)-3-[2-(ethyl-4-{(E)-2-[4-(methylsulfonyl)phenyl]-1,3-diazonylanilino)ethoxy]phenyl]-1,3-isoindolinedione (**3b**)**

**2b** (1.1 g, 3 mmol) was completely dissolved in 30 mL of anhydrous NMP under nitrogen. After the addition of **1** (1.2 g, 3 mmol) and triphenylphosphine (1.6 g, 6 mmol), diethyl azodicarboxylate (1.0 mL, 1.04 g, 6 mmol) was added dropwise. The

reaction mixture was stirred at room temperature for 10 h and then precipitated into 400 mL of ethanol/distilled water. The resulting precipitate was collected by filtration and recrystallized from chloroform/methanol to yield 1.7 g of **3b** (Y = 80%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 7.98 (d, 2H, aromatic H's), 7.89 (q, 4H, aromatic H's), 7.75 (m, 4H, aromatic H's), 7.59 (m, 4H, aromatic H's), 7.31 (d, 2H, aromatic H's), 7.21 (d, 1H, aromatic H's), 7.16 (d, 1H, aromatic H's), 6.61 (d, 2H, aromatic H's), 4.21 (t, 2H, —OCH<sub>2</sub>CH<sub>2</sub>—), 3.69 (t, 2H, —OCH<sub>2</sub>CH<sub>2</sub>—), 3.33 (q, 2H, —CH<sub>2</sub>CH<sub>3</sub>), 3.03 (s, 3H, —SO<sub>2</sub>CH<sub>3</sub>), 1.03 (t, 3H, —NCH<sub>2</sub>CH<sub>3</sub>).

### 2-(2-{Ethyl-[4-(4-methylsulfonylphenylazo)-phenyl]amino}ethoxy)benzene-1,4-diamine (**4b**)

**3b** (1.7 g, 2.4 mmol) was dissolved in 250 mL of THF and refluxed. The solution of hydrazine monohydrate (15 mL, 15.5 g, 300 mmol) in 25 mL of THF was added dropwise. After refluxing for 3 h, the reaction mixture was cooled and the organic layer was separated from the water layer. The solvent was removed and hot ethanol was added and filtered. The solvent was removed from the filtrate and the orange solid was recrystallized from ethanol to yield 0.5 g of **4b** (Y = 46%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 7.95 (d, 2H, aromatic H's), 7.88 (d, 2H, aromatic H's), 7.83 (d, 2H, aromatic H's), 6.79 (d, 2H, aromatic H's), 6.49 (d, 1H, aromatic H's), 6.16 (t, 1H, aromatic H's), 6.12 (d, 1H, aromatic H's), 4.10 (t, 2H, —OCH<sub>2</sub>CH<sub>2</sub>—), 3.81 (t, 2H, —OCH<sub>2</sub>CH<sub>2</sub>—), 3.53 (q, 2H, —CH<sub>2</sub>CH<sub>3</sub>), 3.31 (br, 4H, NH<sub>2</sub>), 3.02 (s, 3H, —SO<sub>2</sub>CH<sub>3</sub>), 1.19 (t, 3H, —NCH<sub>2</sub>CH<sub>3</sub>).

## Polymerization

### PAI-a

To a solution of **RMA** (0.4 g, 1 mmol) in 5 mL of thionyl chloride was added a few drops of DMF and refluxed for 4 h. After the reaction was completed, the solvent was removed by distillation under reduced pressure.<sup>8</sup> The resulting solid (**RMA-COCl**) was dissolved in 4 mL of anhydrous NMP. A solution of **4a** (0.42 g, 1 mmol) in 2 mL of anhydrous NMP and pyridine/triethylamine (1.5 mL/1 mL) was added dropwise and stirred at 0°C for 2 h and then at room temperature for additional 2 h. Triphenylphosphite (0.8 mL, 0.94 g, 3 mmol) was added to the reaction mixture and heated to 120°C and stirred for 12 h. After the reaction was completed, the reaction mixture was cooled and poured into a large

amount of methanol. It was reprecipitated several times from THF into methanol and dried in a vacuum oven at 60°C until a constant mass was maintained to yield 0.5 g of a red solid (conversion = 60%).

IR (KBr pellet, cm<sup>-1</sup>): 3405 (br, —NH), 2988–2872 (br, —CH, aliphatic), 1783 (w, C=O, imide), 1712 (s, C=O, imide), 1512 (s, —N=O asym), 1332 (s, —N=O sym).

### PAI-b

This polymer was synthesized similarly to **PAI-a** from **RMA** (0.4 g, 1 mmol) and **4b** (0.45 g, 1 mmol) to yield 0.4 g of a red solid (conversion = 46%).

IR (KBr pellet, cm<sup>-1</sup>): 3405 (br, —NH), 2988–2872 (m, —CH, aliphatic), 1781 (w, C=O, imide), 1712 (s, C=O, imide), 1388 (m, —S=O asym), 1130 (s, —S=O sym).

## Characterization

FTIR spectra were recorded on a Midac FTIR spectrophotometer by using a KBr pellet and window. <sup>1</sup>H-NMR spectra were obtained on a JEOL JNM-LA300 (300 MHz). UV/vis spectra were recorded on a Shimadzu UV-2101PC double-beam spectrophotometer. Differential scanning calorimetry (DSC) measurement was carried out on a Perkin-Elmer DSC 7 at a heating rate of 10°C/min. Thermogravimetric analyses (TGA) were carried out with a DuPont 2950 at a heating rate of 10°C/min under a nitrogen atmosphere and air.

## Fabrication of Polymer Film

The solution of **PAI-a** and **PAI-b** in THF was spin-coated onto a slide glass. The residual solvent was removed at 150°C in a vacuum oven for several days. Film thickness was measured with a TENCOR P-10 profilometer. Optically clear polymer films of 400–500 nm thickness were obtained and used for the measurement of SHG and photoinduced birefringence.

## SHG Measurement

Transparent films of high optical quality were obtained by spin-coating and were poled by the corona poling method. The sample was placed 1 cm below a sharpened tungsten needle electrode charged at 5 kV and the temperature of the film was then heated to 150°C for 15 min. After cooling to ambient temperature, the poling field was turned off. SHG at 532 nm of the poled polymer was measured in transmission. The 1064-nm fun-

damental beam was provided by a Q-switched Nd-YAG laser operating at a 10-Hz repetition rate and a 10-ns pulse duration.

SHG experiments and data analysis were carried out by the standard Maker fringe method.<sup>11</sup> A quartz crystal was used as a reference, allowing for the calibration measurements. The sample cell was able to rotate and was kept between two polarizers, allowing an adequate choice of the polarizations of the fundamental and second-harmonic beams.

### Measurement of Photoinduced Birefringence

A writing laser beam of 532-nm wavelength was used to induce birefringence in the polymer films. The samples were placed between two crossed polarizers *P* and *A* in the path of a probing He-Ne laser. They were irradiated with a writing laser beam, linearly polarized at 45° with respect to the direction of transmission of *P* and *A*. The optical anisotropy, induced in the sample under the action of the writing beam, caused a light signal to pass through the analyzer *A*. The photoinduced birefringence ( $\delta n$ ) was obtained by the following equation:

$$\delta n = \lambda \arcsin[(I/I_0)^{0.5}]/(\pi d)$$

where *I* is the intensity of the transmitted light after *A*; *I*<sub>0</sub>; the intensity of the light passing through the pair of polarizers; *d*, the thickness of the sample; and  $\lambda$ , the wavelength of the probe beam (632.8 nm).

## RESULTS AND DISCUSSION

### Syntheses of Monomers and Polymers

The synthetic route to the rosin-based monomer (**RMA-COCl**) is shown in Scheme 1 and those to the azo-dye diamines are shown in Schemes 2 and 3. Literature methods were successfully adopted for the synthesis of **RMA-COCl** and **4a**. The rosin consists of 90% abietic acid, which is apt to isomerize into levopimaric acid by heat or in an acidic condition. The isomerized product, that is, levopimaric acid, readily underwent a Diels-Alder reaction with maleic anhydride to give **RMA**. The net yield of **RMA** from the gum rosin was 35%. **RMA** was reacted with thionyl chloride into **RMA-COCl** easily. For frequency doubling, chromophores absorbing at the shorter wavelength

region are preferred for enhanced speed and stability.<sup>12</sup> So, we synthesized a different azo chromophore (**2b**) with sulfone as an electron-withdrawing group (Scheme 2), which had more blue-shifted absorption than did **2a**. From this compound, **4b** was synthesized by a similar method adopted for the synthesis of **4a**.<sup>2</sup> All the compounds shown in Schemes 1–3 were identified by NMR and IR characterization.

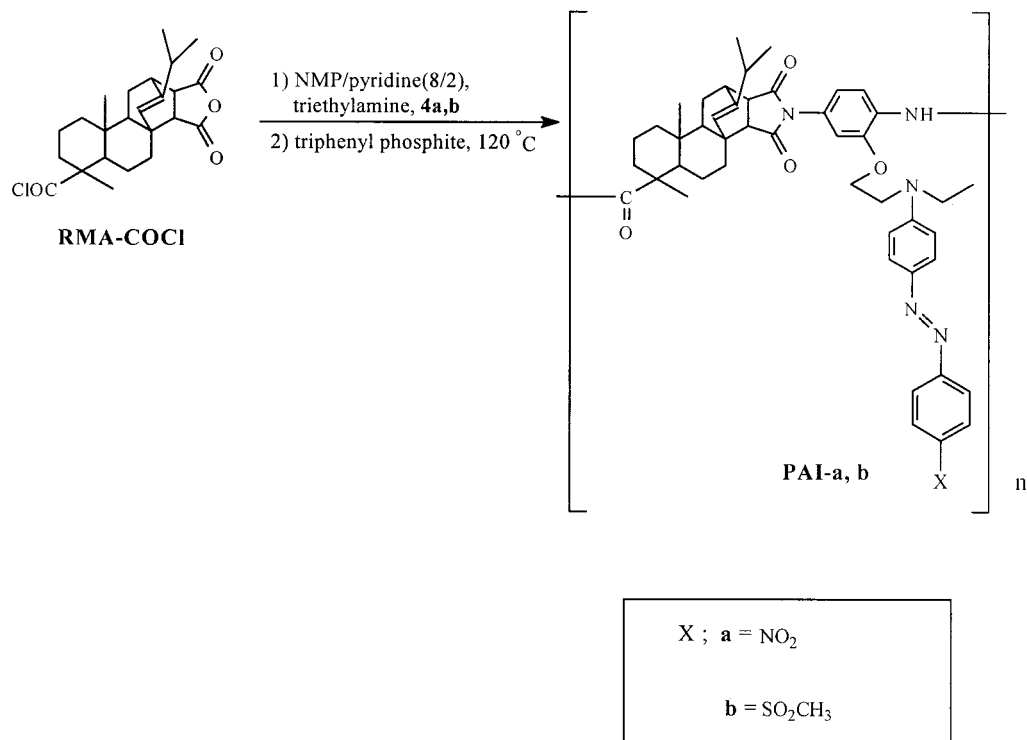
The polymerization procedure of **PAI-a** and **PAI-b** is shown in Scheme 4. Acyl halide and anhydride functional groups of **RMA-COCl** were reacted with azo-dye diamines (**4a**, **4b**) into the polyamideimide structure. Triethylamine and pyridine were used as an acid scavenger and triphenylphosphite was used for the condensation catalyst. Figure 1 shows the FTIR spectra of **PAI-a** and **PAI-b**. The chemical structure of polymers were characterized by the distinct carbonyl absorption of imide at 1783 and 1712 cm<sup>-1</sup> and nitro absorption at 1512 and 1332 cm<sup>-1</sup> for **PAI-a** and the distinct carbonyl absorption of imide at 1781 and 1712 cm<sup>-1</sup> and sulfone absorption at 1388 and 1130 cm<sup>-1</sup> for **PAI-b**.

### Properties of Polymers

The properties of **PAI-a** and **PAI-b** are summarized in Table I. Both polymers were highly soluble in methylene chloride, chloroform, tetrachloroethane, NMP, DMF, and tetrahydrofuran due to the bulky alicyclic rosin structure in the backbone. The number-average molecular weights were relatively low (measured to be 2000–4000) but the mechanically tough and transparent film of high optical quality were easily obtained by the spin-coating method. Low molecular weights of these polymers are possibly due to the nature of sterically hindered functional groups and also the bulkiness of **RMA-COCl**.

The thermal properties of polymers were evaluated by DSC and TGA. From the DSC measurement, the glass transition temperature (*T*<sub>g</sub>) was found to be 146°C for **PAI-a**. Although it was not detected by DSC, the *T*<sub>g</sub> of **PAI-b** is considered to be not much different from that of **PAI-a**. As shown in Figure 2, **PAI-a** and **PAI-b** were very stable up to 250°C. It is speculated that the decomposition of a chromophore starts at this temperature.

The UV-visible absorption spectra of the polymers are shown in Figure 3. **PAI-a** showed maximum absorption at 480 nm and a cutoff wavelength around 620 nm. In contrast, **PAI-b** showed

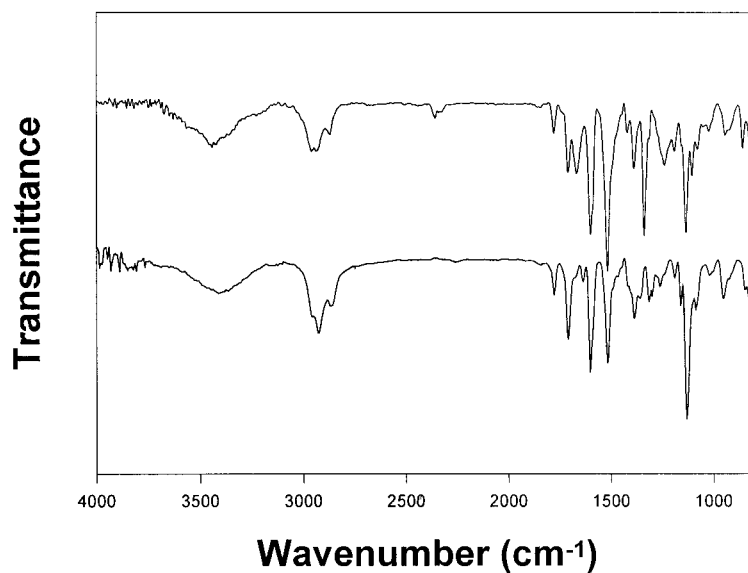


**Scheme 4** Synthesis of rosin-based photoactive polyamideimides.

maximum absorption at 444 nm and a cutoff wavelength around 560 nm. This blue-shifted absorption is advantageous in practical use for frequency doubling. Blue-shifted absorption of **PAI-b** compared to that of **PAI-a** originates from

the weaker electron-withdrawing effect of sulfone than that of the nitro group.

Figure 4 shows the Maker fringe pattern of **PAI-a**. The calculated SHG coefficients of rosin-based azo polymers are shown in Table II. **PAI-a**



**Figure 1** IR spectra of (upper curve) **PAI-a** and (lower curve) **PAI-b**.

**Table I** Synthesis and Molecular Weights of PAI-a and PAI-b

Polymer	Conversion (%)	$\eta_{inh}$ (dL/g) <sup>a</sup>	$M_n$ <sup>b</sup>	$M_w$ <sup>b</sup>	$M_w/M_n$
<b>PAI-a</b>	60	0.12	4200	8300	1.95
<b>PAI-b</b>	46	0.10	2100	4100	1.91

<sup>a</sup> Inherent viscosity measured with 0.5% (w/v) solution in NMP at 30°C.

<sup>b</sup> Measured by GPC in THF, using polystyrene;  $M_n$ : number-average molecular weight;  $M_w$ : weight-average molecular weight.

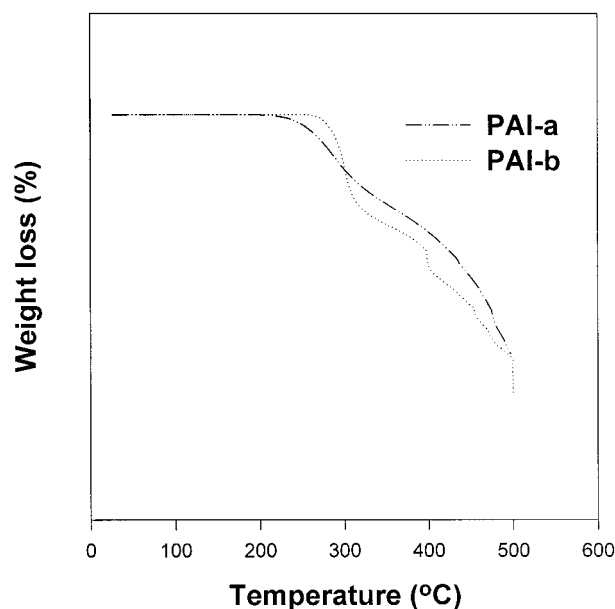
showed a larger SHG coefficient ( $d_{33} = 83$  pm/V,  $d_{31} = 16$  pm/V) than that of **PAI-b** ( $d_{33} = 54$  pm/V,  $d_{31} = 12$  pm/V), although the order parameters were comparable. It is explained by the fact that chromophore **2a** has a larger  $\beta$  (first hyperpolarizability) and more resonance enhancement at 1064 nm than has **2b** because of the stronger electron-withdrawing ability of the nitro group than that of sulfone.

Figure 5 shows a typical sequence of writing and erasing of birefringence in rosin-based azo polymers. Birefringence was induced to a saturation level by a linear polarized laser beam and relaxation occurred when the laser beam was turned off. When the circularly polarized laser beam was turned on, the induced birefringence was erased instantaneously. It was observed that **PAI-a** had a larger saturation level of birefringence in comparison to **PAI-b**, which probably comes from the fact that **PAI-a** has a larger dipole moment and a higher absorbance at 532 nm than

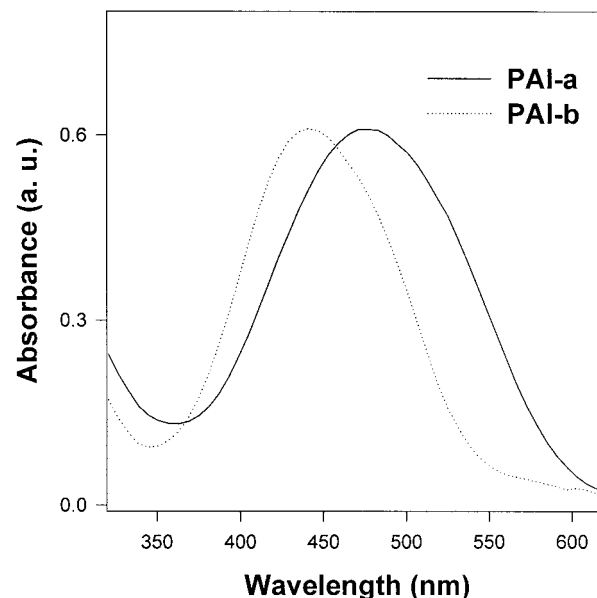
those of **PAI-b** (see Fig. 3). Birefringences as high as 0.072 for **PAI-a** and 0.035 for **PAI-b** could be induced and erased repeatedly by the irradiation of linearly polarized and circularly polarized 532-nm light. On the other hand, **PAI-b** showed a faster writing rate, which presumably resulted from the fact that dipolar rearrangement in the writing process was easier due to the relatively lower molecular weight and smaller dipole moment. It was particularly noted that the rosin-based azo polymers **PAI-a** and **PAI-b** are potentially very useful for an optical storage application due to the large value of photoinduced birefringence and excellent optical quality. Further studies on the writing and erasing kinetics of the photoinduced birefringence in terms of the polymer structure are in progress.

## CONCLUSIONS

Rosin-based photoactive polyamideimides (**PAI-a**, **PAI-b**) were synthesized and characterized. These

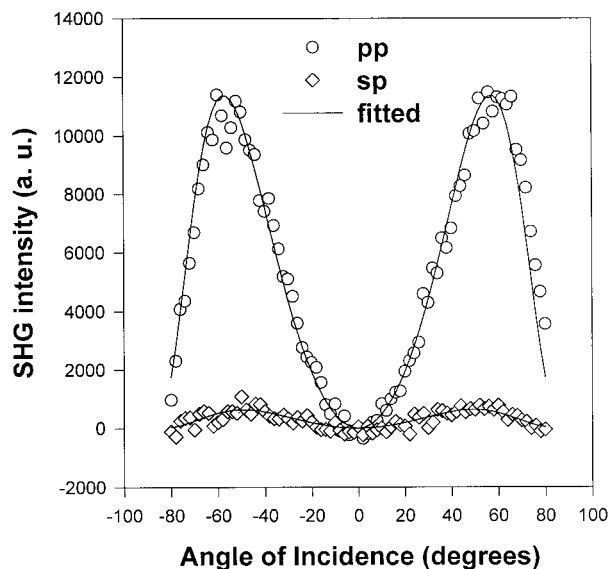


**Figure 2** TGA thermograms of **PAI-a** and **PAI-b**.



**Figure 3** UV-visible absorption spectra of **PAI-a** and **PAI-b**.





**Figure 4** SHG Maker fringe curve of corona-poled PAI-a.

polymers had excellent solubility in various organic solvents such as methylene chloride, chloroform, tetrachloroethane, NMP, DMF, and tetrahydrofuran and showed moderate-to-high thermal stability. They could easily be processed into a thin film of high optical quality by spin-coating. The measured second-order nonlinear optical coefficients ( $d_{33}$ ) of the polymers were 83 pm/V for PAI-a and 54 pm/V for PAI-b. Large photoinduced birefringences as high as 0.072 for PAI-a and 0.035 for PAI-b could be induced and erased repeatedly by the irradiation of linearly polarized and circularly polarized 532 nm light, respectively.

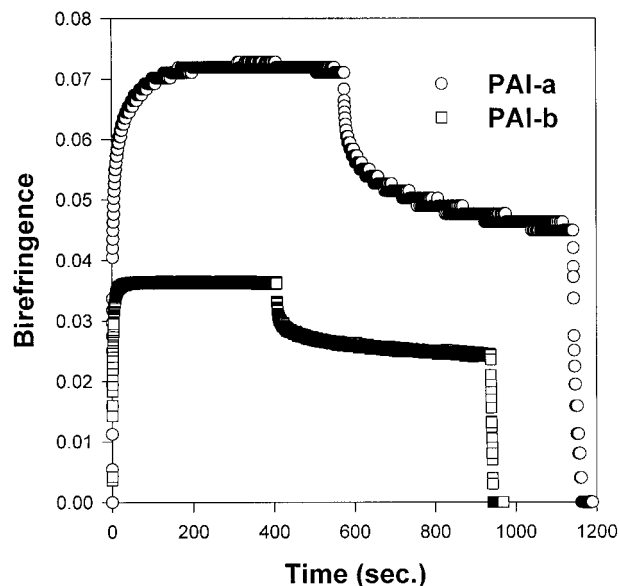
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**Table II** Second-order Nonlinear Optical Properties of PAI-a and PAI-b

Polymer	$\varphi^a$	$d_{33}$ (pm/V)	$d_{31}$ (pm/V)	$d_{33}/d_{31}$
PAI-a	0.15	83 <sup>b</sup>	16 <sup>b</sup>	5.2
PAI-b	0.16	54 <sup>b</sup>	12 <sup>b</sup>	4.5

<sup>a</sup> Order parameter  $\varphi = 1 - A_p/A_0$ ,  $A_p$ : absorbance after poling;  $A_0$ : absorbance before poling.

<sup>b</sup> Corona poling: 5 kV, 15 min at 150°C, measured using a Nd-YAG laser (1064 nm).



**Figure 5** Photoinduced birefringence of PAI-a and PAI-b written with a 532-nm laser. For PAI-a, time = 0 s: linearly polarized laser ON; time = 580 s: laser OFF; time = 1150 s: circularly polarized laser ON. For PAI-b, time = 0 s: linearly polarized laser ON; time = 410 s: laser OFF; time = 940 s: circularly polarized laser ON.

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