

# Synthesis and Nonlinear Optical Properties of Polyphosphazenes with Binaphtholyl and Indole Side Groups

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**ABSTRACT:** New polyphosphazenes (**P2** and **P3**) that contain indole-based chromophore and binaphtholyl moieties as side chains are prepared by a new postfunctional strategy. Molecular structural characterization for the high polymers was presented by <sup>1</sup>H-NMR, IR and UV-Visible spectra, gel permeation chromatography, and differential scanning calorimetry. The glass transition temperature of **P2** was determined to be 168°C, higher than those polyphosphazenes reported previously in the literatures. **P2** and **P3** are thermal stable and easily soluble in high polar sol-

vents. The maximum absorption of **P2** in chloroform was at 425 nm and cuts off at about 550 nm, while that of **P3** was 393 nm and 500 nm, respectively, which resulted in a wide transparency window. The poled films of **P2** and **P3** reveal a resonant  $d_{33}$  value of 20 pm/V and 14 pm/V, respectively, by second harmonic generation measurements. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 365–371, 2007

**Key words:** polyphosphazene; synthesis; indole; nonlinear optical property

## INTRODUCTION

Polyphosphazenes with the general formula  $[\text{NP}(\text{R})_{2-x}(\text{R}')_x]_n$  ( $\text{R} = \text{R}'$ , homopolymers;  $\text{R} \neq \text{R}'$ , copolymers) are a very important class of inorganic polymers. The inorganic backbone has some unique properties such as high thermooxidative and photolytic stability, excellent optical transparency from 220 to 800 nm. Most polyphosphazenes have very high molecular weight, and they are usually amorphous, soluble, and easily prepared.<sup>1–4</sup> Because of these advantages, they were considered as an excellent candidate for electro-optical (EO) applications.<sup>5–7</sup> In 1991, a second-order nonlinear optical (NLO) chromophore, dispersed red-1 (DR-1), was first linked to the phosphorus–nitrogen backbone by Allcock et al.<sup>5</sup> to synthesize new NLO polymeric materials; the resultant polyphosphazenes showed good properties such as stability and processibility and demonstrated that polyphosphazenes might be promising polymeric materials for the NLO applications, except that  $T_g$  was only 58°C. Then in 1996 and 1998, they also synthesized some other polyphosphazenes with higher loading of the NLO chromophores by alternative approaches.<sup>6,7</sup>

In 1996, Carriedo et al.<sup>8</sup> prepared a new type of phosphazene polymer containing 2,2'-dioxybiphenyl groups by using the corresponding difunctional reagents, and among them, one polyphosphazene possesses very high glass transition temperature ( $T_g$ ): 164°C. This result was exciting. And in 2000, Lopez and coworkers<sup>9</sup> linked 4-[(4'-nitrophenyl)azo]phenoxy and 2,2'-dioxybiphenyl groups to phosphazene backbone to yield the NLO-active polyphosphazene, and the  $T_g$  was still very high (about 150°C). They studied the resultant high  $T_g$  NLO-active polyphosphazene in detail with the corresponding doped system, and provided much useful information. However, the  $d_{33}$  value was tested to be only 1.7–6.0 pm/V. This might be due to the low  $\beta$  value of the chromophore and there was no flexible spacer between the phosphazene backbone and the chromophore side groups, which directly decreased the nonlinear property of the polymer by affecting the effective poling of the chromophore moieties under the electric field. Therefore, to achieve the high  $d_{33}$  value in the system of polyphosphazenes, the chromophore with higher  $\beta$  value should be used, and there should be a suitable spacer between the chromophore side chains and the backbone, just as Allcock et al. did previously.<sup>5,10</sup> On the other hand, Park and coworkers recently showed that the polymers with indole-based chromophores possessed very high  $d_{33}$  values.<sup>11</sup> And also, the maximum absorption of the resultant polymers showed blue-shifted compared with that of polymers containing DR-1 as NLO chromophore. This is another advant-

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age since the device-quality NLO materials should possess a wide transparency window (low optical loss), besides the large macroscopic optical nonlinearity and high stability to meet the requirements of the practical application.<sup>12–15</sup>

In this article, a new postfunctional strategy was explored to synthesize new polyphosphazenes (**P2** and **P3**) that contained indole-based chromophore and binaphtholyl moieties as side chains. Thus, polyphosphazene (**P1**) with binaphtholyl and indole groups as side chains was first obtained by the direct nucleophilic substitution reaction from a highly reactive macromolecular intermediate, poly(dichlorophosphazene), and then a post azo coupling of *p*-nitrobenzenediazonium fluoroborate or *p*-ethylsulfonylbenzenediazonium fluoroborate toward the indole ring in **P1** afforded the indole-based chromophore-functionalized polyphosphazene (**P2** and **P3**). The synthetic route is simple, and the purification of the products is very easy. The resultant polyphosphazenes are well soluble in common solvents and showed good comprehensive properties. Therefore, it is believed that this method can be applied to prepare many other NLO polymers with indole-based side groups, especially sulfonyl-indole based chromophores as there is no other group report about the usage of *p*-ethylsulfonylbenzenediazonium fluoroborate for the preparation of NLO polymers.

## EXPERIMENTAL

### Materials and measurements

Tetrahydrofuran (THF) and petroleum ether (60–90°C) were dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. *N*-(hydroxyethyl) indole was prepared as reported previously.<sup>11</sup> The *p*-nitrobenzenediazonium fluoroborate was synthesized following a procedure described in the literature.<sup>16</sup> *p*-ethylsulfonylaniline was synthesized according to the literature.<sup>17</sup> *N*-methylpyrrolidone was dried over and distilled from CaH<sub>2</sub> under an atmosphere of dry nitrogen. Ethanol was treated as normal procedure. All other reagents were used as received. Poly(dichlorophosphazene) was obtained from the thermal ring-opening polymerization of phosphonitrile chloride trimer.<sup>18</sup> Sodium hydride was weighted in the dry box. The substitution reactions of poly(dichlorophosphazene) were carried out in a dry nitrogen atmosphere using Schlenk technique.

<sup>1</sup>H-NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer. FTIR spectra were recorded on a Testscan Shimadzu FTIR 3000 series in the region of 3000–400 cm<sup>-1</sup> on KBr pellets. UV-visible spectra were obtained using a Shimadzu 160A spectrometer in the polymer chloroform solution. Differential scanning calorimetry (DSC) analy-

ses were performed in a Rigaku Themoflex DSC8131 at a scan rate of 10°C/min. Molecular weights were determined in THF solution by Waters 2960D separation Module containing Styragel HR1 THF column and Waters 2410 Refractive Index Detector with a calibration curve for polystyrene standards. Thermal analysis was performed on SHIMADZU DT-40 thermal analyzer at a heating rate of 20°C/min in nitrogen at a flow rate of 50 cm<sup>3</sup>/min for thermogravimetric analysis.

### Synthesis of *p*-ethylsulfonylbenzenediazonium fluoroborate

*p*-ethylsulfonylaniline (0.56 g, 3 mmol) was dissolved in fluoroboric acid (40%), and then the solution was cooled to 0°C. A solution of sodium nitrite (0.21 g, 3 mmol) in water (1.5 mL) was added dropwise. The resultant mixture was stirred at 0°C for half an hour. The yellow solid was filtered quickly and washed with cold ethanol and ether for several times. After this, the product was stored in the refrigerator (0.7 g).

### Synthesis of polyphosphazene (**P1**)

Binaphthol (0.61 g, 2.1 mmol) and some triethylamine were added to a solution of poly(dichlorophosphazene) (0.47 g, 4.0 mmol) in 30 mL THF, and the mixture was stirred at 60°C for 30 h. Twenty milliliters of a solution of the sodium salt of *N*-(hydroxyethyl)indole [prepared from *N*-(hydroxyethyl)indole (0.65 g, 4.0 mmol) and sodium hydride (0.096 g, 4.0 mmol) in THF] was added, and the mixture was stirred at 60°C for 2 days. Then 15 mL of the solution of NaOCH<sub>2</sub>CH<sub>3</sub> [prepared from sodium (0.18 g, 7.8 mmol) and ethanol (0.8 g, 17.4 mmol)] was added, and the resultant mixture reacted for another 3 days at 60°C. After the bulk of THF in the mixture was removed under vacuum, the mixture was poured into 300 mL water, and the white solid was filtered, washed with water, and air-dried. The solid was dissolved in THF, and the insoluble residue was filtered out. The filtrate was evaporated to remove the bulk of THF. Some methanol was added to precipitate the solid. The resultant solid was purified by several precipitations from THF into methanol. The solid was dried in vacuum at 40°C to yield the product (0.32 g). <sup>1</sup>H-NMR(δ, CDCl<sub>3</sub>): 8.1–6.2 (m, aromatic rings), 3.4–2.3 (m, —NCH<sub>2</sub>, —OCH<sub>2</sub>), 1.2–1.1 (t, —CH<sub>3</sub>).

### Preparation of polyphosphazene (**P2** and **P3**)

Polyphosphazene **P1** (0.13 g) was dissolved in 1 mL of *N*-methylpyrrolidone, and then *p*-nitrobenzenediazonium fluoroborate (70 mg) was added under cooling with an ice bath. The color of the solution changed to red immediately. After stirring for 8 h at

0°C, excessive anhydrous potassium carbonate was added and the mixture was stirred for additional 1 hour, and then filtered. The residue was washed with THF, and the filtrates were collected and THF was removed under reduced pressure. Then some methanol was added dropwise to precipitate the polymer. The resultant solid was purified by several precipitations from THF into methanol. The solid was dried in vacuum at 40°C to yield 60 mg orange red product. <sup>1</sup>H-NMR (δ, CDCl<sub>3</sub>): 8.4–8.0 (m, aromatic rings), 7.9–7.4 (m, aromatic rings), 7.4–6.1 (m, aromatic rings), 2.3–3.4 (m, –NCH<sub>2</sub>, –OCH<sub>2</sub>), 1.2–1.1 (t, –CH<sub>3</sub>).

**P3** was prepared by the similar procedure as **P2**, but *p*-ethylsulfonylbenzenediazonium fluoroborate was used instead of *p*-nitrobenzenediazonium fluoroborate. <sup>1</sup>H-NMR(δ, CDCl<sub>3</sub>): 8.2–7.8 (m, aromatic rings), 7.8–7.7 (m, aromatic rings), 7.6–7.4 (m, aromatic rings), 7.2–6.2 (m, aromatic rings), 3.8–3.6 (m, –OCH<sub>2</sub>), 3.5–3.3 (m, –NCH<sub>2</sub>), 3.2–3.0 (m, –SO<sub>2</sub>CH<sub>2</sub>), 1.4–1.1 (t, –CH<sub>3</sub>).

### Polymer film preparation

Polyphosphazenes **P2** and **P3** were dissolved in THF, and the solution (5 wt %) was filtered through syringe filters. Polymer films were spin coated onto indium-tin-oxide-coated glass substrates (which were cleaned by N, N-dimethylformide, acetone, distilled water, and THF subsequently in ultrasonic bath) (2500 rpm). Residual solvent was removed by heating the films in a vacuum oven at 45°C for 2 days. The film thickness of **P2** and **P3** was 0.36 and 0.48 μm, respectively, measured by TENCOR 500 Surface Profiler.

### Characterization of poled films

The second-order optical nonlinearity of polyphosphazenes **P2** and **P3** was determined by *in situ* second harmonic generation (SHG) experiments using a closed temperature-controlled oven with optical windows and three needle electrodes. The film, which was kept at 45° to the incident beam, was poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature: 160°C for **P2** and 130°C for **P3**, voltage: 8.5 kv at the needle point, gap distance: 0.8 cm. SHG measurements were carried out with a Nd:YAG laser operating with a 10 Hz repetition rate and an 8 ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

## RESULTS AND DISCUSSION

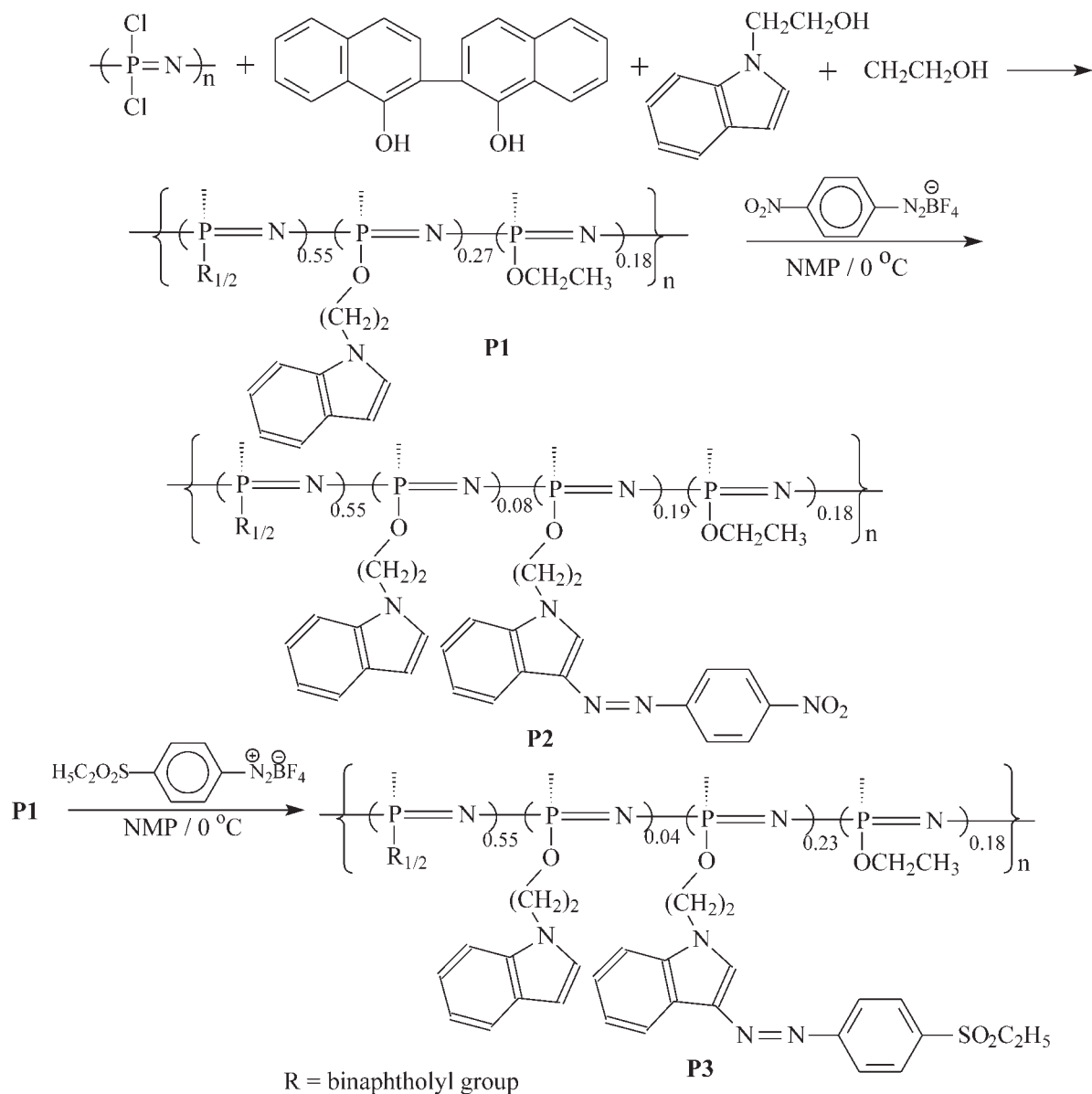
### Synthesis

Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of phosphonitrile

chloride trimer.<sup>18</sup> Separation of the phosphonitrile chloride trimer from the poly(dichlorophosphazene) was very important. We used petroleum ether (60–90°C) to wash the unpolymerized trimer because the poly(dichlorophosphazene) was not dissolved in petroleum ether. By comparison of the amount of the trimer before and after the polymerization, we could easily know the quantity of the poly(dichlorophosphazene).<sup>19–22</sup>

The synthetic route to **P1–3** is shown in Scheme 1. **P1** was obtained from the highly reactive macromolecular intermediate, poly(dichlorophosphazene), by nucleophilic substitution reaction. In the report of Carriedo et al., the difunctional reagents reacted with the chlorine atoms of poly(dichlorophosphazene) at the presence of K<sub>2</sub>CO<sub>3</sub> as the base.<sup>8</sup> Here in our case, the binaphtholyl groups were linked to the polyphosphazene backbone while some triethylamine was present instead of K<sub>2</sub>CO<sub>3</sub> since it was soluble in THF and the resultant mixture was in the same phase. The binaphtholyl and indole groups can not react with all the chlorine atoms because of the steric shielding effect. However, if some chlorine atoms remain in the polymer without being reacted, crosslinking may take place and the polymer becomes insoluble when it is exposed to moisture or water.<sup>23</sup> So, an excess of NaOCH<sub>2</sub>CH<sub>3</sub> was added into the reacting solution to replace all the remaining chlorine atoms completely.

**P2** was synthesized via a post azo coupling reaction, which has been developed by us recently, and proved to be a convenient method to introduce indole azo chromophores into the side chains of NLO active polymers.<sup>19</sup> Here, we further developed the postfunctional method by using a novel reagent, *p*-ethylsulfonylbenzenediazonium fluoroborate, to synthesize **P3**. Though there was no report about its preparation, we still expect that it could be synthesized as both sulfonyl and nitro groups are strong acceptors, and both of *p*-alkylsulfonylaniline and *p*-nitroaniline could form diazonium salts in hydrochloric acid. And according to the literatures and our previous work, the chromophores exhibited similar first molecular hyperpolarizability (β) when the nitro groups were replaced by the sulfonyl groups, but the sulfonyl compounds showed much wider transparency in visible region (with hypsochromic shift of 20–40 nm) and the synthetic flexibility.<sup>24–26</sup> The overall synthesis of the polyphosphazenes **P2** and **P3** was carried out through only two steps. The synthetic route was very simple, and the purification of the products was very easy. Another advantage of this method was that the concentration of the indole-based chromophore in **P2** and **P3** could be controlled by adjusting the quantity of the compound of *p*-nitrobenzenediazonium fluoroborate or *p*-ethylsulfonylbenzenediazonium fluoroborate in the azo coupling reaction. We hope that this new post functional method would promote the prep-



Scheme 1

aration of more other polymers containing indole-based or sulfonyl-based chromophore and other polyphosphazenes with high glass transition temperature for NLO applications.

#### Structural characterization of P1 and P2

In the IR spectra of P1–3 (Fig. 1), the 1250–1200  $\text{cm}^{-1}$  bands were attributed to an intense P=N stretching vibration and the 750  $\text{cm}^{-1}$  band to an in-phase P–N–P stretch. An apparent new strong absorption band, appeared at 1332  $\text{cm}^{-1}$  in the IR spectrum of P2, was assignable to the absorption of the nitro unit. Also, in P3, a new strong absorption bands appeared at about 1137  $\text{cm}^{-1}$  was due to the absorption of the sulfonyl groups (Fig. 2). This confirmed that the *p*-

nitrobenzenediazonium fluoroborate or *p*-ethylsulfonylbenzenediazonium fluoroborate had reacted with the indole ring and the nitro or sulfonyl units were introduced into the polymer side chains.

The signals of the binaphtholyl and indole rings of P1 in the  $^1\text{H-NMR}$  spectra appeared in the downfield, the proton resonance of  $-\text{NCH}_2-$ ,  $-\text{OCH}_2$  groups at 2.3–3.4 ppm, and the proton resonances of methyl groups around 1.0 ppm. In P2, after the azo coupling reaction, some resonance peaks appeared in the downfield, which were due to the *p*-nitro phenyl moieties, also confirmed that the azo coupling reaction was successful and the azo chromophore really formed. The ratios of the side chains could be calculated by analyzing the  $^1\text{H-NMR}$  peak integration carefully, and were shown in Scheme 1. Similarly, the

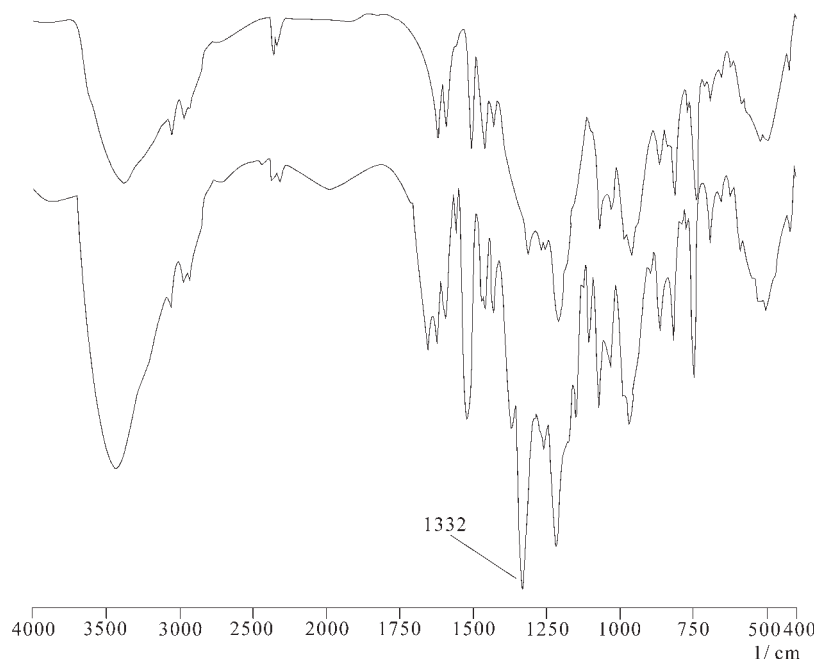


Figure 1 The IR spectra of P1-2.

structure of **P3** could be determined as shown in Scheme 1.

**P1-3** have good solubility in common organic solvents, such as  $\text{CHCl}_3$ , THF, DMSO, and DMF, etc. Figure 3 showed the UV-Visible spectra of **P1-3** in the solution of chloroform. After the post azo coupling reaction, a new strong absorption maximum of the  $\pi-\pi^*$  transition of indole-based chromophore in **P2** appeared at about 425 nm, with a cutoff at ca. 550 nm, while that of **P3** was 393 nm and 500 nm, respectively. The maximum absorption of **P2** and **P3** was

much blue-shifted compared with that of polymers containing DR-1 as NLO chromophore and resulted in a wide transparency window. And the results further proved that when the nitro groups were replaced by the sulfonyl groups, the sulfonyl compounds showed much wider transparency in visible region.

The polyphosphazenes did not show any significant low-temperature weight loss. The high-temperature weight loss for the polymers commenced at about 285°C and increased gradually at high temperature. Generally, the  $T_g$  of polyphosphazenes was very

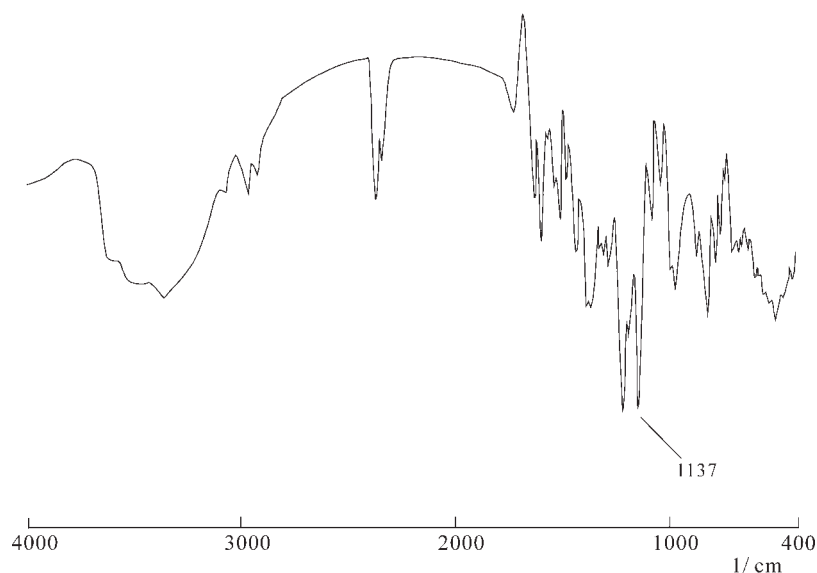
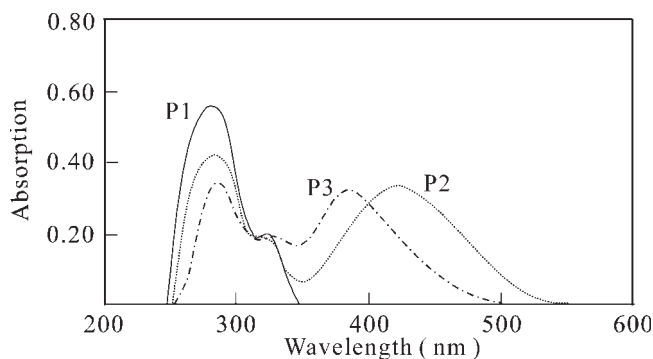


Figure 2 The IR spectra of P3.



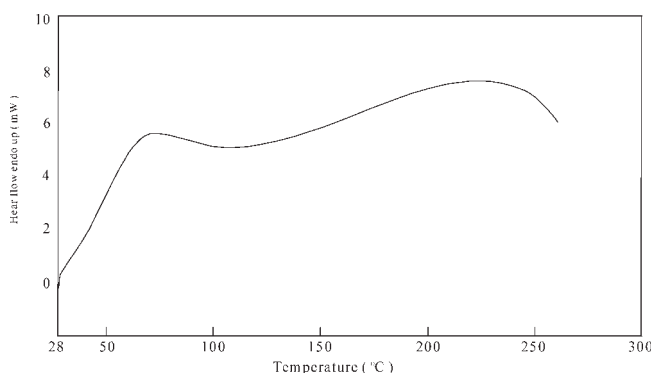


**Figure 3** The UV-Vis spectra of **P1–3** in  $\text{CHCl}_3$ .

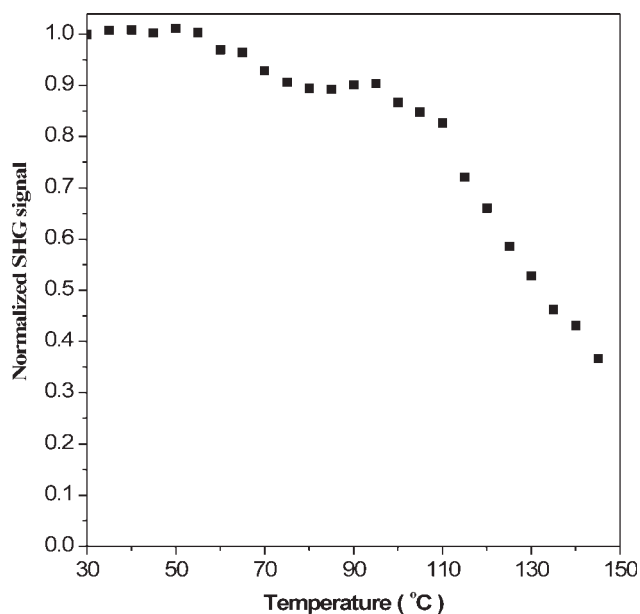
low due to the high flexibility of the phosphazene backbone.<sup>1–4</sup> Here in **P2**, some units were linked with the binaphtholyl groups, and the free rotation of the backbone was limited in a great degree, so the  $T_g$ s of **P2** and **P3** should increase dramatically as reported previously.<sup>9</sup> The DSC thermogram exhibited a glass transition temperature ( $T_g$ ) at about 168°C of **P2** (Fig. 4). And that of **P3** was not obtained, but the  $T_g$  of **P3** should also be high as the structure of **P3** and **P2** was similar. Perhaps 168°C is the highest  $T_g$  in polyphosphazenes found so far, and will benefit much to the stability of the NLO property of **P2**.

The molecular weights of **P1–3** were determined by gel permeation chromatography with refractive index detector. The  $M_n$  and  $M_w$  of **P3** were  $1.6 \times 10^5$  and  $2.7 \times 10^5$ , respectively, **P2** were  $1.8 \times 10^5$  and  $3.0 \times 10^5$ , respectively, while those of **P1** were  $1.4 \times 10^5$  and  $1.9 \times 10^5$ , respectively. It was obvious that the molecular weights of polymers did not change much during the post azo coupling reaction as the reaction conditions are mild.

To evaluate the NLO activity of the poled polymer films, thin films of polyphosphazene **P2** and **P3** were prepared for SHG measurement. The thin films of **P2** and **P3** could be prepared very easily under high spinning rate (2500 rpm, much high than that reported before<sup>9</sup>), and the quality was very high. Cal-



**Figure 4** DSC curve of **P2**.



**Figure 5** Decay of the SHG coefficient signals as a function of temperature for **P2**.

ulation of the  $d_{33}$  value for the poled **P2** is based upon the equation as shown below,<sup>27</sup>

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{\frac{I_s l_{c,q}}{I_q l_s} F}$$

where the  $d_{11,q}$  is  $d_{11}$  of the quartz crystals, which is 0.45 pm/V,  $I_s$  and  $I_q$  are the SHG intensities of the sample and the quartz, respectively,  $l_{c,q}$  is the coherent length of the quartz,  $l_s$  is the thickness of the polymeric films, and  $F$  is the correction factors of the apparatus and equals 1.2 when  $l_c [dmt] l_s$ . The  $d_{33}$  values of **P2** and **P3** were calculated to be 20 and 14 pm/V, respectively, at 1064-nm fundamental wavelength. Generally, the  $d_{33}$  value of the same NLO polymer can be different when measured by different methods or different testing systems. Compared with the values of other polymers containing similar azo chromophores tested by the same equipment, the  $d_{33}$  values of **P2** and **P3** are relatively high.<sup>28–33</sup> They should be due to the high  $\beta$  value of indole azo chromophores<sup>10</sup> and the presence of some spacer between the chromophore side chains and the backbone. The dynamic thermal stability of the SHG signal was investigated through a depoling experiment in which the real time decay of the SHG signal is monitored as the poled film was heated at a rate of 4°C/min in the range of 35–200°C. Figure 5 showed that the decay onset of the SHG signals occurred around 110°C, and the half-decay temperature of the signals was 133°C.

Normally, there are three main requirements for the EO materials: high NLO property, low optical loss, and good stability and processability.<sup>12–15</sup> Here,

the  $T_g$  of **P2** and **P3** is relatively high, which will benefit much to the stability of its NLO properties. The  $d_{33}$  value of **P2** and **P3** was not low. The maximum absorption was much blue-shifted (comparing the normal chromophores), which resulted a wide transparency window. The processability of **P2** and **P3** should be very good as its thin films could be prepared very easily, and also polyphosphazenes possess good thermal and photo stability. Therefore, **P2** and **P3** may be promising candidates for the practical NLO uses.

### CONCLUSIONS

New polyphosphazenes **P2** and **P3** with binaphtholyl groups and indole-based chromophores as side chains is prepared by a two-step method. Thus polyphosphazene (**P1**) with binaphtholyl and indole groups as side chains was first obtained by the direct nucleophilic substitution reaction from a highly reactive macromolecular intermediate, poly(dichlorophosphazene), and then a post azo coupling of *p*-nitrobenzenediazonium fluoroborate or *p*-ethylsulfonylbenzenediazonium fluoroborate toward the indole ring in **P1** afforded the indole-based chromophore-functionalized polyphosphazenes (**P2** and **P3**). This synthetic route is simple, and the purification of the products was easy. Especially, *p*-ethylsulfonylbenzenediazonium fluoroborate was synthesized and used at the first time as a novel post azo coupling reagent. To our knowledge, there are no other group reports about the synthesis of polymers with sulfonyl chromophore by the post azo coupling reactions. It is believed that many other polyphosphazenes containing NLO chromophores with high glass transition temperature and polymers with sulfonyl-based chromophores as side chains for NLO applications could be prepared by the similar method. The poled films of **P2** and **P3** reveals a resonant  $d_{33}$  value of 20 and 14 pm/V by SHG measurements. As their  $T_g$ s are relatively high, the transparency window is wide, and they possesses good all-around properties, **P2** and **P3** may be used as EO materials for the practical applications.

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