

## Synthesis and Nonlinear Optical Property of a Polyphosphazene with High Glass Transition Temperature

Zhen LI<sup>1</sup>, Jin Gui QIN<sup>1\*</sup>, Zhou YANG<sup>2</sup>, Cheng YE<sup>2</sup>

<sup>1</sup>Department of Chemistry, Wuhan University, Wuhan 430072

<sup>2</sup>Center for Molecular Science, Organic Solids Lab., Institute of Chemistry, The Chinese Academy of Science, Beijing 100080

**Abstract:** A new polyphosphazene containing binaphtholyl and indole azo chromophores as side chains with high glass transition temperature ( $T_g$ ) was synthesized by a post-functional method. The polymer was well characterized. Its  $T_g$  was tested to be 168 °C, and the poled film of **P2** reveals a resonant  $d_{33}$  value of 20 pm/V by second harmonic generation (SHG) measurements.

**Keywords:** Polyphosphazene, synthesis, SHG.

Considerable interest exists in the development of organic nonlinear optical (NLO) chromophore-containing polymeric materials due to their potential photonics applications and many advantages over single crystals, such as the superior chemical flexibility, processability, and low cost<sup>1,2</sup>. The previous studies proved that polyphosphazenes were considered as an excellent candidate for nonlinear optical (NLO) applications due to their unusual properties, such as high thermooxidative and photolytic stability, optical transparency of the backbone, easy preparation and high functionalization<sup>4-8</sup>. However, the NLO studies on polyphosphazenes are still very rare, especially the polyphosphazenes with high  $T_g$ , which is a very important parameter for the electro-optical materials.

Recently we have synthesized a new polyphosphazene with binaphtholyl and indole azo chromophores. The synthetic route was very simple, and the purification of the product was very easy. Herein, we would like to report the synthetic procedure and structural characterization, and the NLO property of the end product.

The synthetic route was shown in **Scheme 1**. Polyphosphazene (**P1**) with binaphtholyl and indole groups as side chains was obtained by the direct substitution reaction from a highly reactive macromolecular intermediate, poly(dichlorophosphazene), and then a post azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the indole ring in **P1** afforded the indole-based chromophore-functionalized polyphosphazene (**P2**).

### Results and Discussion

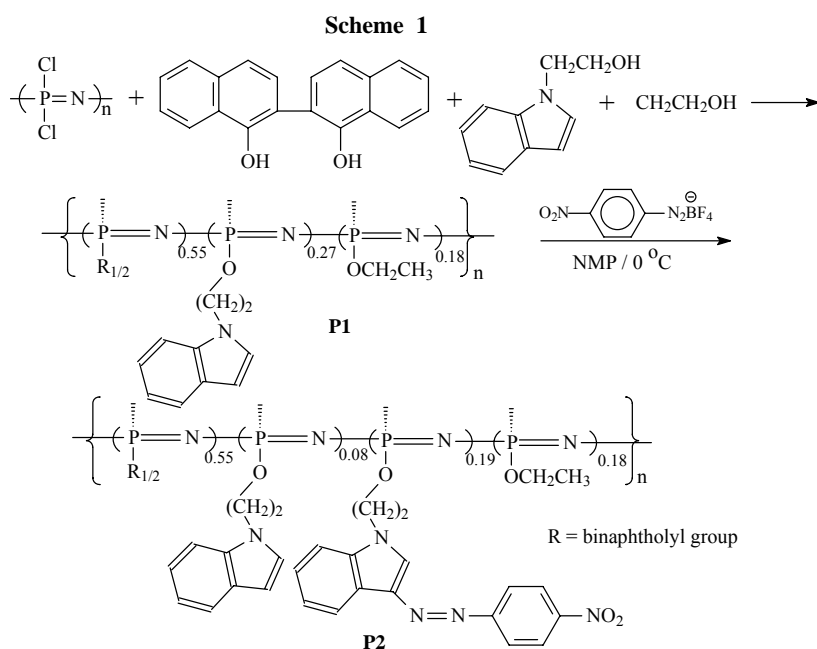
**P1** and **P2** were soluble in common organic solvents, such as CHCl<sub>3</sub>, THF, DMSO and

---

\* E-mail: jgqin@whu.edu.cn

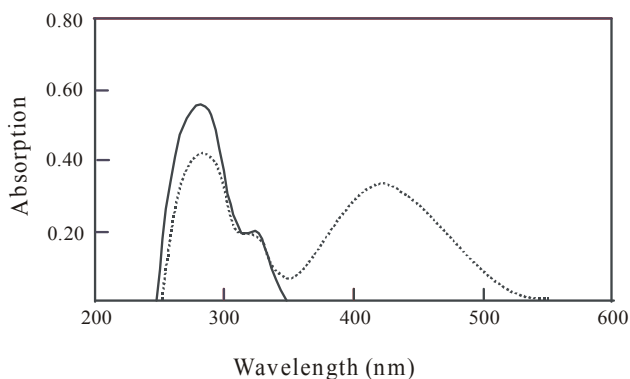
DMF, *etc.* The UV-Vis spectra of **P1** and **P2** in chloroform was shown in **Figure 1**.

After the post azo coupling reaction, a new strong maximum absorption of the  $\pi$ - $\pi^*$  transition of indole-based chromophore appeared at about 425 nm, with a cutoff at *ca.* 550 nm in **P2**. This confirmed that the *p*-nitrobenzenediazonium fluoroborate had reacted with the indole ring and the nitro groups were introduced into the polymer side chains<sup>8</sup>.



In the IR spectrum of **P1** and **P2**, 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**, which was assignable to the absorption of the nitro unit. The IR data further proved the success of the post azo coupling reaction.

**Figure 1** The UV-Vis spectra of **P1** ( solid line ) and **P2** ( dash line ) in  $\text{CHCl}_3$



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. This result 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 as shown in **Scheme 1**.

Generally, the  $T_g$  of polyphosphazenes was lower than 60 °C due to the high flexibility of the phosphazene backbone<sup>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  $T_g$  of **P2** should increase dramatically as reported previously<sup>7</sup>. The DSC thermograms of polymers exhibited a glass transition temperature ( $T_g$ ) at about 168 °C of **P2**. Perhaps this is the highest  $T_g$  in polyphosphazenes found so far, and will benefit to the stability of the NLO property of **P2**.

The molecular weights of **P1** and **P2** were determined by gel permeation chromatography with refractive index detector. The  $M_n$  and  $M_w$  of **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..

To evaluate the NLO activity of the poled polymer films, thin films of polyphosphazene **P2** on indium-tin-oxide- (ITO-) coated glass substrates were prepared by spin-coating method. The poled film of **P2** exhibits a resonant  $d_{33}$  value of 20 pm/V by second harmonic generation (SHG) measurements. Since polyphosphazenes showed some good unusual characteristics and **P2** possessed a relative high temperature, this polymer would be a good NLO polymer for the potential applications.

In conclusion, a new polyphosphazene with high glass transition temperature was synthesized. The resonant  $d_{33}$  value was determined to be 20 pm/V. It can be expected that many other polyphosphazenes with binaphtholyl and NLO chromophore groups could be easily prepared by the similar synthetic route reported here, and the research is still under way in our group.

### Acknowledgments

We are grateful to the National Natural Science Foundation of China, the Science Foundation of Hubei Province (2003ABA074) and the National Fundamental Key Research Program of China for financial support

### References

1. W. E. Moerner, A. G. Jepsen, C. L. Thompson, *Annu. Rev. Mater. Sci.*, **1997**, 32, 585.
2. S. R. Marder, B. Kippelen, A. K. Y. Jen, N. Peyghambarian, *Nature*, **1997**, 388, 845.
3. H. R. Allcock, *Appl. Organometal. Chem.*, **1998**, 12, 659.
4. Z. Li, C. Zhan, J. Qin, *J. Funct. Polym.(in Chinese)*, **2000**, 13, 240.
5. R. H. Neilson, P. W. Neilson, *Chem. Rev.*, **1988**, 88, 541.
6. H. R. Allcock, R. Ravikiran, M. A. Olshavsky, *Macromolecules*, **1998**, 31, 5206.
7. G. Rojo, G. Martin, F. A. Lopez, *et al.*, *Chem. Mater.*, **2000**, 12, 3603.
8. Z. Li, J. Qin, S. Li, C. Ye, J. Luo, Y. Cao, *Macromolecules*, **2002**, 35, 9232.

Received 28 March, 2003