Notes

Polyphophazene Containing Indole-Based Dual Chromophores: Synthesis and Nonlinear Optical Characterization

Zhen Li,[†] Jingui Qin,*[,†] Shaojun Li,[‡] Cheng Ye,[‡] Jie Luo,[§] and Yong Cao[§]

Department of Chemistry, Wuhan University,
Wuhan 430072, China;
Center for Molecular Science, Organic Solids Lab.,
Institute of Chemistry, The Chinese Academy of Science,
Beijing 100080, China; and
College of Materials Science,
South China University of Technology,
Guangzhou, 510640, China

Received May 20, 2002
Revised Manuscript Received August 9, 2002

Introduction

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.[1,2] Polyphosphazenes are inorganic polymers with a backbone of alternating phosphorus and nitrogen atoms and two side groups linked to the phosphorus atoms. In recent years, they have attracted growing attention due to their unique range of unusual properties, such as the excellent flexibility of the backbone, high thermal and oxidative stability, optical transparency from 220 nm to the near-IR region, and the ease of syntheses. Compared to the ordinary polymers with only one functional side group per unit, the polyphosphazenes provide double sites for further functionalization.[3−7] In 1991, NLO chromorphores were introduced to the backbone of polyphosphazene by Allcock et al. for the first time and yielded the NLO-active polyphosphazenes.[8] Among them, the polyphosphazene with DR-1 moieties as side chains showed a d_{33} value of 34 pm/V though the chromophore loading was relatively low. This result was encouraging. Then in 1996 and 1998, they synthesized some other polyphosphazenes with higher loading of the chromophores by alternative appoaches.[9,10] In 2000, Lopez et al. reported a new NLO-active polyphosphazene with high glass-transition temperature.[11] Thus, the previous work demonstrated that polyphosphazenes could fulfill many of the requirements of the NLO-active polymers and were promising candidates for the practical applications. However, the NLO studies on polyphosphazenes are still very scarce. On the other hand, Park et al. recently showed that the polymers with indole-based chromophores possessed very high d_{33} values.[12,13] These results prompted us to introduce the indole chromophores onto the backbone of polyphosphazene and study the second nonlinear optical properties of the resultant polyphosphazenes. As the synthetic route for the indole-based chromophores in the case of Park is relatively long and the purification of the small molecules is not so easy, we also would like to explore another synthetic method to simplify the preparation procedure.

In this paper, a new and easier synthetic route is presented with the aim to develop polyphosphazenes containing the indole-based chromophore. Thus, a polyphosphazene (**P1**) with indole as side group was first synthesized (Scheme 1). Then the post-azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the indole ring afforded the indole-based chromophore-functionalized polyphosphazene (**P2**) (Scheme 2).

Experimental Section

Materials and Measurements. Tetrahydrofuran (THF) and petroleum ether (60−90 °C) was dried over and distilled from K−Na alloy under an atmosphere of dry nitrogen. The *p*-nitrobenzenediazonium fluoroborate was synthesized following a procedure described in the literature.[14] *N*-Methylpyrrolidinone (NMP) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. All other reagents were used as received. Poly(dichlorophosphazene) was obtained from the thermal ring-opening polymerization of phosphonitrile chloride trimer.[15] Sodium hydride was weighted in the drybox. The substitution reactions of poly(dichlorophosphazene) were carried out in a dry nitrogen atmosphere using the Schlenk technique.

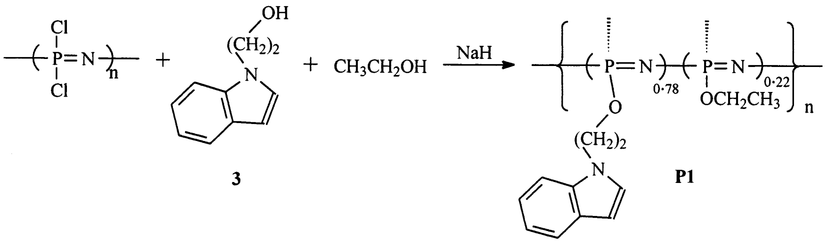
^1H NMR spectroscopy study was conducted with a Varian Mercury300 spectrometer. FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 series in the region of 3000−400 cm^{-1} on KBr pellets. UV−vis spectra were obtained using a Schimadzu 160A spectrometer in the polymer DMF solution. Differential scanning calorimetry (DSC) analyses were performed in a Rigaku Themoflex DSC8131 at a scan rate of 10 °C/min. Molecular weights were determined in THF solution by a Waters 2960D separation module containing a Styragel HR1 THF column and a Waters 2410 refractive index detector with a calibration curve for polystyrene standards. Thermal analysis was performed on a SHIMADZU DT-40 thermal analyzer at a heating rate of 20 °C/min in nitrogen at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA).

Synthesis of *N*-(Hydroxyethyl)indole (3). Powdered potassium hydroxide (12 g) was stirred with DMF (60 mL) at room temperature for 30 min. The mixture was then stirred with indole (5.0 g, 42.6 mmol) at room temperature for 2 h. 2-Chroloethanol (4.2 mL, 62 mmol) in DMF (10 mL) was added slowly, and the resultant mixture was allowed to stir at room temperature for 24 h. Then the mixture was poured into water (1 L), and the aqueous mixture was extracted with chloroform. The extract solution was dried with Na_2SO_4 for several days, and the solvent was removed at reduced pressure. The liquid residue was fractionally distilled off (0.3 mmHg, 152 °C) in vacuo to give 5.5 g of yellow viscous liquid (81%). ^1H NMR ($CDCl_3$): $\delta = 7.63$ (m, 1H), 7.40 (d, 1H), 7.21 (t, 1H), 7.05 (d, 2H),6.58 (d, 1H), 4.17 (t, 2H), 3.80 (t, 2H), 3.50 (t, 1H).

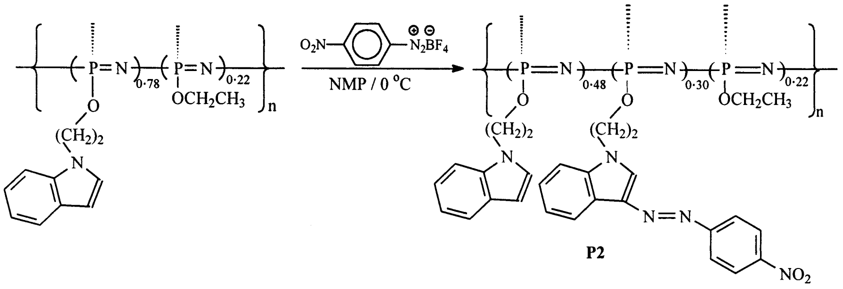
[†] Wuhan University.
[‡] The Chinese Academy of Science.
[§] South China University of Technology.

10.1021/ma020769r CCC: $22.00

Scheme 1



Scheme 2



Synthesis of Polyphosphazene (P1). Twenty milliliters of a solution of the sodium salt of compound **3** (prepared from the compound **3** (1.29 g, 8 mmol) and sodium hydride (0.19 g, 8 mmol) in THF) was added to a solution of poly(dichlorophosphazene) (0.58 g, 5 mmol) in 30 mL of THF, and the mixture was stirred at 50 °C for 2 days. Then 15 mL of the solution of $NaOCH_2CH_3$ (prepared from sodium (0.23 g, 10 mmol) and ethanol (0.8 g, 17.4 mmol) in THF) was added, and the resultant mixture reacted for another 2 days at 50 °C. After the main part of THF in the mixture was removed under vacuum, the mixture was poured into 400 mL of water. The solid was filtered, washed with water, and air-dried. Then, 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 chloroform into methanol. The solid was dried under vacuum at 40 °C to yield **P1** (0.6 g).

Preparation of Polyphosphazene (P2). Polyphosphazene **P1** (0.20 g) was dissolved in 1.4 mL of *N*-methylpyrrolidinone (NMP), and then *p*-nitrobezenediazonium fluoroborate (79 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, an excess of anhydrous potassium carbonate was added, and the mixture was stirred for an additional 1 h 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 solid was dried in a vacuum at 40 °C to yield 0.18 g of orange-red **P2**.

Polymer Film Preparation. Polyphosphazene **P2** was dissolved in THF, and the solution (3 wt %) was filtered through syringe filters. Polymer films were spin-coated onto indium tin oxide (ITO)-coated glass substrates (which were cleaned in the ultrasonic bath with *N*,*N*-dimethyformide, acetone, distilled water, and THF subsequently). The residual solvent was removed by heating the films in a vacuum oven, at 45 °C, for 2 days. The film thickness was 0.47 μm measured by a TENCOR 500 surface profiler.

Characterization of Poled Films. The second-order optical nonlinearity of polyphosphazene **P2** 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, 80 °C; voltage, 7.5 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 was used as the reference.

Results and Discussion

Synthesis. *N*-(Hydroxyethyl)indole (**3**) was prepared in a modified manner according to the literature.[12] At the presence of the potassium hydroxide in the solvent DMF, indole directly reacted with 2-chloroethanol to give the product. This reaction condition was much milder than the reported one, as 2-chloroethanol was used instead of ethylene carbonate.

Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of phosphonitrile chloride trimer.[15] 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 soluble in this medium. By comparison of the amount of the trimer, before and after the polymerization, a quantity of the poly(dichlorophosphazene) can be easily deduced.[16−18]

The synthetic route to **P1** and **P2** is shown in Schemes 1 and 2. **P1** was obtained from the highly reactive macromolecular intermediate, poly(dichlorophosphazene), by the nucleophilic substitution reaction. Indole groups cannot react with all the chlorine atoms because of the steric shielding effect. However, if some chlorine atoms remain in the polymer without being reacted, cross-linking may take place and the polymer becomes insoluble when it is exposed to moisture or water. So an excess of $NaOCH_2CH_3$ 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 recently utilized as a convenient method to introduce azo chromophores into the side chains of NLO-active polymers. This method was used by some groups[19,20] and also by our group.[21] However, in all the reported cases, the reacting polymers contained aniline groups as the side chains, and the position which the azo salts attacked at was the para position. In our case, **P1** bears an indole group, and we expect the azo coupling reaction will take place as indicated in the **P2** structure.

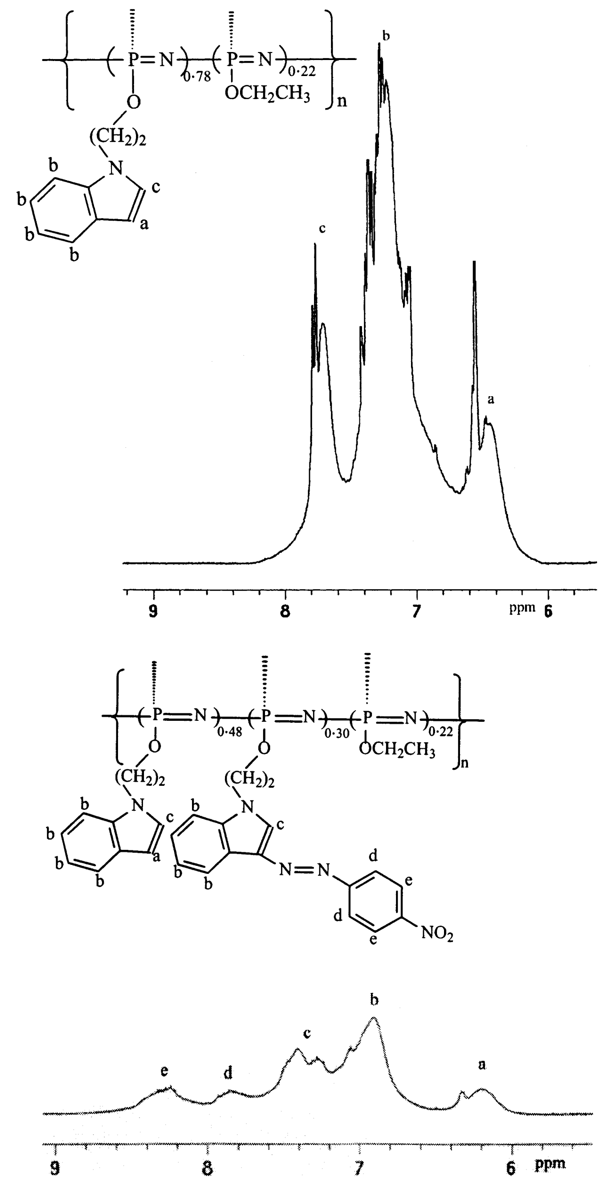


Figure 1. (a, top) ^{1}H NMR spectrum of polyphosphazene **P1**. (b, bottom) ^{1}H NMR spectrum of polyphosphazene **P2**.

The overall synthesis of the polyphosphazene **P2** was carried out through only two steps. The synthetic route and the purification of the products were very easy. Another advantage of this method was that the concentration of the indole-based chromophore in **P2** could be easily controlled by adjusting the quantity of the compound of *p*-nitrobezenediazonium fluoroborate in the azo coupling reaction.

Structural Characterization of P1 and P2. In the IR spectra of **P1** and **P2**, the 1250−1200 cm^{-1} bands of the P=N stretching vibration and the 750 cm^{-1} band of the in-phase P−N−P stretch were present. An apparent new strong absorption band appeared at 1330 cm^{-1} in the IR spectrum of **P2** assignable to the absorption of the nitro unit. This confirmed that the *p*-nitrobenzenediazonium fluoroborate had reacted with the indole ring, and the nitro units were introduced into the polymer side chains.

The component concentrations in the polymers could be calculated by analyzing the ^{1}H NMR peak integration carefully and are shown in Schemes 1 and 2. Figure 1 showed the ^{1}H NMR spectrum of **P1** and **P2** and the assignment of peaks downfield for comparison. The ratio of the indolyl and ethoxy moieties in **P1** was estimated to be 3.5:1 by comparing the aromantic proton integration and the methyl proton integration in Figure 1a. Some resonance peaks appearing downfield in Figure 1b, which were due to the *p*-nitrophenyl moieties, also confirmed that the azo coupling reaction was successful, and the azo chromophore really formed. The ratio of the two kinds of indole units in **P2**, indolyl and azo indolyl moieties, was estimated to be 8:5 by analyzing the spectrum carefully.

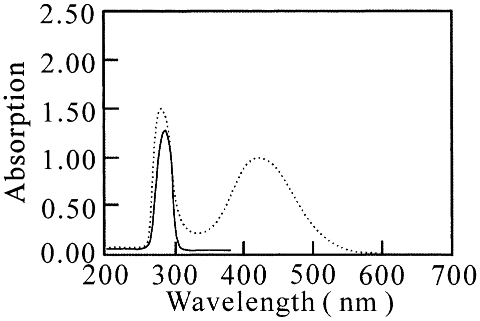


Figure 2. UV−vis spectra of polyphosphazene **P1** and **P2** in DMF.

P1 and **P2** have excellent solubility in common organic solvents, such as CHCl$_3$, THF, DMSO, and DMF, etc. Figure 2 shows the UV−vis spectra of **P1** and **P2** in the solution of DMF. The only strong absorption band in **P1** with λ_{max} at about 286 nm was due to the indole rings. After the post-azo coupling reaction, this absorption band remained in **P2**, as there were still many unreacted indole ring, while a new strong absorption maximum of the $\pi-\pi^*$ transition of indole-based chromophore appeared at about 425 nm, with a cutoff at ca. 570 nm.

The polyphosphazenes did not show any significant low-temperature weight loss. The high-temperature weight loss for the polymers commenced at about 280 °C and increased gradually at high temperature. The DSC thermograms of polymers exhibited a glass transition (T_g) at about 37 °C of **P1** and 86 °C of **P2**. The T_g's are relatively low, indicating that the backbone has good flexibility. The T_g of **P2** is higher than that of **P1** due to the rigid indole-based chromophore side chains in **P2** after the azo coupling reaction. The molecular weights of **P2** were determined by gel permeation chromatography with refractive index detector. The M_n and M_w of **P2** were 2.7 × 10^4 and 8.1 × 10^4, respectively.

To evaluate the NLO activity of the poled polymer films, thin films of polyphosphazene **P2** were prepared for SHG measurement. Calculation of the d_{33} value for the poled **P2** is based upon the following equation:[22]

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

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 $l_c \gg l_s$. The d_{33} value of **P2** was calculated to be 32 pm/V at 1064 nm fundamental wavelength. This value was relatively high. Also, indole-based chromophores are dual functional moieties which are responsible for both the photoconductivity and NLO activity as demonstrated by Park et al.[12,13] Generally, the photorefractive (PR) effect can occur in materials that simultaneously possess electrooptical activity and photoconductivity.[1] Here in **P2**, almost every unit contains one indole group, and 60% of the units contain one indole azo chromorphore; both of them could act as charge-transporting agents. Therefore, the indole groups are close enough in space due to its high density and the good flexibility of polyphosphazene backbone, and the charge carrier may transport between the indole moieties. This is another improvement, besides the easy synthesis, compared to the polymers of Park et al., in which the alkyl components in the copolymers do not contribute to the photoconductivity. As **P2** has demonstrated the second-order nonlinear optical property, and some indole-based polymers have shown the photoconductivity in the literature;[12,13] therefore, it is expected that **P2** could show the PR effect. We will study the PR properties of **P2** in the near future.

Conclusion

A new polyphosphazene **P2** with a high density of the dual indole-based chromophore is prepared by a novel easy two-step method. First, a polyphosphazene **P1** with indole as side chains was first synthesized, and then the post-azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the indole ring afforded a mulifunctional indole-based chromophore-functionalized polyphosphazene **P2**. The polymers exhibit excellent solubility in common organic solvents such as $CHCl_3$, THF, DMSO, and DMF. The poled film of **P2** reveals a resonant d_{33} value of 32 pm/V by second harmonic generation (SHG) measurements. It is believed that many other polymers containing multifunctional indole-based chromophores for nonlinear optical applications could be easily prepared by this new synthetic strategy.

Acknowledgment. We are grateful to the National Science Foundation of China and the National Fundamental Key Research Program of China for financial support.

References and Notes

(1) Moerner, W. E.; Jepsen, A. G.; Thompson, C. L. *Annu. Rev. Mater. Sci.* 1**997**, *32*, 585.
(2) Marder, S. R.; Kippelen, B.; Jen, A. K. Y.; Peyghambarian, N. *Nature (London)* **1997**, *388*, 845.
(3) Kim, C.; Allcock, H. R. *Macromolecules* **1987**, *20*, 1726.
(4) Allcock, H. R.; Pucher, S. R.; Scopelianos, A. G. *Macromolecules* **1994**, *27*, 1.
(5) Allcock, H. R. *Adv. Mater.* **1994**, *6*, 106.
(6) Li, Z.; Zhan, C.; Qin, J. *J. Funct. Polym. (Chinese)* **2000**, *13*, 240.
(7) Allcock, H. R.; Kim, C. *Macromolecules* **1990**, *23*, 3881.
(8) Allcock, H. R.; Dembek, A. A.; Kim, C.; et al. *Macromolecules* **1991**, *24*, 1000.
(9) Allcock, H. R.; Cameron, C. G.; Skloss, T. W.; et al. *Macromolecules* **1996**, *29*, 233.
(10) Allcock, H. R.; Ravikiran, R.; Olshavsky, M. A. *Macromolecules* **1998**, *31*, 5206.
(11) Rojo, G.; Martin, G.; Lopez, F. A.; Carriedo, G. A.; Alonso, F. J. G.; Martinez, J. I. F. *Chem. Mater.* **2000**, *12*, 3603.
(12) Moon, H.; Hwang, J.; Kim, N.; Park, S. Y. *Macromolecules* **2000**, *33*, 5116.
(13) Hwang, J.; Sohn, J.; Lee, J.; Lee, J.; Chang, J.; Lee, G. J.; Park, S. Y. *Macromolecules* **2001**, *34*, 4656.
(14) Starkey, E. B.; Smith, L. I.; Ungnade, H. E. *Org. Synth. Collect. Vol.* **1943**, *2*, 225.
(15) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(16) Li, Z.; Luo, J.; Li, J.; Zhan, C.; Qin, J. *Polym. Bull. (Berlin)* **2000**, *45*, 105.
(17) Li, Z.; Li, J.; Qin, J. *React. Funct. Polym.* **2001**, *48*, 113.
(18) Li, Z.; Qin, J.; Deng, X.; Cao, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3428.
(19) Schilling, M. L.; Katz, H. E.; Cox, D. I. *J. Org. Chem.* **1988**, *53*, 5538.
(20) Wang, X.; Kumar, J.; Tripathy, S. K.; et al. *Macromolecules* **1997**, *30*, 219.
(21) Tang, H.; Luo, J.; Qin, J.; Kang, H.; Ye, C. *Macromol. Rapid Commun.* **2000**, *21*, 1125.
(22) Dalton, L. R.; Xu, C.; Harper, A. W.; Ghosn, R.; Wu, B.; Liang, Z.; Montgomery, R.; Jen, A. K.-Y. *Nonlinear Opt.* **1995**, *10*, 383.

MA020769R