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Second-order nonlinear optical property of polyphosphazenes containing charge-transporting agents and indole-based chromophore

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Abstract

A new post functional strategy was developed to prepare polyphosphazenes with a high density of the indole based chromophore (nitro-indole or sulfonyl-indole chromophores) and carbazolyl side groups. Thus polyphosphazene (**P1**) with carbazolyl and indole groups was first prepared by direct nucleophilic substitution reaction with poly(dichlorophosphazene). Then, polyphosphazenes (**P2**–**P4**) containing charge-transporting agent (carbazolyl groups) and indole azo chromophores were synthesized via a post azo coupling reaction between **P1** and *p*-nitrobezenediazonium fluoroborate or *p*-ethylsulfurylbenzenediazonium fluoroborate in *N*-methylpyrrolindone (NMP). The structures of **P1**–**P4** were characterized, and the poled film of **P2**–**4** revealed a resonant d_{33} values in the range of 7–26 pm/V by second harmonic generation (SHG) measurements.

Keywords: Polyphosphazene; Synthesis; Indole

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1. Introduction

In the past decades, second order nonlinear optical (NLO) polymers, including electro-optical (EO) and photorefractive (PR) polymers, have attracted much attention. Many NLO polymers were prepared and studied due to their potential applications in photonics such as holographic data storage, real-time image processing and optical switching. Also, they possess a number of advantages (for example, the superior chemical flexibility, processability, and low cost) over single crystals [1–4]. Polyphosphazene, initially reported in 1965 by Allcock et al. [5], is a kind of inorganic polymer with a backbone of alternating phosphorus and nitrogen atoms and two side groups linked to the phosphorus atoms. These polymers are considered a promising candidate for NLO applications due to their unusual properties, such as a high thermo-oxidative and photolytic stability, optical transparency from 220 to 800 nm. Furthermore, most polyphosphazenes have very high molecular weight, and they are usually amorphous, soluble, and easily prepared [6–12].

On the other hand, Park et al. recently showed that the polymers with indole-based chromophores possessed very high NLO properties [13,14] except the synthetic route is relatively long and the purification of small molecules is not easy. Also in 2001, Brustolin et al. reported the syntheses and charge-transfer properties of a series of poly(1-vinylindole)s [15]. However, the NLO studies on polymers with indole moieties are still very scarce. Here, we would like to present a new post-functional method for the syntheses of new polyphosphazenes with indole-based chromophore as side chains under the mild reaction conditions. Also, the carbazolyl moieties were linked to the phosphazene backbone as cosubstituent to improve the NLO properties as Park et al. proposed [13] though they use small molecules, *N*-ethyl carbazole, as dopant directly. First, polyphosphazene (**P1**) with carbazolyl and indole groups was prepared by direct nucleophilic substitution reaction with poly(dichlorophosphazene), and then polyphosphazenes (**P2**–**P4**) containing charge-transporting agents (carbazolyl groups) and indole azo chromophores

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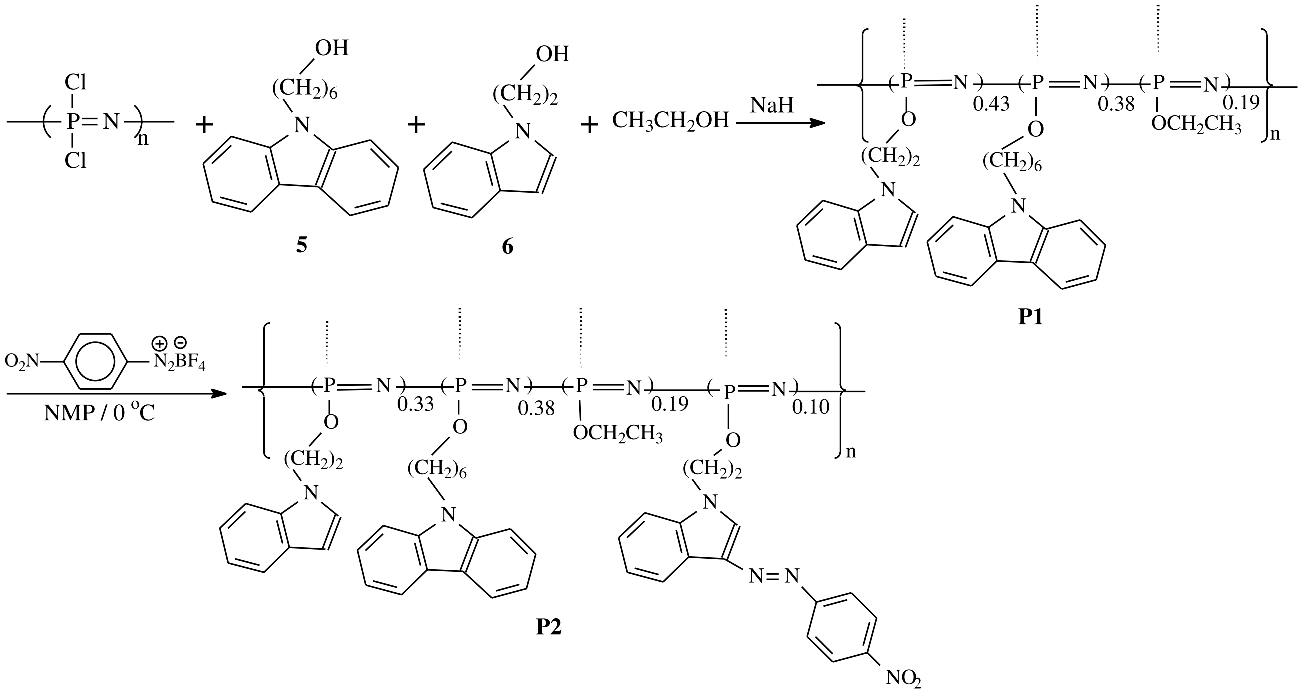

Scheme 1.

were obtained via a post azo coupling reaction (Scheme 1). The synthetic route is simple, and the purification of the products is very easy. The resultant polyphosphazenes are soluble in common solvents and showed good comprehensive properties (including the stability, NLO properties and the transparency etc.). 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 report by other groups about the usage of *p*-ethylsulfurylbenzenediazonium fluoroborate for the preparation of NLO polymers.

2. Experimental

2.1. Materials and measurements

Tetrahydrofuran (THF) and petroleum ether (60–90 °C) was dried over and distilled from K–Na alloy under dry nitrogen atmosphere. *N*-methylpyrrolindone (NMP) was dried over and distilled from CaH_2 under dry nitrogen atmosphere. All other reagents were used as received. *p*-Nitrobenzenediazonium fluoroborate was synthesized following a procedure described in the literature [16]. *p*-Ethylsulfonylaniline was synthesized according to the literature [17]. *N*-(6-Hydroxyhexanyl)carbazole (**5**) was prepared as reported previously [18,19]. *N*-(Hydroxyethyl) indole (**6**) was synthesized from 2-chloroethanol and indole in DMF in the presence of excess of KOH as the base [13]. Poly(dichlorophosphazene) was obtained from thermal ring-opening polymerization of phosphonitrile chloride trimer [5] and purified as we reported previously [18–20]. Sodium hydride was weighted in the dry box. The substitution reactions of poly(dichlorophosphazene) were carried out in dry nitrogen atmosphere using Schlenk technique.

^1H NMR was measured with a Varian Mercury 300 spectrometer. FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 spectrometer in the region of 3000–400 cm^{-1} on KBr pellets. UV–vis spectra were obtained using a Schimadzu 160A spectrometer in DMF. Molecular weights were determined in THF by Waters 2960D separation Module containing Styragel HR1 THF column and Waters 2410 Refractive Index Detector with a calibration curve of polystyrene standards. Differential scanning calorimetry (DSC) was performed in a Rigaku Themoflex DSC8131 with a scan rate of 10 °C/min.

2.2. 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 0.5 h. 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).

2.3. Synthesis of polyphosphazene (*P1*)

Compound **5** (1.7 g, 6.4 mmol) reacted with sodium