

Synthesis and Properties of Novel Y-Shaped Nonlinear Optical Polymers Containing Imidazole-Based Chromophores

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ABSTRACT: This article describes the synthesis and second-order nonlinearity study of several new polyphosphazene polymers, which are composed of a new type of nonlinear optical chromophore attached to polyphosphazene. They were obtained via a post-azo coupling reaction. The resulting materials were characterized with $^1\text{H-NMR}$, $^{31}\text{P-NMR}$, Fourier transform infrared, ultraviolet-visible, gel permeation chromatography, and differential scanning calorimetry. Chromophore contents up to 14 mol % were realized. The polymers had good optical transparency, and poled films revealed resonant d_{33} values in the range of 18–37 pm/V by second harmonic generation measurements. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2802–2807, 2008

Key words: azo polymers; functionalization of polymers; NLO; nonlinear polymers; synthesis

INTRODUCTION

The development of organic nonlinear optical (NLO) chromophore-containing polymeric materials has drawn considerable attention for their potential photonics applications over the last decade.^{1–5} Significant interest exists in the design and development of organic materials with large molecular hyperpolarizability (β) values, improved optical transparency, and good thermal stability. However, this enhancement of β is always accompanied with a redshift in the λ_{max} peak, which is a so-called nonlinearity–transparency tradeoff. Y-shaped chromophores^{6–9} show improved tradeoff compared to classical one-dimensional dipolar chromophores because of the contribution of the large, off-diagonal β tensorial components.

It has been theoretically and experimentally shown by Fichou and others that heteroaromatic-based chromophores^{10–13} and multidipolar chromophores^{14–21} have larger macroscopic nonlinearities, higher thermal stability, and better orientational order and stability than one-dimensional, donor–acceptor disubstituted π -conjugated molecules. Heterocyclic compounds have lower delocalization energy than benzene, so they can offer better effective conjugation than benzene in donor–acceptor compounds. The multidipolar chromophores improve the ability to

form noncentrosymmetric structures and reduce the tendency toward aggregation. Another advantage of the multidipolar chromophores is that they can increase the polar order in poled polymers with respect to that of their monomeric units. Therefore, how to provide general laws predicting NLO properties of multidipolar chromophores is still a big challenge. This problem should be solved to further push the development of NLO polymeric materials and bring this kind of promising material into practical applications.

Polyphosphazenes are inorganic-backbone polymers²² resulting from the repetition of the $-\text{P}=\text{N}-$ monomer unit with two side groups linked to the phosphorous atoms. They present a number of useful features for practical devices, such as excellent flexibility of the backbone, high thermal and oxidative stability, optical transparency from 220 nm to the near-IR region, and controlled incorporation of covalent chromophores, which can be easily accomplished over a broad concentration range. Recently, some new synthetic routes^{23–29} have been developed for the preparation of polyphosphazenes with large β values and high glass-transition temperature (T_g) values.

A combination of the advantages of heteroaromatic-based and multidipolar chromophores could produce a new type of chromophore that presents high electro-optical coefficients and good temporal stability. In this article, the synthesis and characterization of some efficient imidazole-based NLO polymeric materials are reported.

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EXPERIMENTAL

Materials and measurements

All chemicals were purchased from commercial suppliers. Tetrahydrofuran (THF), petroleum ether (60–90°C), and ethanol were dried over and distilled from a sodium alloy under an atmosphere of dry nitrogen. 4-(4,5-Diphenyl-1*H*-imidazol-2-yl)-phenol (compound **1**) was obtained with a reaction of diphenylethanedione, 4-hydroxybenzaldehyde, and ammonium acetate in the solvent glacial acetic acid³⁰ and dried *in vacuo* at 25°C to remove the water. *p*-Chlorobenzenediazonium fluoroborate, *p*-fluorobenzenediazonium fluoroborate, and *p*-iodobenzenediazonium fluoroborate were synthesized according to a procedure described in the literature.³¹ All other reagents were used as received. The substitution reaction of polydichlorophosphazene was carried out in a dry nitrogen atmosphere.

The ¹H-NMR spectra were collected at 400 MHz on a Varian Mercury plus 400 spectrometer (Varian Medical Systems, Inc., Palo Alto, CA), ³¹P-NMR spectra at 162 MHz were obtained. The Fourier transform infrared measurements were conducted on a PerkinElmer Paragon 1000 Fourier transform spectrometer (Boston, MA) at room temperature (25°C). The samples were mixed with KBr powder and then pressed into flakes. Ultraviolet–visible (UV–vis) spectra were recorded on a Paragon 1000 spectrometer. Solution UV–vis spectra were measured as 1×10^{-5} M solutions in THF at 25°C. Differential scanning calorimetry analyses were performed on a Pyris 1 differential scanning calorimeter under a nitrogen atmosphere at a heating rate of 10°C/min. Molecular weights were determined in a dimethylformamide solution with a series 200 with a calibration curve for polystyrene standards.

Synthesis of P1

A solution (30 mL) of the sodium salt of compound **1** [prepared from compound **1** (0.55 g, 1.76 mmol) and sodium hydride (0.0424 g, 1.76 mmol) in THF] was added to a solution of polydichlorophosphazene (0.68 g, 5.8 mmol) in 15 mL of THF, and the mixture was stirred at 20°C for 48 h under an atmosphere of dry nitrogen. After that, 10 mL of a solution of NaOCH₂CH₃ [prepared from ethanol (0.59 g, 12.8 mmol) and sodium hydride (0.30 g, 12.8 mmol) in THF] was added, and the resultant mixture reacted for 24 h at 20°C. After the THF in the mixture was removed *in vacuo*, the solid was poured into 100 mL of water. The solid was filtered, washed with water, and dried *in vacuo*. The solid was dissolved in THF, and the insoluble residue was filtered out. The filtrate was dropped into ethanol to precipitate the solid. The resultant solid was purified by several

precipitations from THF into ethanol. The solid was dried *in vacuo* at 25°C to yield polyphosphazene **P1** (0.79 g).

¹H-NMR (dimethyl sulfoxide-*d*₆, 400 MHz, δ): 7.92 [Br, 2H, C=C–Ar (para-H)], 7.42 [Br, 4H, C=C–Ar (meta-H)], 7.34 [Br, 4H, C=C–Ar (ortho-H)], 7.21 [Br, 4H, P–O–Ar (meta-H)], 7.13 [Br, 4H, P–O–Ar (ortho-H)], 3.83 (Br, 4H, OCH₂), 1.01 (Br, 6H, CH₃), 12.51 (Br, 2H, NH).

The preparation procedure of **P2** was similar to that of **P1**.

Synthesis of P3

P1 (0.17 g) was dissolved in 5 mL of THF, and then *p*-chlorobenzenediazonium fluoroborate (0.39 g) was added under cooling with an ice bath. After 2 h of stirring at 0°C, an excess of anhydrous potassium carbonate was added. The color of the solution changed from no color to red gradually. The mixture was stirred for 60 h at 0°C and then filtered. THF was removed *in vacuo*, and the solid was poured into 50 mL of water. The solid was filtered, washed with water, and dried *in vacuo* at 25°C to yield **P3** (0.18 g).

The preparation procedure of **P4–P8** was similar to that of **P3**.

Polymer film preparation

P3–P8 were dissolved in cyclohexanone, and the solutions (ca. 2 wt %) were filtered through syringe filters. Polymer films were spin-coated onto indium tin oxide coated glass substrates. The residual solvent was removed by the heating of the films in a vacuum oven at 45°C for 60 h. The film thickness was measured with a Tencor 500 surface profiler (Tencor Instrument, Inc., San Jose, CA) and is shown in Table I.

Characterization of the poled films

The second-order optical nonlinearity of **P3–P8** was determined by *in situ* second harmonic generation (SHG) experiments. SHG measurements were carried out with an Nd:YAG laser operating with a 10-Hz repetition and an 8-ns pulse width at 1064 nm. A Y-cut quartz crystal was used as the reference. To induce molecular ordering in the spin-coated films and so break the centrosymmetry, a corona poling technique was used.³² A needle, at a static potential 10 kV, was positioned at 0.9 cm above the grounded sample. The temperature during poling was different for each film (Table I) and was close to T_g to facilitate molecular orientation. Under these conditions, a steady state corresponding to thermodynamic equilibrium in the presence of the field appears to be achieved.

TABLE I
Some Characterization Data of P1–P8

Polymer	T_g (°C)	λ_{\max} (nm)	T_p (°C)	$M_n \times 10^4$	$M_w \times 10^4$	d_{33} (pm/V)	d (μm)
P1	148	303	—	2.9	3.5	—	—
P2	122	—	—	2.4	3.0	—	—
P3	158	363	146	3.2	4.2	29	1.97
P4	140	—	128	2.7	3.1	21	2.02
P5	157	372	145	3.3	3.9	37	2.39
P6	136	—	125	2.7	3.0	28	1.89
P7	169	365	155	3.7	4.4	23	2.11
P8	145	—	132	2.8	3.3	18	2.26

d , thickness of the thin film; M_n , number-average molecular weight; M_w , weight-average molecular weight; T_p , poling temperature.

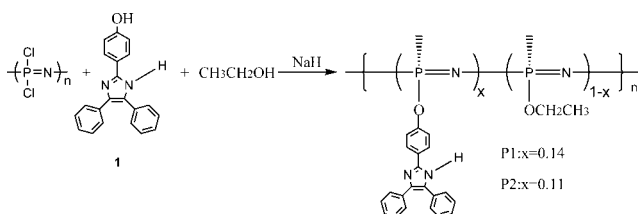
RESULTS AND DISCUSSION

Synthesis

The syntheses of P1–P8 are illustrated in Schemes 1 and 2. P1 and P2 with imidazole as a side group were first synthesized (Scheme 1). Then, the post-azo coupling of *p*-chlorobenzenediazonium fluoroborate, *p*-fluorobenzenediazonium fluoroborate, and *p*-iodobenzenediazonium fluoroborate toward the benzene rings afforded imidazole-based, chromophore-functionalized P3–P8 (Scheme 2). Polydichlorophosphazene was synthesized following a procedure described in the literature.³³ It is a simple and convenient one-pot synthesis according to the literature. P1 and P2 were obtained from the highly reactive macromolecular intermediate, polydichlorophosphazene, by the nucleophilic substitution reaction. To get soluble polymers, compound 1 could not react with all or most of the chlorine atoms. At the end of the substitution reaction, an excess of NaOCH₂CH₃ was added to the reacting mixture to replace all the remaining chlorine atoms completely. Here, *p*-nitrobenzenediazonium fluoroborate, *p*-fluorobenzenediazonium fluoroborate, and *p*-iodobenzenediazonium fluoroborate were used to attack the benzene rings to prepare polymers containing NLO chromophores.

Structural characterization of P1–P8

In the IR spectra of P1–P8, the 1200–1225-cm⁻¹ bands were attributed to a P=N stretching vibration, and the 765–770-cm⁻¹ band was attributed to an in-

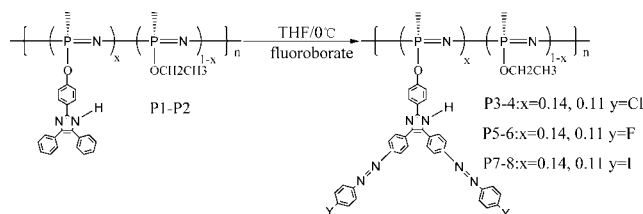


Scheme 1 Synthesis of P1 and P2.

phase P–N–P stretch. The new absorption band appeared at 1646–1668 cm⁻¹ in the IR spectra of P3–P8 and was assignable to the absorption of N=N; other new absorption bands appeared at about 670 cm⁻¹ and were assignable to the absorption of –Cl. Those appearing at about 1345 and 500 cm⁻¹ were assignable to the absorption of –F and –I. Figure 1 shows the IR spectra of some polymers.

The component concentrations in the polymers could be calculated from the ¹H-NMR peak integration of phenyl proton resonances and the proton resonances of –OCH₂ groups. It is very important because it has great influence on the nonlinearity, transparency, T_g , and solubility. The higher the component concentrations are, the better the nonlinearity and T_g are and the worse the transparency and solubility are. It is important to find an applicable range. Figure 2 shows the ¹H-NMR spectra of P3, P5, and P7 and the assignment of peaks downfield for comparison. A ³¹P-NMR study was conducted with a Varian Mercury Plus 400 spectrometer. There were two peaks at about –7.8 and –13.5 ppm in P1, two peaks at about –10.1 and –15.2 ppm in P3, two peaks at about –7.0 and –14.3 ppm in P5, and two peaks at –7.6 and –14.0 ppm in P7.

The molecular weights of P1–P8 were determined by gel permeation chromatography with a refractive-index detector (Table I). The differential scanning calorimetry thermograms of polymers P3–P8 exhibited high T_g values. P7 had a higher T_g value than P3 and P5, as iodo groups were bigger than other groups. That is good for keeping the orientation after polarization.



Scheme 2 Synthesis of P3–P8.

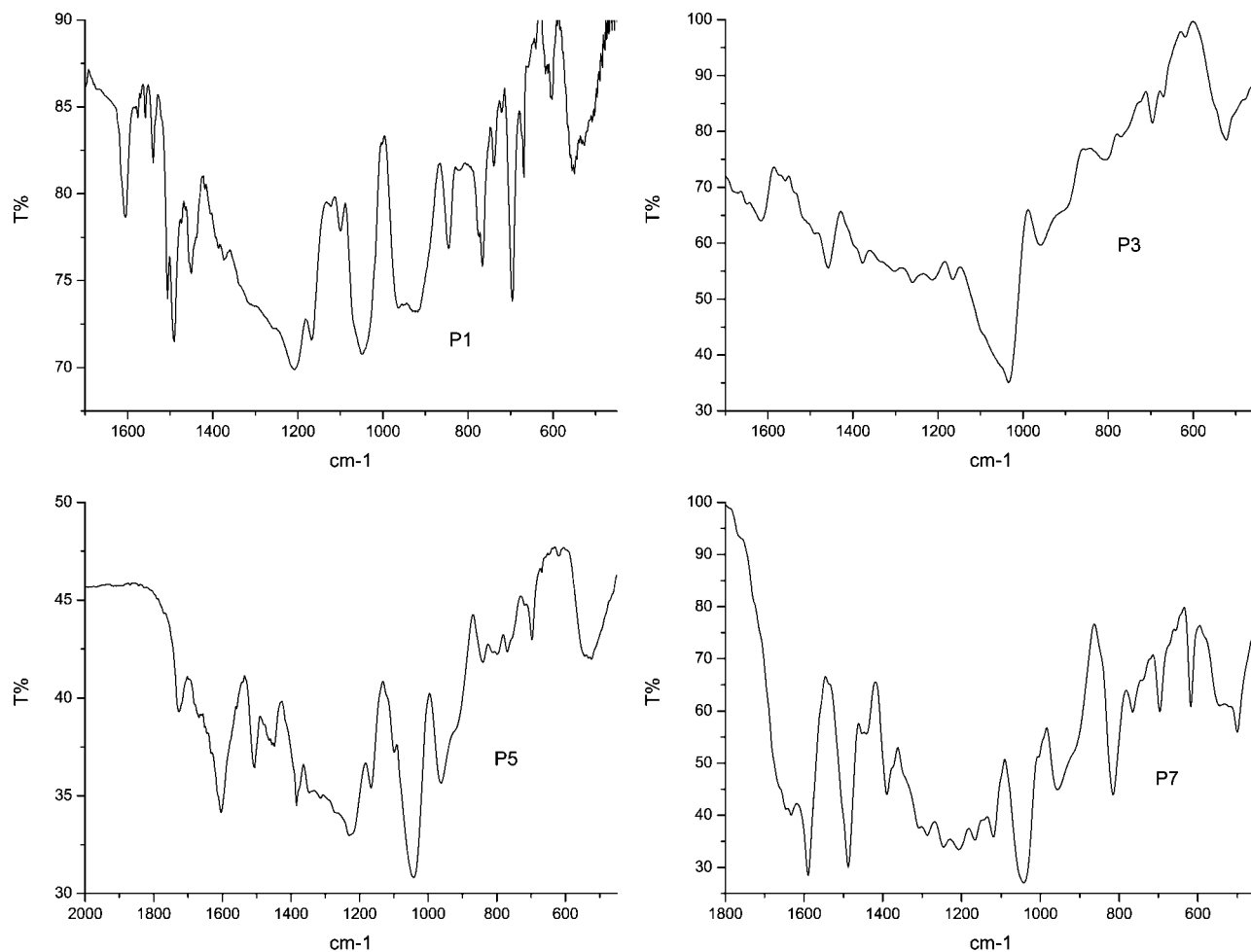


Figure 1 IR spectra of P1, P3, P5, and P7.

These polymers have good solubility in common organic solvents, such as THF, dimethyl sulfoxide, dimethylformamide, and CHCl_3 . Figure 3 shows the UV-vis spectra of some polymers in a solution of THF. It was obvious that P1 had two absorption bands and λ_{max} at about 303 nm. After the post-azo coupling reaction, some new absorption bands for the π - π^* transition of the imidazole-azo chromophore appeared, and the absorption maxima are collected in Table I, with a cutoff at about 480 nm. The polymers presented relative blueshifts,²²⁻²⁵ which should contribute to low optical loss and confirmed the advantages of halogen-based chromophores again. P5 showed a higher maximal absorption wavelength and a narrower transparency window than P3 and P7, and this coincided with the strongest withdrawing power of the fluoro groups.

NLO property

The calculation of the d_{33} values for poled P3–P8 is based on the following equation:³⁴

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

where $d_{11,q}$ 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 factor of the apparatus and equals 1.2 when $l_c \geq l_s$. The d_{33} values of P3–P8 were calculated, and the results are shown in Table I. It is clear, however, from the data in Table I that, among the series, the magnitude of the d_{33} values increases with increasing donor-acceptor strength. It is reasonable that P5 possessed a higher d_{33} value than P3 and P7 as fluoro groups were the strongest acceptors. The second highest d_{33} value was found in P3, which was close to that of P5. The lowest d_{33} value was in P7 because the iodo groups are not as strong acceptors as fluoro groups and chloro groups.

CONCLUSIONS

Some new polymers with imidazole-based and multiple charge-transfer Y-shaped chromophores were prepared by an easy two-step method. The polymers

displayed a markedly blueshifted optical maximum (363–372 nm in THF) while maintaining relatively large d_{33} values by SHG measurements. They also presented good solubility in common organic solvents.

This work demonstrates an approach to developing second-order NLO materials offering improved nonlinearity–transparency tradeoff characteristics. It is believed that further studies will focus on opti-

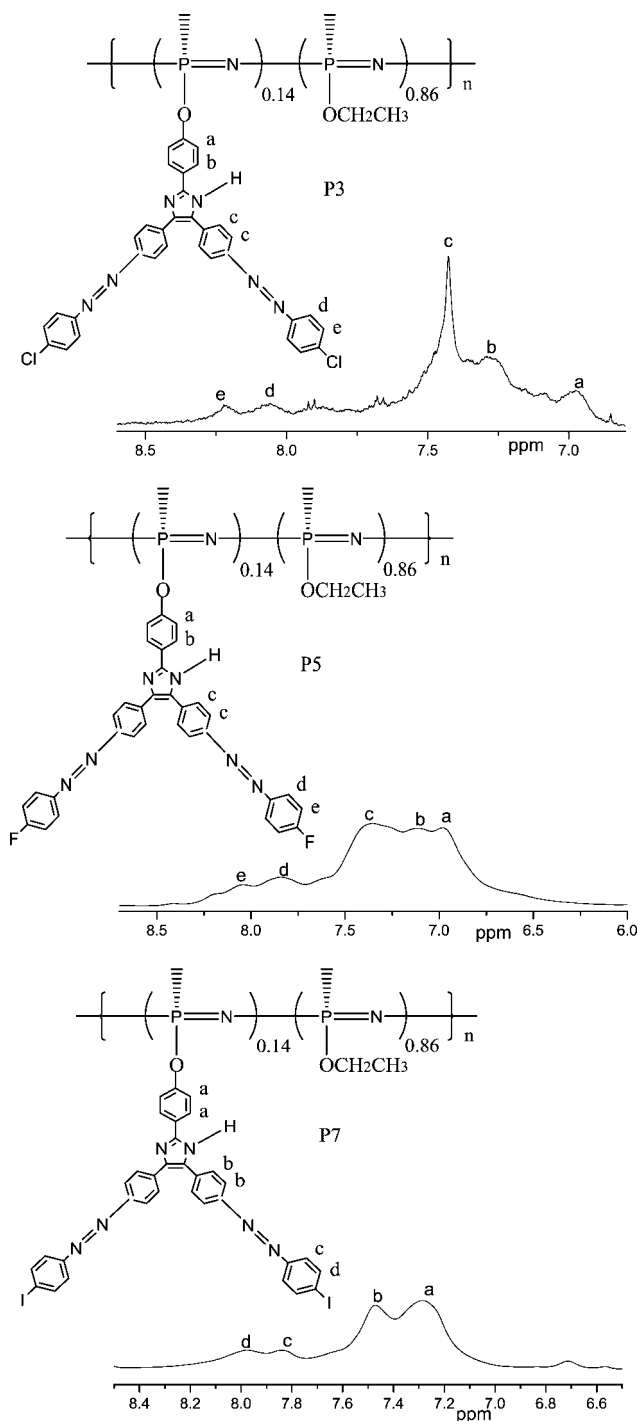


Figure 2 $^1\text{H-NMR}$ spectra of **P3**, **P5**, and **P7**.

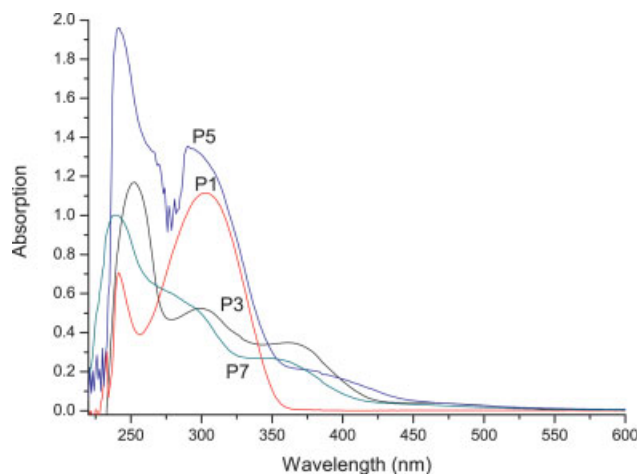


Figure 3 UV-vis spectra of **P1**, **P3**, **P5**, and **P7** in THF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mizing the β response and optical properties as well as an in-depth understanding of this special nonlinearity–transparency relationship by a combination of molecular modeling and modification.

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