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Short communication

Synthesis and characterization of a new high-T_g photorefractive material

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Abstract

The synthesis and characterization of a new high-T_g photorefractive polymer, polyphosphazene P2, was described. It was obtained via a post-azo coupling reaction. The resulting material has been characterized by means of ^{1}H NMR, ^{31}P NMR, FT-IR, UV–vis, GPC and DSC. Chromophore contents up to 14 mol% have been realized. The molecular weights of polyphosphazene P2 are 3.3×10^4 (M_n) and 4.3×10^4 (M_w), respectively; and the glass-transition temperature is high (170 °C). Measurements reveal that it possesses relatively large magnitude of photoinduced birefringence (4.2–4.7×10^{-3}).

Keywords: Azo polymers; Imidazole; NLO; Photorefractive effects; Polyphosphazene

1. Introduction

The materials combine photosensitivity, photoconductivity, and electrooptical (EO) activity can be regarded as suitable materials for photorefractive (PR) applications [1]. The refractive indices of these materials can be modulated by light via a photoinduced space-charge field and the EO effect. In 1991, the PR effect was demonstrated in polymeric materials for the first time [2]. Then, many routes toward organic PR materials have been developed, and the PR effect in various organic materials has been extensively investigated for many years [3].

Azobenzene polymers are promising materials for optical in the field of photonics applications [4]. Such applications include reversible optical data storage [5–8], fabrication of diffractive elements with specific polarization properties [9,10], optical switching and/or slab waveguides [11,12] and many other purposes. The mechanism by which birefringence is obtained in azobenzene polymer films is based on the photoinduced *trans–cis–trans* isomerization of the azobenzene groups, accompanied by their movement and rearrangement perpendicular to the laser polarization direction.

High-T_g systems have received much attention in the past few years [13–15]. In these systems, efficient PR materials could be get when a combination of strong EO effects, large charge-carrier generation efficiencies, and high charge mobilities is achieved. In addition, the high-T_g materials with

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single-component are superior to low-T_g composites, which may suffer from phase separation or crystallization on long time scales.

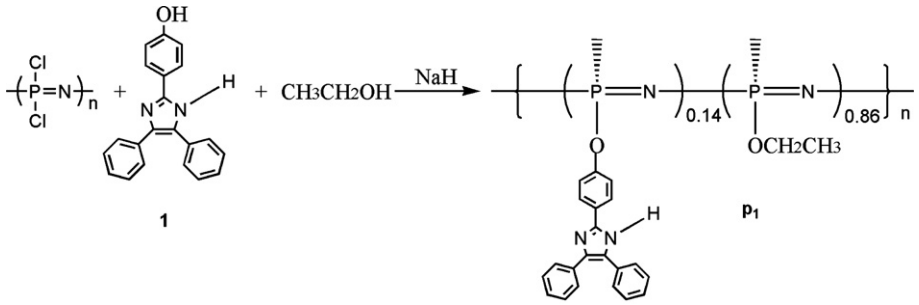
Polyphosphazenes are inorganic-backbone polymers [16] resulting from the repetition of the —P=N— monomer unit and with two side groups linked to the phosphorus atoms. They present a number of useful features for practical devices, such as the excellent flexibility of the backbone, high thermal and oxidative stability, optical transparency from 220 nm to the near-IR region, and controlled incorporation of covalently chromophores can be easily accomplished over a broad concentration range. Recently, some new synthetic routes [17–19] have been developed for the preparation of polyphosphazene PR materials. In this paper, we report the synthesis and characterization of a new multifunctional high-T_g PR material via a post-azo coupling reaction. A polyphosphazene (P1) with imidazole as side group was first synthesized (Scheme 1). Then, the post-azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the benzene rings afforded the imidazole-based chromophore-functionalized polyphosphazene (P2) (Scheme 2).

2. Experimental

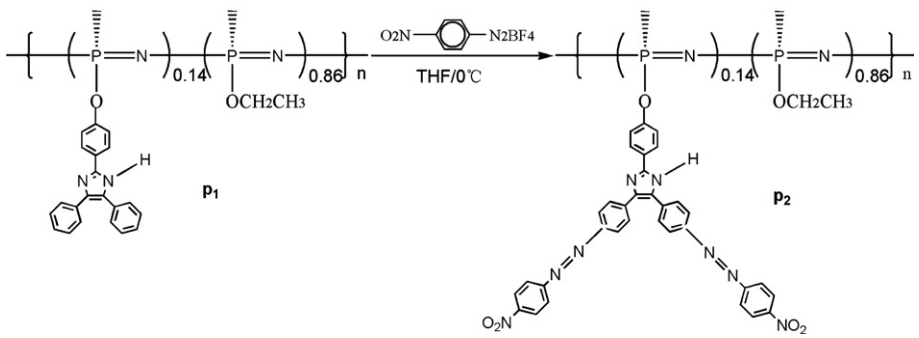
2.1. Materials and measurements

All chemicals were purchased from commercial suppliers. Tetrahydrofuran (THF) and petroleum ether (60–90 °C) were dried over and distilled from Na alloy under an atmosphere of dry nitrogen. The 4-(4,5-diphenyl-1*H*-imidazol-2-yl)-phenol (compound 1) was obtained using reaction of diphenylethanedione, 4-hydroxy-benzaldehyde and ammonium acetate in solvent glacial acetic acid [20]. The *p*-nitrobenzenediazonium fluoroborate was synthesized following a procedure described in the literature [21]. All other reagents were used as received. The substitution reaction of poly(dichlorophosphazene) was carried out in a dry nitrogen atmosphere.

The ^{1}H NMR spectra were collected at 400 MHz on a Varian Mercury plus 400 spectrometer, ^{31}P NMR spectra at 162 MHz were obtained. The FT-IR measurements were conducted on a Perkin–Elmer Paragon 1000 Fourier transform spectrometer at room temperature (25 °C). The samples



Scheme 1. Synthesis of P1.



Scheme 2. Synthesis of P2.

were mixed with the powder of KBr and then pressed into the flakes. UV–vis spectra were recorded on a PARAGON 1000 spectrometer. DSC analyses were performed on a PYRIS 1 DSC under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Molecular weights were determined in DMF solution by a Series 200 with a calibration curve for polystyrene standards.

2.2. Synthesis of polyphosphazene P1

30 ml of a solution of the sodium salt of compound 1 (prepared from the compound 1 (0.50 g, 1.6 mmol) and sodium hydride(0.0385 g, 1.6 mmol) in THF) was added to a solution of poly(dichlorophosphazene) (0.62 g, 5.3 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 $NaOCH_2CH_3$ (prepared from ethanol (0.49 g, 10.7 mmol) and sodium hydride (0.256 g, 10.7 mmol) in THF) was added, and the resultant mixture reacted for 24 h at 20 °C. After the THF in the mixture was removed under vacuum, the solid was poured into 100 ml of water. The solid was filtered, washed with water, and dried under vacuum. The solid was dissolved in THF, and the insoluble residue was filtered out. The filtrate was dropped to ethanol to precipitate the solid. The resultant solid was purified by several precipitations from THF into ethanol. The solid was dried under vacuum at 25 °C to yield polyphosphazene P1 (0.73 g).

2.3. Synthesis of polyphosphazene P2

Polyphosphazene P1 (0.25 g) was dissolved in 5 ml of THF, and then *p*-nitrobenzenediazonium fluoroborate (0.37 g) was added under cooling with an ice bath. After stirring for 2 h at 0 °C, an excess of anhydrous potassium carbonate was added, and the mixture was stirred for 48 h at 0 °C and then filtered. THF was removed under vacuum, and the solid was poured into 50 ml of water. The solid was filtered, washed with water, and dried under vacuum at 25 °C to yield polyphosphazene P2 (0.19 g).

2.4. Polymer film preparation

The polyphosphazene P2 was dissolved in cyclohexanone, and the solution (2.1 wt%) was filtered through syringe filters. Polymer films were spin-coated onto glass substrates. The solvent was removed by heating the films in a vacuum oven at 30 °C for 36 h. The film thickness was measured by a TENCOR 500 surface profiler.

2.5. Characterization of the films

The photoinduced birefringence was investigated with a He–Ne laser at 633 nm as the probing light, and a continuous wave (cw) second harmonic generation (SHG) output of yttrium-aluminum-garnet (YAG) laser at 532 nm with intensity of 100 mW/cm^2 as the writing light. The samples were placed between two crossed polarizer P and A in the path of the He–Ne laser beam. They were irradiated with the writing laser linearly polarized at ±45° with respect to the directions of transmission of P and A. The optical anisotropy which was induced in the samples under the action of writing light caused a signal light behind the analyzer A.

3. Results and discussion

3.1. Synthesis

The synthesis of polyphosphazenes P1 and P2 are illustrated in Schemes 1 and 2. Poly(dichlorophosphazene) was synthesized following a procedure described in the literature [22]. It is a simple and convenient one-pot synthesis according to the literature. Polyphosphazene P1 was obtained from the highly reactive macromolecular intermediate, poly(dichlorophosphazene), by the nucleophilic substitution reaction. To get soluble polymers, 4-(4,5-diphenyl-1*H*-imidazol-2-yl)-phenol (compound 1) cannot react with all or most of the chlorine atoms. At the end of the substitution reaction, an excess of $NaOCH_2CH_3$ was added into the reacting mixture to replace all the remaining chlorine atoms completely. Polyphosphazene P2 was synthesized via a post-azo coupling reaction. Here, *p*-nitrobenzenediazonium fluoroborate was used to attack the benzene rings to prepare polymers containing NLO chromophores.

3.2. Structural characterization of polyphosphazenes P1 and P2

In the IR spectra of polyphosphazenes P1 and P2, the 1200–1220 cm^{-1} bands were attributed to a P═N stretching vibration and the 770 cm^{-1} band to an in-phase P–N–P stretch. The new absorption band appeared at 1650 cm^{-1} in the IR spectrum of

polyphosphazene P2 assignable to the absorption of N=N, other new absorption bands appeared at 1512 cm^{-1} and 1372 cm^{-1} assignable to the absorption of $-NO_2$. These confirmed that the *p*-nitrobenzenediazonium fluoroborate had reacted with the benzene rings.

The component concentrations in the polymers could be calculated from the ^1H NMR peak integration of phenyl proton resonances and the proton resonances of $-OCH_2$ groups. Fig. 1 showed the ^1H NMR spectra of polyphosphazenes P1 and P2 and the assignment of peaks downfield for comparison. The ratio of the NLO chromophores and methylene moieties in polyphosphazene P2 was estimated to be 1:6. ^{31}P NMR study was conducted with a Varian Mercury plus 400 spectrometer. There are two peaks at about −7.8 and −13.5 ppm in polyphosphazene P1, and there are two peaks at about −9.4 and −15.1 ppm in polyphosphazene P2, which move toward highfield.

The molecular weights of polyphosphazene P2 were determined by gel permeation chromatography with refractive index detector. The M_n and M_w of polyphosphazene P2 were 3.3×10^4 and 4.3×10^4, respectively. The DSC thermograms of polymers exhibited a glass transition (T_g) at about 148 °C of polyphosphazene P1 and 170 °C of polyphosphazene P2. The high-T_g is good to avoid phase separation or crystallization.

These two polymers have good solubility in common organic solvents, such as THF, DMSO, DMF, and $CHCl_3$, etc. Fig. 2 showed the UV–vis spectra of polyphosphazenes P1 and P2 in the solution of THF. It was obvious that polyphosphazene P1 has two absorption bands and the λ_{max} at about 303 nm. After the post-azo coupling reaction, a new absorption band for the π–π^* transition of imidazole-azo chromophore appeared at about 363 nm, with a cutoff at about 430 nm. It presents a wide transparency window and should contribute to the low optical loss of polyphosphazenes.

Calculation of the Δn value for the polyphosphazene P2 is based upon the following equation [23]:

$$I_\perp = I_0 \sin^2(\pi \Delta n d/\lambda)$$

where $I_\perp$ is the intensity of the transmitted light behind A, I_0 is the total transmitted He–Ne laser intensity (through the pair of parallel polarizers before irradiation), d is the thickness of the sample, Δn is the birefringence, and λ is the wavelength of He–Ne laser (633 nm). Some samples were made, and the film thickness was 2.32 μm, 2.97 μm, 3.15 μm and 2.26 μm. The Δn value was calculated to be 4.5×10^{-3}, 4.2×10^{-3}, 4.7×10^{-3} and 4.4×10^{-3} at room temperature (25 °C), respectively. The value is smaller than typically reported for low-T_g PR materials [24,25], which is expected due to the lack of orientational enhancement [26]. Nevertheless, it

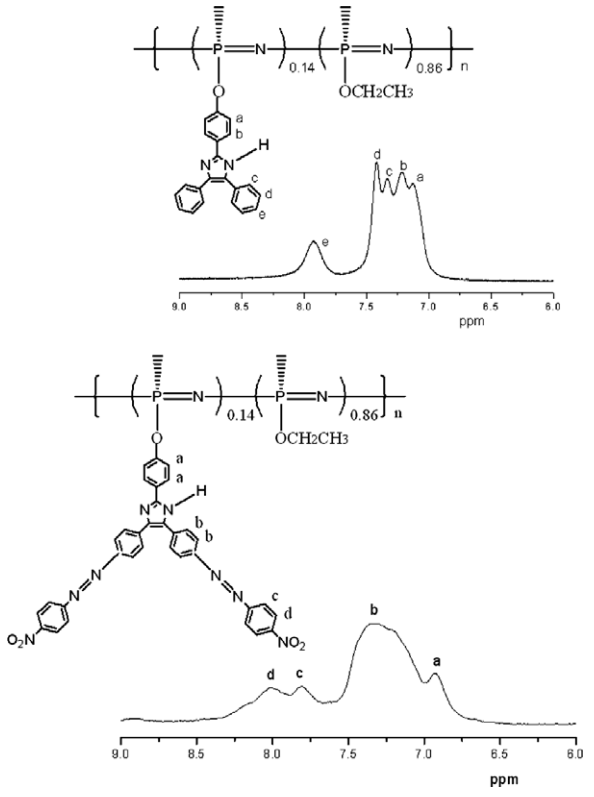


Fig. 1. ^1H NMR spectra of polyphosphazene P1 (top) and P2 (bottom).

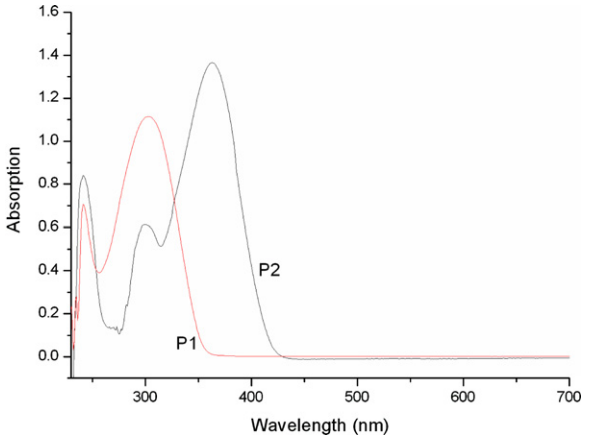


Fig. 2. UV–vis spectra of polyphosphazene P1 and P2 in THF.

is one of the highest photoinduced birefringence reported so far for high-T_g PR polymer systems [13,15,27].

4. Conclusion

In summary, a new polyphosphazene P2 with imidazole-based chromophore is prepared by an easy two-step method. The polymer presents relatively high photoinduced birefringence value ($4.2–4.7 \times 10^{-3}$), good optical transparency, high-T_g (170 °C) and good solubility in common organic solvents. We hope that this strategy will be used to the preparation of more other polymers containing heteroaromatic-based and multi-dipolar chromophores as nonlinear optical applications.

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References

[1] Gunter P, Huignard JP. Photorefractive materials and their applications. Berlin: Springer-Verlag; 1988.
[2] Ducharme S, Scott JC, Twieg RJ, Moerner WE. Phys Rev Lett 1991;66.
[3] Moerner WE, Grunnet-Jepsen A, Thompson CL. Annu Rev Sci 1997;27:585.
[4] Blanc D, Pelissier S, Saravanamatu K, Najafi S, Andrews M. Adv Mater 1999;11:1508.
[5] Cimrova V, Neher D, Kostromine S, Bieringer T. Macromolecules 1999;32:8496.
[6] Natansohn A, Rochon P. Chem Rev 2002;102:4139.
[7] Han M, Ichimura K. Macromolecules 2001;34:82.
[8] Changshun W, Haosheng F, Yong Q, Yanqiang Y, Zhengqian W. Appl Phys Lett 1999;74:19.
[9] Lagugne-Labarthet F, Buffeteau T, Sourisseau CJ. Appl Phys 2001;90:3149.
[10] Lagugne-Labarthet F, Rochon P, Natansohn A. Appl Phys Lett 1999;75:1377.
[11] Stockermans R, Rochon P. Appl Optics 1999;38:3714.
[12] Delarie JA, Nakatani K. Chem Rev 2000;100:1817.
[13] Peng Z, Gharavi AR, Yu L. J Am Chem Soc 1997;119:4622.
[14] Barrett C, Choudhury B, Natansohn A, Rochon P. Macromolecules 1998;31:4845.
[15] Hattemer E, Zentel R, Mecher E, Meerholz K. Macromolecules 2000;33:1972.
[16] Allcock HR. Adv Mater 1994;6:106.
[17] Allcock HR, Ravikiran R, Olshavsky MA. Macromolecules 1998;31:5206.
[18] Zhen L, Jun L, Jingui Q. React Funct Polym 2001;48:113.
[19] Allcock HR, Bender JD, Chang Y. Chem Mater 2003;15:473.
[20] Isikdag I, Meric A. Boll Chim Farm 1999;138:24.
[21] Starkey EB, Smith LI, Ungnade HE. Org Synth Collect Vol 1943;2:225.
[22] Carriedo GA, Alonso FJG, Gomez-Elipe P, Fidalgo JI, Alvarez JLG, Presa-Soto A. Chem Eur J 2003;9:3833.
[23] Todorov T, Nikolova L, Tomova N. Appl Optics 1984; 23:4309.
[24] Iftime G, Natansohn A, Rochon P. Macromolecules 2002; 35:365.
[25] Freiberg S, Lagugne-Labarthet F, Rochon P, Natansohn A. Macromolecules 2003;36:2680.
[26] Moerner WE, Slience SM, Hache F, Bjorklund GC. J Opt Soc Am B 1994;22:320.
[27] Yu L, Chen YM, Chan WK. J Phys Chem 1995;99:2797.