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Novel polyphosphazenes containing charge-transporting agent and chromophore as pendant groups

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Summary

Two novel functionalized polyorganophosphazenes containing charge-transporting agent and electro-optical chromophore as side chains for the photorefractive application are synthesized. The structure characterization was carried out by ^{1}H-NMR, IR and UV-Visble spectra, gel permeation chromatograply and differential scanning calorimetry. Due to the good flexibility of the backbone and the high degree of functionalization, polyphosphazenes are expected to be a good candidate for photorefractive polymeric materials.

Introduction

The photorefractive (PR) effect refers to spatial modulation of refraction generated by a specific mechanism: light-induced charge redistribution in a material in which the index of refraction depends upon electric field (1). Since the first polymeric photorefractive material was reported in 1991 (2), the PR polymers have attracted growing attention in recent years due to their potential applications in coherent optical systems including holographic data storage, real-time image processing and optical switching, and several advantages over the inorganic crystals (1,3,4). The necessary functionalities for PR polymers are photoconductivity and electro-optic response. There have been different approaches investigated in the past to develop photorefractive polymers. The popular approach is to mix all of the necessary functional species into polymer matrices, forming so called guest-host systems. Most of the reported high performance PR polymers are of this kind. However, another class of PR polymers, namely fully functionalized polymers, in which both the nonlinear optical (NLO) chromophore and the charge-transporting molecule were attached to the polymer backbone, has been considered as promising candidate for PR materials. Generally, because of their single component, the fully functionalized PR polymers are more stable against phase separation and sublimation during sample preparation than the guest-host polymers, and the stability of the electrooptic coefficient are much better. While several issues for fully functionalized PR polymers as shown below must be addressed before the performance of this type of PR polymers is competitive with those of the guest-host polymers. The first is the possibility of interrupting conduction pathways for the charge-transporting molecules by the dilution of other functional groups. The second is that most of the fully functionalized polymers to date are tedious to make, thus it is not a trivial task to optimize the PR properties of the polymers by modulating the

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relative concentration of the functional groups. Furthermore, another disadvantage of fully functionalized polymers is that the improvement of stability is usually accompanied by reduction of the materials flexibility. This reduction, in some degree, does not facilitate their PR properties. Therefore, new strategies are required to be explored to develop novel fully functionalized PR polymers, and a major challenge is to design and synthesize fully functionalized polymers simultaneously possessing high degree of functionalization and good flexibility (3).

Polyphosphazenes have the repeating unit structure of $[-N=P(R^1R^2)-]$, where R^1 and R^2 are the two side-chain of the polymers. Compared to the ordinary polymers with only one functional side group per unit, the polyphosphazenes provide double sites for further functionalization. The backbone of polyphosphazene is transparent from 200 to 800 nm and very flexible. Furthermore, they are photochemically and thermo-oxidatively stable (5). Therefore, polyphosphazenes may be considered as a good candidate for fully functionalized polymers.

With a view to develop fully functionalized PR polymers based on polyphosphazenes, we have recently designed and synthesized two new polyphosphazenes bearing carbazolyl groups and chromophore groups as the side chains. To our knowledge, this is the first time that polyorganophosphazenes were designed and synthesized for PR materials. Carbazolyl groups are good charge-transporting agents (3) for photoconductivity and the chromophores offer electro-optic response, so the polymers may have potential PR effect. Herein we would like to report the synthesis and structural characterization of these polymers.

Experimental

Materials and Instruments:

N-(2-hydroxyethyl)carbazole (**1**) and 6-Bromohexanol were prepared by following a literature procedure (6, 7). Phosphonitrile chloride trimer (Aldrich) was purified twice by vacuum sublimation (60°C/13Pa) before use. Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Ethanol was dried using a common method. All other reagents were used as received. The substitution reactions of poly(dichlorophosphazene) were carried out in a dry nitrogen atmosphere.

^{1}H-NMR spectra were conducted with a varian Mercury300 spectrometer. FT-IR spectra were recorded on a Testscan Shimaedzu FT-IR 3000 series in the region of 3000-400 cm^{-1} on KBr pellets. Differential scanning calorimetry (DSC) analyses were performed in a Rigaku Themoflex DSC8131 at a scan rate of 10°C/min. UV-visible spectra were obtained using a Schimadzu 160A spectrometer in the polymer THF solution. Molecular weights were determined by gel permeation chromatography (GPC) combined with light scattering (LS) in THF solution.

Synthesis

2, 5 -Dimethyl -(p -nitrophenylazo)phenol (***2*** *)* 4-Nitroaniline (4.7 g, 34 mmol) was dissolved in a solution of concentrated hydrochloric acid (10 ml) in 20 ml water. The mixture was cooled to 0°C in an ice bath, and then a solution of sodium nitrite (2.5 g, 36 mmol) in 10 ml water was added slowly to the 4-nitroaniline solution. After stirred below 2°C for 20 min, some sodium acetate was added to the above mixture to adjust pH about 7.0. Then the resultant mixture was added to a solution prepared from 2, 5-dimethylphenol (5 g, 41 mmol) and NaOH (1.36 g, 34 mmol) in 50 ml water. The mixture was agitated below 2 °C for 10 hrs. The orange red precipitate was filtered, washed with water, and air-dried. The solid was recrystallized from acetone/methanol to give 8.38 g product (91%). ^{1}HNMR ($CDCl_3$) δ(ppm): δ2.24 (s, 3H, Ar-CH_3), δ2.72 (S, 3H, Ar-CH_3), δ6.73 (s, 1H, ArH), δ7.57

(s, 1H, ArH), δ7.94 (d, 2H, ArH), δ8.26 (d, 2H, ArH). FT-IR (cm^{-1}, KBr): 1559, 1328 (-NO_2), 1253, 1087 (C-O).

2-[2, 5-dimethyl-4-(p-nitrophenylazo)phenoxy]ethanol (***3*** *)* Compound **2** (4.9 g, 18 mmol) and KOH (1 g, 18 mmol) in 40 ml DMF were stirred at room temperature for 30 min, and then 2-chloroethanol (2.2 g, 27 mmol) in 10 ml DMF was added slowly in 20 min. The resultant mixture was allowed to stir at 80 °C for 12 hrs. The mixture was poured into 500 ml water, and the brown red solid was filtered, washed with water, and air-dried. The solid was recrystallized from acetone/methanol to yield 4.3 g product (75%). ^{1}HNMR (acetone-d^6) δ2.2 (s, 3H), δ2.72 (s, 3H), δ3.0 (s, 1H), δ3.9 (t, 2H), δ4.2 (t, 2H), δ7.0 (s, 1H), δ7.6 (s, 1H), δ7.96-8.44 (m, 4H). FT-IR (cm^{-1}, KBr): 1602 (-C=C-), 1522, 1339 (-NO_2), 1249, 1072 (C-O).

N-(6-Hydroxyhexanyl)carbazole (***4*** *)* Powdered potassium hydroxide (12 g) was stirred with DMF (150 ml) at room temperature for 15 min. The mixture was then stirred with carbazole (14 g) at room temperature for 1hr. 6-Bromohexanol (13 ml) was added slowly, and the resultant mixture was allowed to stir at room temperature for 24 hrs. Then the mixture was poured into water (2 L) and the white solid was filtered, washed with water, and air-dried. The solid was recrystallized from ethanol/water to yield N-(6-Hydroxyhexyl)carbazole (80%). ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.4 (m, 8H, C-$(CH_2)_4$-C-O), 3.6 (t, 2H, -O-CH_2-), 4.3 (t, 2H, -N-CH_2-), 7.15 (m, 2H, ArH), 7.45 (m, 4H, ArH), 8.12 (d, 2H, ArH); FT-IR (cm^{-1}, KBr): 1593 (-C=C-), 1230 (C-N).

N-hydroxyethyl-N-methyl-4-(p -nitrophenylazo)aniline (***5*** *)* The synthesis procedure was just like the preparation of Compound **3.** A small difference was that N-hydroxyethyl-N-methylaniline was added instead of the sodium salt of 2, 5-dimethylphenol. The yield is 85%. ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.16 (s, 3H, -NCH_3), 3.60 (t, 2H, -NCH_2-), 3.84 (t, 2H, -OCH_2-), 6.76 (d, 2H, ArH), 7.90 (d, 4H, ArH), 8.28 (m, 2H, ArH); FT-IR (cm^{-1}, KBr): 1602 (-C=C-), 1506, 1331 (-NO_2), 1258 (C-N).

Poly(dichlorophosphazene) (***6*** *)* Phosphonitrile chloride trimer (2.5 g) was weighed directly into an ampule tube. The tube was evacuated to 13 Pa for 3 hrs and then sealed. The sealed ampule tube was placed into a 250 °C oil bath until the clear melting mixture became highly viscous but slightly mobile. The tube was broken and taken into a schlenk vessel, and dried petroleum ether (100 ml) was added . Then the resultant mixture was stirred at 50 °C for 3 hrs. After this, the cooled $N_3P_3Cl_6$ solution was transferred to another flask using a cannula, removed the ether, unreacted trimer was weighted, so the amount of poly(dichlorophosphazene) could be calculated. Then dry THF was added to the schlenk vessel to dissolve the polymer.

Polymers ***7*** *and* ***8*** The polymers were prepared in a similar manner. The synthetic procedure of Polymer **7** was shown as following.

Fifteen milliliters of a solution of the sodium salt of Compound **1** (prepared from the compound **3** (0.46 g, 1.46 mmol) and sodium hydride (0.035 g, 1.45 mmol) in THF) was added to a solution of poly(dichlorophosphazene) (**6**) (1.06 g, 9.13 mmol) in 80 ml THF, and the mixture was stirred at 60 °C for two days. Then the sodium salt of Compound **1** (prepared from Compound **1** (1.93 g, 9.2 mmol) and NaH (0.22 g, 9.1 mmol)) in 20 ml THF was added, and the mixture was again stirred at 60 °C for two days. Finally, 20 ml of the solution of $NaOCH_2CH_3$ (prepared from sodium (0.46 g, 20 mmol) and ethanol (0.92 g, 20mmol)) was added, and the resultant mixture reacted for another four days at 60 °C. The mixture was poured into 800 ml water, and the red solid was filtered, washed with water, and air-dried. The solid was dissolved in THF, and the insoluble residue was filtered out. The filtrate was evaporated to remove the bulk of THF. Then the solid was isolated and purified by several precipilations from THF into methanol. The solid was vacuum dried at 40 °C to yield the product.

Results and discussion:

Preparation of poly(dichlorophosphazene) The presence of traces of water in the polymerization tube affects the polymerization process considerably (8). It was found that within the range of 0.02% to 0.1 mol % water in $(NPCl)_3$, increasing amounts of water increased the rate of polymerization (9). So the polymerization duration is not always unchanged because the amount of water is not the same. During the polymerization of phosphonitrile chloride trimer, we put the sealed ampule tube into a 250 °C oil bath until the clear melting mixtures became highly viscous but still slightly mobile. Generally speaking, the polymerization duration varies from two hours to two days (10) depending on the amounts of water.

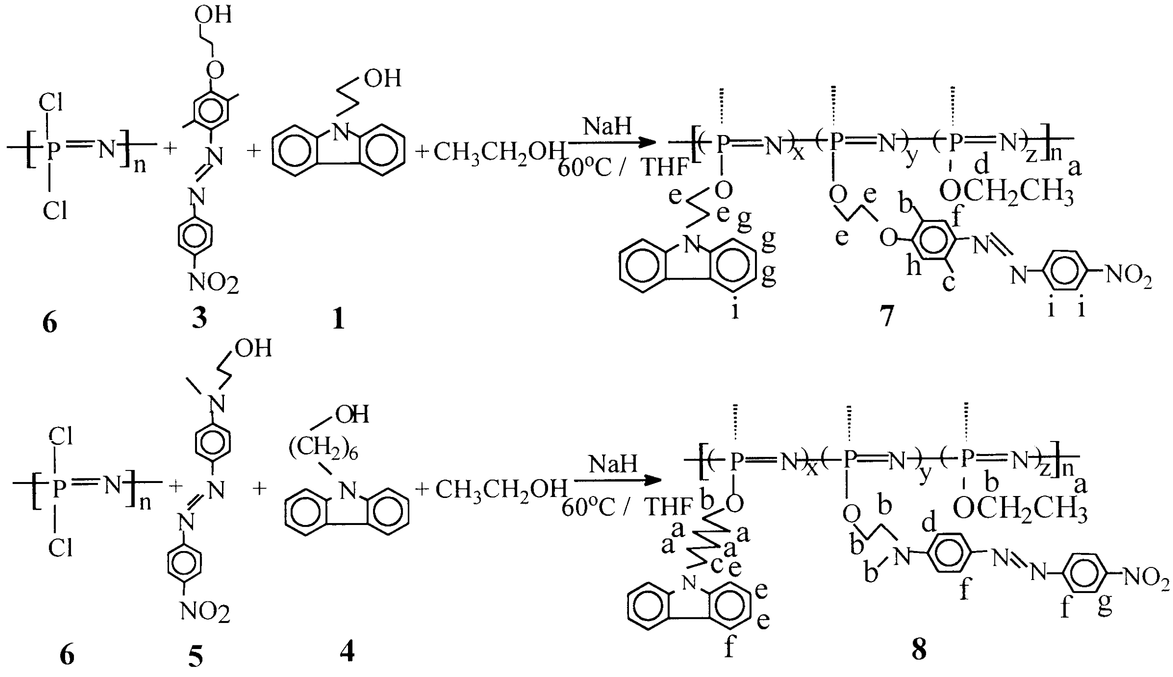
Purification of the poly(dichlorophospphazene) was very important. Allcock et al (11) cooled the ampule tube in liquid nitrogen and then warmed to room temperature three times before opening. After this, the tube was opened and the residual trimer was separated by vacuum sublimation (11). In our work, a more convenient separation method has been explored because the poly(dichlorophosphazene) was not dissolved in petroleum ether, petroleum ether was used to dissolve the unpolymerized trimer and then transferred away. Also from the amount of trimer before and after the polymerization, the quantity of the poly(dichlorophosphazene) could be easily estimated.

*Synthesis of Polymers **7** and **8*** The synthetic route to Polymers **7** and **8** is shown in **Scheme I**. Poly(dichlorophosphazene) (**6**), which is the precursors for following functionalization, was successively reacted with the sodium salts of N-2-hydroxyethyl-N-methyl-4-(p-nitrophenylazo)aniline, 6-carbazolylhexanol, and then ethanol to afford Polymer **7**. Polymer **8** was synthesized in a similar manner like Polymer **7**.

This synthetic route and the reaction conditions were chosen for the following reasons:

1.The steric hindrance associated with the polymer chain will slow down the rate of chlorine replacement by other nucleophilic reagents, especially after each phosphorus atom bears one organic side groups (12). For this reason, during the synthetic procedure, Polymer **6** was first reacted with chromophore agents due to their small size and low concentration.

Scheme I



2. One of the necessary functionalities for PR polymers is photoconductivity. And, in PR polymers, charge transporting function is generally provided by a network of charge-transporting agents (1,3). In Polymers **7** and **8**, carbazolyl groups at 1 equiv were introduced onto the main chain, so each phosphorus atom may bear one carbazolyl side group. The carbazolyl groups will be close enough in space due to its high density and the good flexibility of polyphosphazenes. Therefore, the charge carrier may transport from carbazolyl group to carbazolyl group because carbazolyl groups are good charge-transporting agents.

3. The phosphorus-nitrogen backbone may cleave at high temperature after a long time during nucleophilic reaction. On the other hand, if the reaction was carried out at room temperature, the reaction rate is very slow, and poly(dichlorophosphazene) was only partially substituted. According to Allcock et al (13), at a temperature of 50 °C, a good compromise between high degree of functionalization and minimized polymer backbone cleavage has been obtained. While in our cases, due to the bulky size and properties of the nucleophiles, a temperature of 60 °C is better. It has been found that, at this temperature, the cleavage of the backbone was minimized and the functional groups could be linked to the backbone successfully in few days.

4. Carbazolyl and chromophore groups can not react with all the chlorine atoms because of the steric shielding effect (14). 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.

Structural characterization of polymers The compositions of the polymers (Table 1) could be determined by ^{1}H-NMR spectra (Figure 1). The peaks shown in Figure 1 were noted in the structure of Polymers **7** and **8** (Scheme I).

Infrared spectroscopy (Figure 2) was compatible with the structure of Polymers **6** and **7**. The bands at 1250 — 1200 cm^{-1} were attributed to an intense P=N stretching vibration and the band at 750cm^{-1} to an in-phase P-N-P stretch. In addition, the absorbances for the aromatic ring are at 1598, 1458, 722 cm^{-1} and the NO_2 unit at 1328 cm^{-1}.

Table 1. Component concentration ratio in Polymers **7** and **8**

Polymer	x	y	z
7	0.50	0.05	0.45
8	0.47	0.08	0.45

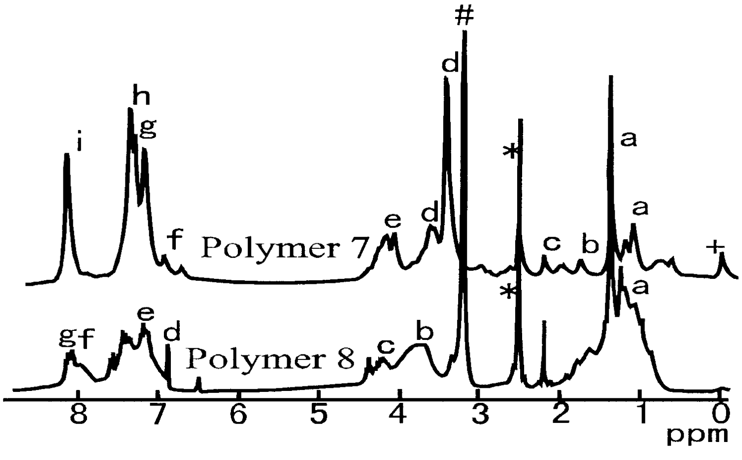


Figure 1. ^{1}H-NMR of Polymer **7** and **8** ($^+$ TMS; * solvent (DMSO); $^\#$ H_2O)

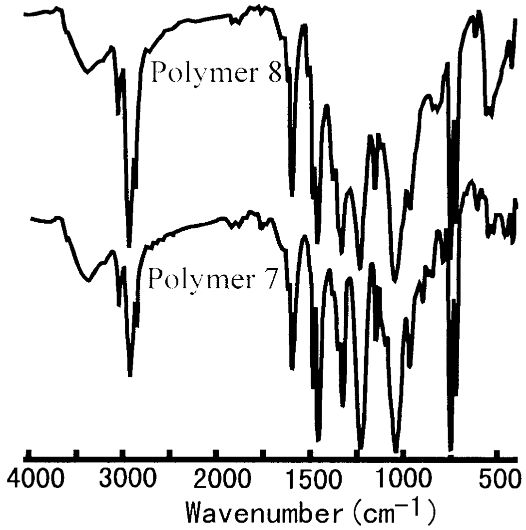


Figure 2. FT-IR spectra of Polymers **7** and **8**

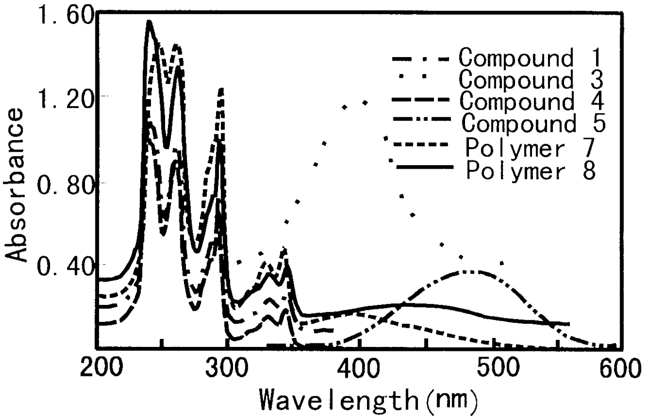


Figure 3. UV-Vis spectra of the compounds (concentration: **1, 4, 5** (0.04 mg / ml), **7** and **8** (0.09 mg / ml), **3** (0.15 mg / ml))

The molecular weights of polymers **7** and **8** were determined by gel permeation chromatography combined with light scattering. The M_n and M_w of polymer **7** were $1.96x10^4$ and $2.05x10^4$, while $8.21x10^4$, $1.21x10^5$ of Polymer **8** respectively.

These two polymers have good solublity in common organic solvents, such as THF, DMSO, DMF, etc. The UV-Visible spectra of the polymers in THF were recorded and were compared to the absorption spectra of the functional molecules(see Figure 3). Both Polymers **7** and **8** showed a hypsochromic shift relative to the chromophore groups, and it was more signigicant in Polymer **8**. It may be due to electronic interactions between the backbone and the side groups in the polymers.

Differential scanning calorimetric (DSC) analysis showed the glass transition temperature (T_g) of Polymer **7** at 71 °C, and Polymer **8** at 74 °C. Although high degree of functionalization has been achieved, their T_gs are relatively low, indicating that the flexibility of the two polymers has not been significantly reduced.

Conclusion

Novel polyorganophosphazenes with highly functionalized charge-transporting agent and electro-optical chromophore as side chains are successfully synthesized. The characterization of photo-conductivity, electro-optical effect and photorefractive effect is in due course.

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