Postfunctionalization Strategy for Developing Polyphosphazene with a High Loading of Highly Polar Molecules in the Side Arms

Zhen Li, Jingui Qin, Hongding Tang, Yunyang Liu

Department of Chemistry, Wuhan University, Wuhan, China, 430072

ABSTRACT: A new postfunctionalization strategy for developing polyphosphazene functionalized with a high density of highly polar molecules was explored, and the moiety loading was up to 0.84 per unit. A polyphosphazene with *N,N*-dialkyl-substituted aniline as side chains was first synthesized by a direct substituted reaction, and then post azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the aniline groups afforded functionalized polyphosphazenes with highly polar molecules. The structural characterization was performed with ^{1}H-NMR, IR, and ultraviolet–visible spectroscopy and gel permeation chromatography. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2989–2993, 2003

Key Words: polyphosphazene; synthesis; functionalization of polymers

INTRODUCTION

Polyphosphazenes are inorganic polymers with backbones of alternating phosphorus and nitrogen atoms, and they are considered excellent candidates for electrooptic applications because of the unusual advantages of their inorganic backbones, such as high thermooxidative and photolytic stability and optical transparency from 220 to 800 nm. Most polyphosphazenes have very high molecular weights, and they are usually amorphous, soluble, and easily prepared.[1–3] In the past decade, Allcock's group has performed systematic studies in this area; for example, disperse red 1 (DR-1)-bonded polyphosphazenes have been studied in detail, DR-1 being a highly polar molecule. In 1991, DR-1 was first linked to the phosphorus–nitrogen backbone for the synthesis of new nonlinear optical (NLO) polymeric materials, and the loading of DR-1 was 33%.[4] As the loading of DR-1 was relatively low, the synthetic procedure was not easy by a direct reaction, Allcock et al.[2] improved their synthetic methods to raise the loading up to 46% via reactions that involved functionalized poly(organophosphazene)s. However, soluble polyphosphazenes with higher percentages of DR-1 moieties could not be obtained by this method. They ascribed these results to the intrinsically high polarity of the donor–acceptor structure of DR-1, the low solubility of the sodium salt of the DR-1 alcohol, and the close packing or stacking of rigid aromatic side groups.[2,4–6] As a result, Allcock's group raised two questions: what is the maximum loading of DR-1 groups possible in the polyphosphazene systems, and is there a polyphosphazene bearing two DR-1 moieties per repeat unit? Their studies showed that polyphosphazenes with higher loadings of DR-1 moieties could be prepared by changes in the synthetic method. Therefore, is it possible to further raise the loading of DR-1 moieties directly linked to the phosphazene backbone by another synthetic route?

However, the azo coupling reactions between polymers and diazonium salts enable the introduction of NLO chromophores. This method was first used by Katz et al.[7] to functionalize a copolymer of methyl methacrylate and methacrylate ester of *N*-ethyl-*N*-(hydroxyethyl) aniline in acetic acid. As an acidic medium is not a favorite solvent medium for most polymers, Tripathy et al.[8] developed this method by using polar organic solvents such as dimethylformamide (DMF) or dimethylacetamide. In our previous studies, we easily synthesized DR-1-containing polysilanes by the azo coupling reaction in *N*-methylpyrrolidone (NMP) with high reaction yields.[9] In this study, this method was further extended to the synthesis of polyphosphazenes with high DR-1 loadings. Therefore, polyphosphazenes with *N,N*-dialkyl-substituted anilines as side chains were first synthesized by the direct substituted reaction, and then the post azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the aniline groups afforded polyphosphazenes
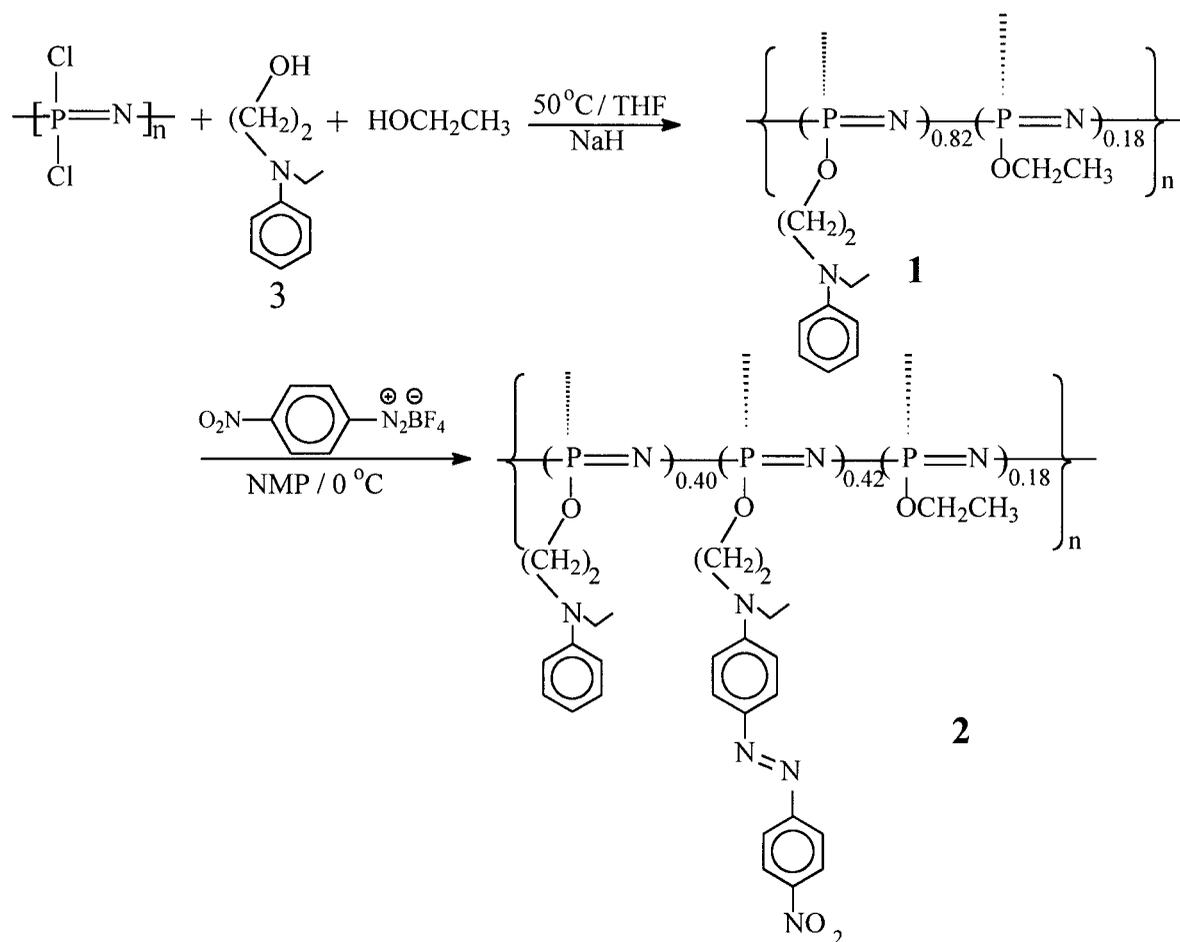
Scheme 1

with high chromophore loadings. Here we report the synthesis and structural characterization of these polymers.

EXPERIMENTAL

Materials and instruments

N-Ethyl-*N*-(2-hydroxyethyl)aniline (**3**) was synthesized from *N*-ethylaniline and 2-chloroethanol.[10] *p*-Nitrobenzenediazonium fluoroborate was synthesized according to a procedure described in the literature.[11] Phosphonitrile chloride trimer (Aldrich, Milwaukee, WI) was purified twice by vacuum sublimation (60°C/13 Pa) before use. Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of phosphonitrile chloride trimer[12] and purified as reported by us previously.[13–15] Tetrahydrofuran (THF) was dried over and distilled from a K–Na alloy under an atmosphere of dry nitrogen. All the other reagents were used as received. The substitution reactions of poly(dichlorophosphazene) were carried out under a dry nitrogen atmosphere with a Schlenk technique.

^{1}H-NMR spectra were recorded with a Varian Mercury 300 spectrometer (Palo Alto, CA). FTIR spectra were recorded on a Shimadzu Testscan FTIR 3000 series (Osaka, Japan) in the region of 3000–400 cm^{-1} on KBr pellets. Ultraviolet–visible (UV–vis) spectra were obtained with a Shimadzu 160A spectrometer in a polymer *N,N*-dimethylformide solution. The molecular weights were determined in THF solutions with a Waters 2960D separation module (Milford, MA) containing Styragel HR1 THF columns and a Waters 2410 refractive-index detector with a calibration curve for polystyrene standards.

Synthesis

Preparation of polyphosphazenes 1

N-Ethyl-*N*-hydroxyethylaniline (1.94 g, 11.7 mmol) reacted with sodium hydride (0.27 g, 11.3 mmol) in THF (20 mL) at 50°C for 10 h, and then the resultant solution of the sodium salt of compound **3** was added to a solution of poly(dichlorophosphazene) (0.68 g, 5.8 mmol) in 80 mL of THF; the mixture was stirred at 50°C for 2 days. Then, 10 mL of a solution of
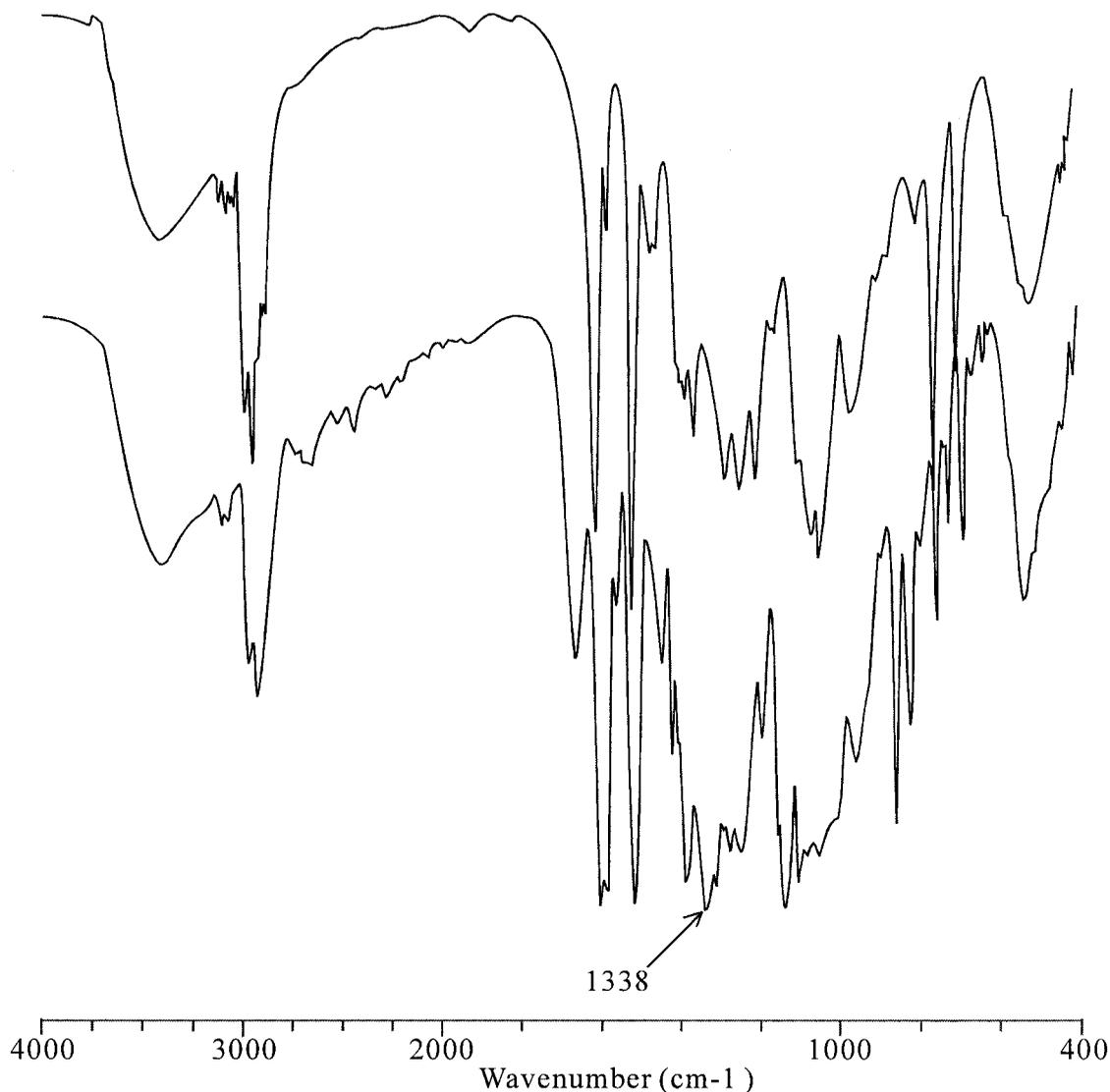
Figure 1   IR spectra of polymers **1** and **2**.

NaOCH$_2$CH$_3$ prepared from sodium (0.27 g, 11 mmol) and ethanol (0.8 g, 17 mmol) in THF] was added, and the resultant mixture was stirred at 50°C for another 2 days. The mixture was poured into water (400 mL), and the white 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 further purified by several precipitations from THF into methanol. The solid was vacuum-dried at 40°C to yield the product (0.70 g).

Preparation of polyphosphazenes 2

1 (150 mg) was dissolved in NMP (1 mL), and then *p*-nitrobenzenediazonium fluoroborate (155 mg) was added under cooling with an ice bath. The color of the solution changed to dark red immediately. After 8 h of stirring at 0°C, excessive anhydrous potassium car-

bonate was added, and the mixture was stirred for 1 h more and then filtered. The residue was washed with THF, the filtrates were collected, and THF was removed under reduced pressure. Then, some methanol was added dropwise to precipitate the polymer. Reprecipitation gave a dark red product (200 mg).

RESULTS AND DISCUSSION

Synthesis

The synthetic route to these polymers is shown in Scheme 1. **2** was polyphosphazene containing DR-1 moieties as side groups. The overall synthesis of the polyphosphazenes with high chromophore loadings was carried out with ring-opening polymerization and macromolecular substitution. Subsequent azo coupling reactions were carried out on aniline-bearing **1** to give the required polymer with a high chro-
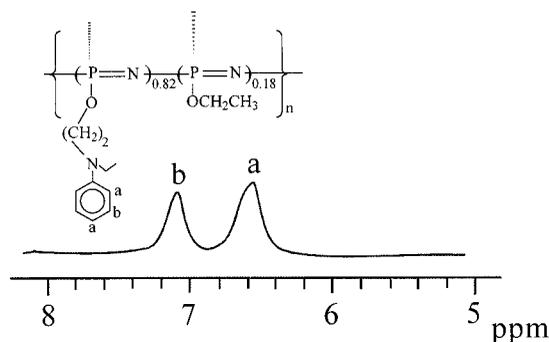
Figure 2 Part of the ^{1}H-NMR spectrum of polymer **1**.

mophore loading. The DR-1-containing polyphosphazene was dark red and soluble in DMF, dimethyl sulfoxide (DMSO), and NMP.

Aniline groups could not react with all the chlorine atoms because of a steric shielding effect. However, if some chlorine atoms remained in the polymer without being reacted, crosslinking could take place, and the polymer became insoluble when it was exposed to moisture or water. Therefore, an excess of $NaOCH_2CH_3$ was added to the reacting solution to replace all the remaining chlorine atoms.

The quantum of NMP in the azo coupling reaction was very important. Generally, the less there was, the better it was. If the quantum was large, the product polymer could not precipitate from the reacting solution even when excess methanol was added. This might be due to the good solubility of the product polymer in NMP. Therefore, in the reaction, only the quantum needed for solubilizing **1** was added.

Structural characterization of the polymers

The molecular weights of the polymers were determined by gel permeation chromatography experiments with THF as a solvent. The number-average and weight-average molecular weights of **1** were 2.4 $\times 10^4$ and 1.0 $\times 10^5$, respectively. Data for **2** could not be obtained because it was insoluble in THF.

In the IR spectra (Fig. 1), the intense P=N stretching vibration caused the bands at 1250–1200 cm^{-1}, and the in-phase P—N—P stretch resulted in the band at 750 cm^{-1}. In addition, the absorbances for the aromatic ring were at 1600 and 1446 cm^{-1}, and the strong absorbance of the NO_2 unit at 1338 cm^{-1} appeared in **2**. This confirmed that p-nitrobenzenediazonium fluoroborate reacted with the aniline side groups and that nitro units were introduced into the side chains.

NLO chromophore loading

The component concentrations in the polymers were calculated by a careful analysis of the ^{1}H-NMR peak integration, and they are shown in Scheme 1. For **1**, the

component concentrations were calculated from the ^{1}H-NMR peak integration of the phenyl proton resonances of the aniline groups in the range of 6.50–7.40 ppm, the proton resonance of —NCH_2, —OCH_2 groups at 3.0–4.0 ppm, and the proton resonances of methyl groups around 1.0 ppm (Scheme 1). As the concentration of the ethoxide groups in the polyphosphazene remained the same before and after the post azo coupling reaction, it was easy to estimate the component concentrations in **2** by a comparison of the proton resonances in the downfield. The concentration of DR-1 moieties in **2** was 0.42; that is, the DR-1 loading was 0.84 per repeating unit as one repeating unit bore two side groups in the polymer, and the results are shown in Scheme 1. For a comparison of **1** and **2**, their ^{1}H-NMR spectra for the aromatic regions and the assignments of the peaks are shown in Figures 2 and 3. The resonances at 7.08 and 6.60 ppm corresponded to chemical shifts of benzyl protons in aniline moieties in the case of **1**. After the post azo coupling reaction, the resonance at 6.60 ppm decreased as some aniline moieties were transformed into DR-1 moieties, and the resonance shifted to the downfield as a result of the introduction of electron-withdrawing groups and an increase in the conjugation length (see Fig. 3).

The UV–vis absorption spectra of polymer **1** and **2** were measured and compared with the absorption spectra of the free-form chromophore (Fig. 4). The absorption could be attributed directly to the spectra of the side groups. A new absorption peak appeared in the spectroscopy of **2** at 484 nm as a result of the introduction of electron-withdrawing groups and an increase in the conjugation length. The concentration of the DR-1 moieties in **2** could be determined further by a comparison of the intensities of the maximum
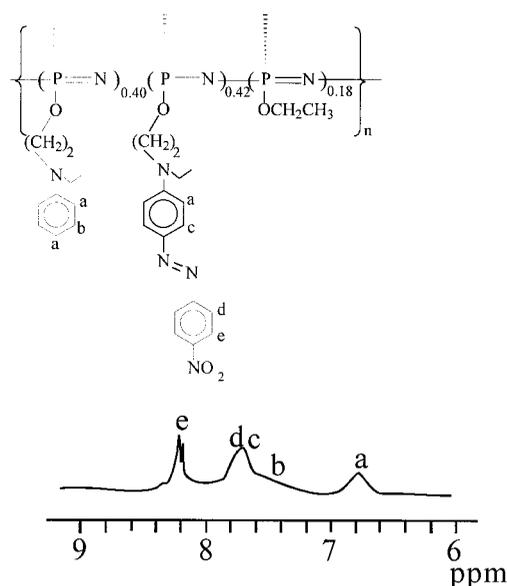

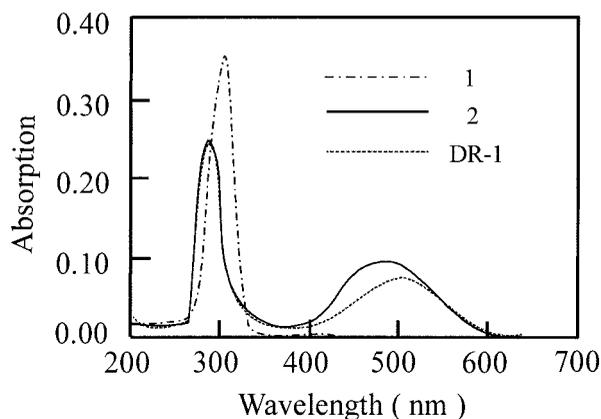
Figure 3 Part of the ^{1}H-NMR spectrum of polymer **2**.

Figure 4 UV–vis spectra of polymers **1** and **2** and DR-1 in DMF.

absorption peak at 483 nm in DMF and that of pure DR-1 molecules in DMF, and the results were similar to those obtained from ^{1}H-NMR spectroscopy of **2**.

Polymer **2** showed a hypsochromic shift in the absorption spectra relative to the side groups. This might be due to electronic interactions between the backbone and the side groups in the polymers, as found previously.[2,13]

Polyphosphazene loaded with 33% DR-1 moieties could be prepared by the direct substituted reaction according to Allcock et al.,[4] but the low solubility of the salt of the DR-1 alcohol limited the substituted reaction to a great extent. In our method, polyphosphazene with *N,N*-dialkyl-substituted aniline as side chains was first synthesized by the direct substituted reaction, and then the post azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the aniline groups afforded the chromophore-loading polyphosphazenes. This approach diminished the effect of the low solubility of the sodium salt of the DR-1 alcohol. The main conflict focused on the reaction between the

aniline groups and *p*-nitrobenzenediazonium fluoroborate. As the aniline groups possessed high reactivity for undergoing the post azo coupling reaction, polyphosphazenes with higher DR-1 moiety loadings of 42% were synthesized.

CONCLUSIONS

A polyphosphazene with a highly polar moiety (DR-1 moiety) loading was synthesized by the post azo coupling method. It was dark red and soluble in DMF, DMSO, and NMP. The structural characterization was carried with ^{1}H-NMR, IR, and UV–vis spectroscopy and gel permeation chromatography. This synthetic strategy could be generalized to other polymers containing aniline groups to produce a series of high-chromophore-functionalized polymers.

References

1. Neilson, R. H.; Neilson, P. W. Chem Rev 1988, 88, 541.
2. Allcock, H. R.; Ravikiran, R.; Olshavsky, M. A. Macromolecules 1998, 31, 5206.
3. Li, Z.; Zhan, C. M.; Qin, J. G. J Funct Polym (in Chinese) 2000, 13, 240.
4. Allcock, H. R.; Dembek, A. A.; Kim, C.; Devine, R. L. S.; Shi, Y.; Steier, W. H.; Spangler, C. W. Macromolecules 1991, 24, 1000.
5. Allcock, H. R.; Kim, C. Macromolecules 1989, 22, 2596.
6. Allcock, H. R.; Kim, C. Macromolecules 1990, 23, 3881.
7. Schilling, M. L.; Katz, H. E.; Cox, D. I. J Org Chem 1988, 53, 5538.
8. Wang, X.; Kumar, J.; Tripathy, S. K.; Li, L.; Chen, J. Macromolecules 1997, 30, 219.
9. Tang, H.; Luo, J.; Qin, J.; Kang, H.; Ye, C. Macromol Rapid Commun 2000, 21, 1125.
10. Samyn, C.; Verbiest, T.; Kester, E.; Broeck, K.V.; Beylen, M.V. Polymer 2000, 41, 6049.
11. Starkey, E. B.; Smith, L. I.; Ungnade, H. E. Org Synth 1943, 2, 225.
12. Allcock, H. R.; Kugel, R. L. J Am Chem Soc 1965, 87, 4216.
13. Li, Z.; Luo, J.; Li, J.; Zhan, C.; Qin, J. Polym Bull 2000, 45, 105.
14. Li, Z.; Li, J.; Qin, J. React Funct Polym 2001, 48, 113.
15. Li, Z.; Qin, J.; Deng, X.; Cao, Y. J Polym Sci Part A: Polym Chem 2001, 39, 3428.