

Synthesis and Structural Characterization of a Polyphosphazene as a Photoconductive Material

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Abstract: The synthesis of a novel polyorganophosphazene that contains charge-transporting agent as side chains for photoconductive application is reported. Structural characterization for the high polymer was presented by $^1\text{H-NMR}$, infrared spectroscopy, gel permeation chromatography (GPC).

Keywords: Photoconductive, polyphosphazene, synthesis, structure.

In the past decades, photoconductive polymers have received much attention either from a fundamental standpoint or for their potential uses^{1,2}. The photoconductivities of many polymers have been reported, such as phenylmethylpolysilane, poly(p-phenylenevinylene), N-poly(vinylcarbazole), and so on.

Recently we have synthesized a novel polyphosphazene that contains charge-transporting agent for photoconductive application. Polyphosphazene was selected because of its photochemical stability, the good transparency between 220 and 800 nm of the backbone, the possibility of electronic interactions between the backbone and the side groups, and the ease with which the functional groups can be introduced to the side chains of the macromolecules by substitution reactions³.

In the present work, we have designed and synthesized a polyphosphazene bonded with carbazolyl and some ethoxy groups. Carbazolyl groups are good charge-transporting agents⁴ and they may assure the photoconductivity of the polymer.

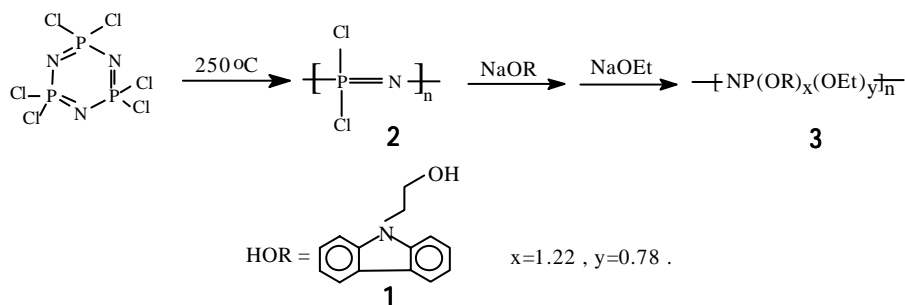
Charge-transporting agent **1** was prepared by the reaction between carbazole and 2-chloroethanol in DMF in the presence of KOH as a hydrogen chloride acceptor⁵. Poly(dichlorophosphazene) **2** was obtained from polymerization of phosphonitrile chloride trimer⁶. Polymer **3** was prepared by allowing 2 equiv of sodium 2-carbazolyloxy (prepared from the compound **1** and NaH) to react with poly(dichlorophosphazene) in THF (dried over and distilled from K-Na alloy) under an atmosphere of dry nitrogen to assure that carbazolylethoxy groups could be covalently linked to the polymer backbone as much as possible. And then an excess of $\text{NaOCH}_2\text{CH}_3$ was added into the reaction mixture to replace all the remaining chlorine atoms to get a fully substituted polymer.

Results and Discussion

Carbazolyl groups are good charge-transporting agents, so we introduced carbazolyl groups to the side chains as much as possible to increase the photoconductivity of the polymer. But carbazolyl groups can not react with all the chlorine atoms because of steric shielding effect. 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 $\text{NaOCH}_2\text{CH}_3$ was added into the reaction mixture to replace all the remaining chlorine atoms completely.

Infrared spectroscopy was compatible with the structure of polymer **3**. The $1250\text{--}1200\text{ cm}^{-1}$ bands were attributed to an intense $\text{P}=\text{N}$ stretching vibration and the 750 cm^{-1} band to an in-phase P-N-P stretch. In addition, the absorbances for the carbazolyl groups are at $1599, 1458, 722\text{ cm}^{-1}$.

The composition ratio of the polymer was estimated by a comparison of the integration of the carbazolyl resonance between 8.0 ppm and 7.2 ppm, and methyl (in ethoxy groups) at 1.0 ppm in $^1\text{H-NMR}$ spectra. The molecular weight of the polymer was determined by gel permeation chromatography (GPC). The M_n and M_w of polymer **3** were 5.7×10^4 and 2.9×10^5 respectively, with M_w/M_n value about 5. The broad, bimodal molecular weight distribution is typical of polyphosphazenes⁷.



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References

1. P. D. Marco, G. Giro, S. Lora, M. Gleria, *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 439.
2. Y. Wang, A. Suna, *J. Phys. Chem. B* **1997**, *101*, 5627.
3. R. H. Neilson, P. W. Neilson, *Chem. Rev.* **1988**, *88*, 541.
4. W. E. Moerner, S. M. Silence, *Chem. Rev.* **1994**, *94*, 127.
5. M. S. Ho, C. Barrett, J. Paterson, *et al.*, *Macromolecules* **1996**, *29*, 4613.
6. H. R. Allcock, R. L. Kugel, *J. Am. Chem. Soc.* **1965**, *87*, 4216.
7. H. R. Allcock, A. A. Dembek, C. Kim *et al.*, *Macromolecules*, **1991**, *24*, 1000.

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