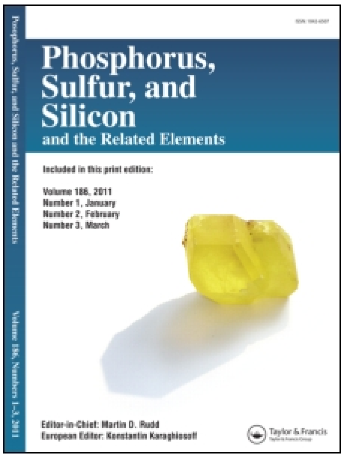

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Chang, Ji Young , Park, Phil Jeung , Han, Man Jung and Chang, Taihyun(1999) 'Copolymers Obtained by Grafting Reaction of 2-Methyl-2-Oxazoline Onto Poly(4-Methylphenoxyphosphazene) and their Micelle Formation', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 197 — 200

To link to this Article: DOI: 10.1080/10426509908546216

URL: http://dx.doi.org/10.1080/10426509908546216

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 197-200
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Copolymers Obtained by Grafting Reaction of 2-Methyl-2-Oxazoline Onto Poly(4-Methylphenoxyphosphazene) and their Micelle Formation

JI YOUNG CHANG[a], PHIL JEUNG PARK[a], MAN JUNG HAN[a] and TAIHYUN CHANG[b]

[a]*Dept. of Applied Chemistry, Ajou University, Suwon 442–749, Korea and*

[b]*Dept. of Chemistry, Pohang University of Science and Technology, Pohang 790–784, Korea*

Poly(dichlorophosphazene) of a low molecular weight was prepared by the thermal polymerization of hexachlorocyclotriphosphazene in the presence of aluminum chloride (10 wt %). The chloro groups were replaced by 4-methylphenoxy groups to give $[NP(OC_6H_4\text{-}p\text{-}CH_3)]_n$. The methyl groups of the polymer were brominated with N-bromosuccinimide and benzoyl peroxide, resulting in $[NP(OC_6H_4\text{-}p\text{-}CH_3)_x(OC_6H_4\text{-}p\text{-}CH_2Br)_y]_n$. The brominated unit content was 5% – 20%. These polymers were employed in initiating polymerization of 2-methyl-2-oxazoline. The weight average molecular weight of the 5% grafted polymer measured by GPC in chloroform was 11,000. Their micelle formation in water was investigated by fluorescence spectroscopy and surface tension measurement.

Keywords: polyphosphazene; graft copolymer; micelle

INTRODUCTION

Several copolymers of polyphosphazene-*graft*-organic polymer have been reported. These polymers have attracted a great attention due to their unique chemical structures, *i.e.*, inorganic polymer backbones with organic polymer side chains, and potential for practical application. Three types of grafting methods have been used, which are radical[1], anionic[2], and stepwise[3] grafting reactions.

In the present work, we studied on cationic grafting reaction of 2-methyl-2-oxazoline onto poly(4-methylphenoxyphosphazene). The graft copolymers were expected to form micelles in water since they had hydrophobic main chains and hydrophilic side chains. To find structural requirements for the micelle formation of the copolymers, we used phosphazene backbones of low molecular weights and controlled the length and the number of organic polymer chains.

EXPERIMENTAL

Materials and Instrumentation

Hexachlorocyclotriphosphazene (Aldrich) was purified by fractional vacuum sublimation at 60 °C in 0.5 mmHg. Poly(dichlorophosphazene) was prepared by the thermal polymerization of hexachlorocyclotriphosphazene at 250 °C in the presence of 10% $AlCl_3$ by weight for 10 h.

The surface tension of the polymers in water was measured by a Fisher tensiometer at 22 °C. For fluorescence measurement, the stock solution of the copolymer in doubly distilled water was prepared. Pyrene was used as a probe. To the solution of pyrene (2.4 mg) in THF (2 ml) was added 100 ml of doubly distilled water and then THF was removed by evaporation under reduced pressure. The concentration of pyrene in each sample solution was made to 6 x 10^{-7} M. Fluorescence spectra were obtained by Kontron SFM-25 spectrometer. Excitation was carried out at 336 nm.

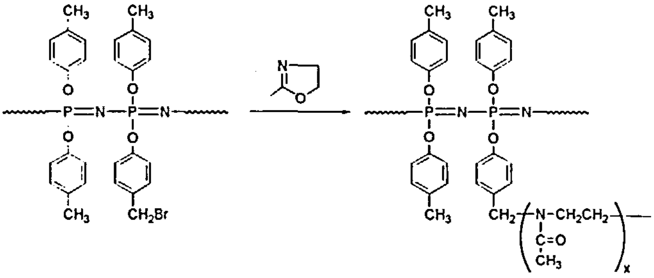
Graft Copolymerization of 2-Methyl-2-oxazoline onto Polyphosphazene

$[NP(OC_6H_4\text{-}p\text{-}CH_3)_2]_n$ and $[NP(OC_6H_4\text{-}p\text{-}CH_3)_x(OC_6H_4\text{-}p\text{-}CH_2Br)_y]_n$ were prepared according to the literature[4]. A typical graft copolymerization was carried out as follows. $[NP(OC_6H_4\text{-}p\text{-}CH_3)_{1.9}(OC_6H_4\text{-}p\text{-}CH_2Br)_{0.1}]_n$ (0.2g) was dissolved in N,N-dimethylformamide (DMF) (10 ml) and the appropriate amount of 2-methyl-2-oxazoline was added to the solution under nitrogen. The polymerization was carried out with stirring at 80 °C. After 10 hr, the reaction mixture was concentrated by evaporation under reduced pressure and added dropwise to diethyl ether. The precipitated polymer was collected by filtration. The polymer was further purified by precipitation twice from the polymer solution in DMF into diethyl ether and dialysis against water with a cellulose membrane (Mw cutoff 1000).

RESULT AND DISCUSSION

Poly(dichlorophosphazene) of a low molecular weight was prepared by the thermal polymerization of hexachlorocyclotriphosphazene at 250 °C for 10 h in the presence of 10% $AlCl_3$ by weight[5]. The conversion of the trimer was almost quantitative. No cross-linked polymer was obtained. Chloro groups of poly(dichlorophosphazene) were replaced by 4-methylphenoxy groups in an usual manner. The weight average molecular weight of the resulting polymer measured by GPC (chloroform, polystyrene standards) was 6,200. Bromination reaction was performed with N-bromosuccinimide and benzoyl peroxide in CCl_4. The brominated methyl group content was controlled to be between 5 - 20% by monitoring the reaction with ^1H NMR spectroscopy.

Benzyl bromide compounds are good initiators for ring-opening polymerization of cyclic iminoethers. The polymerization of 2-methyl-2-oxazoline by initiation with the 5% brominated polymer was carried out in DMF at 80 °C (Scheme 1). Average degree of polymerization of the side chains was determined by ^1H NMR spectroscopy to be 56. Due to the hydrophilicity of the poly(2-methyl-2-oxazoline) side chains, the graft copolymers became soluble in water. They also showed quite different solubilities in organic solvents compared with poly(4-methylphenoxyphosphazene), *i.e.*, soluble in methanol, chloroform, and DMF, but insoluble in tetrahydrofuran, 1,4-dioxane, which were good solvents for poly(4-methylphenoxyphosphazene). After grafting, the weight average molecular weight of the polymer measured by GPC in chloroform increased to 11,000.



Scheme 1

Figure 1 shows the concentration - surface tension relationship of the 5% grafted copolymer in water. The critical micelle concentration (cmc) was found to be 0.025% by weight. Above cmc, the polymer solution showed surface tension of 46 dyne/cm. With the 20% grafted copolymer, the cmc and surface tension were 0.05% and 65 dyne/cm, respectively. The micelle formation of the copolymers was also confirmed by fluorescence spectroscopy. Figure 2 shows the fluorescence spectra of pyrene in water in the presence of the 5% grafted copolymer. Above the cmc, the fluorescence intensity values increased substantially, indicating pyrene transferring into the hydrophobic micelle domain.

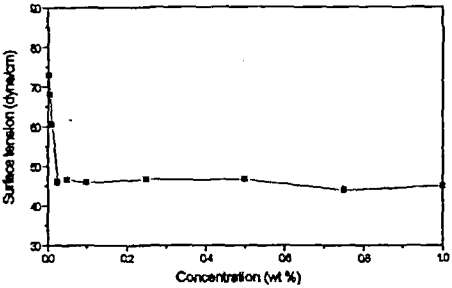


FIGURE 1 Concentration-surface tension relationship for the 5% grafted copolymer.

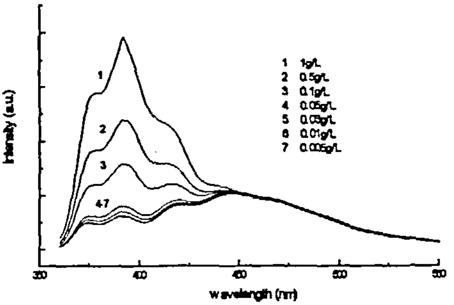


FIGURE 2 Fluorescence emission spectra (λ_{ex} = 336 nm) of pyrene in water in the presence of the 5% grafted copolymer.

Acknowledgments

This work was supported by Korea Science and Engineering Foundation (95-0502-07).

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