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Notes

Influence of the *n*-Hexoxy Group on the Properties of Fluoroalkoxyphosphazene Polymers

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Introduction

Several hundred poly(organophosphazenes) have been synthesized by the replacement of the chlorine atoms in poly(dichlorophosphazene), $(NPCl_2)_n$ (**1**), by organic groups using macromolecular nucleophilic substitution methods.[1] This approach permits the properties of a polymer to be tailored by the introduction of different substituents (or different ratios of two or more cosubstituents). An important subsection of this field revolves around polyphosphazene fluoroelastomers.[1−6] These are low-temperature, fluid-resistant elastomers that have numerous applications in aerospace, automotive, and medical technology. Recently, we discussed the properties of a range of mixed-substituent polyphosphazenes with two different fluoroalkoxy substituents.[6] In that work, we noted that the microcrystallinity detected in polymers with a high content of trifluoroethoxy side groups was not found when ∼10% of the side groups were octafluoropentoxy groups. This low level of the longer fluorinated substituent allowed elastomeric properties to emerge. In view of these results it was of interest to determine the extent to which a less expensive, nonfluorinated, long-chain cosubstituent might inhibit crystallite formation and generate elasticity.

The single-substituent polymer, poly[bis(2,2,2-trifluoroethoxy)phosphazene], $[N{=}P(OCH_2CF_3)_2]_n$, is a semicrystalline material with a T_g at −66 °C, a T_m at 242 °C, and various mesophases in the intervening temperature range. By contrast, poly[bis(*n*-hexoxy)phosphazene] is an amorphous gum with a very low glass transition temperature (∼−100 °C).[1] In the research described here we have synthesized and studied the properties of a series of cosubstituted polyphosphazenes, with different ratios of trifluoroethoxy and *n*-hexoxy substituents. The objective was to examine the structural factors that determine whether a mixed-substituent polyphosphazene will be an elastomer or a microcrystalline material.

Results and Discussion

Synthesis of Cosubstituted Polyphosphazenes 2−6. Polymers **2**−**6** were obtained via the sequential addition of sodium hexoxide and sodium trifluoroethoxide to poly(dichlorophosphazene) (**1**) (Scheme 1 and Table 1). This order of reaction was used to prevent displacement of trifluoroethoxy side groups, already linked to the polymer chain, by sodium hexoxide.[7] The labile chlorine atoms of **1** readily underwent macromolecular replacement, and the progress of the reaction was followed by ^{31}P NMR spectroscopy. ^{1}H NMR spectroscopy was used to determine the ratio of the hexoxy to trifluoroethoxy side groups by integration of the hydrogen peaks of the CH_2 units attached to the oxygen atoms (Table 1). Gel permeation chromatography (GPC) provided estimates of the molecular weights of the polymers (Table 1). These molecular weights and broad polydispersities are typical of macromolecules derived from polymer **1** when it is synthesized by the ring-opening polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$. Some of the molecular weight differences shown in Table 1 are attributed to the use of polymer **1** produced from two different batches.

Table 1. Composition and GPC Characterization Data for Polymers 2−6

polymer	% hexoxy substituent	M_n	M_w	M_w/M_n
2	1.0	110 000	356 000	3.3
3	3.5	159 000	463 000	3.0
4	5.0	126 000	304 000	2.4
5	11.0	212 000	500 000	2.4
6	21.0	250 000	675 000	2.7

Table 2. Properties of Polymers 2−6

% hexoxy substituent	mechanical properties	oxygen index	T_g	mesophase transition	T_m
1.0	semicrystalline	26	−67	61	191
3.5	semicrystalline	26	−62	50	151
5.0	semicrystalline	26	−70	53	
11.0	tough elastomer	26	−70	33	
21.0	gum elastomer	26	−76		

Properties of Polymers 2−6. The characteristics of the cosubstituted polymers are shown in Table 2. As the amount of the hexoxy substituent was increased, the polymers changed from fibrous or rigid semicrystalline materials to elastomers. The polymers with 1% to 5% hexoxy substituents were similar in appearance and physical character. With 11% incorporation of the hexoxy side groups the polymers were tough rubbery materials, and at 21% incorporation the properties were those of a polymeric gum. In addition, the swelling of the cosubstituted polymers in aliphatic organic solvents increased dramatically with increased amounts of the hexoxy substituent. The 100% hexoxy-substituted polyphosphazene is completely soluble in aliphatic solvents.

Differential scanning calorimetry (DSC) results give some insight into these property changes (Figure 1). Increased incorporation of the hexoxy substituent disrupts the crystallinity of the trifluoroethoxy-substituted system. Polymers **2** and **3**, with 1% and 3.5% hexoxy groups, showed mesophase transitions and crystalline

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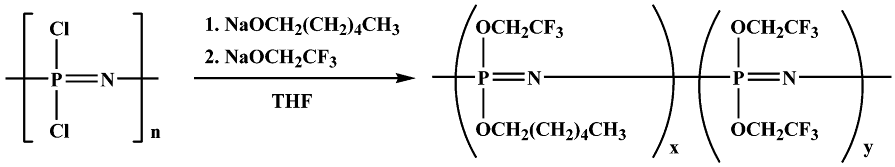
Scheme 1. Synthesis of Cosubstituted Polyphosphazenes 2−6



$$\left[\mathrm{P(Cl)_2{=}N}\right]_n \xrightarrow[\text{THF}]{\text{1. NaOCH}_2\text{(CH}_2)_4\text{CH}_3\ \ \text{2. NaOCH}_2\text{CF}_3} \left(\mathrm{P(OCH_2CF_3)(OCH_2(CH_2)_4CH_3){=}N}\right)_x\left(\mathrm{P(OCH_2CF_3)_2{=}N}\right)_y$$

melting transitions. However, polymers **4** and **5**, with 5% and 11% hexoxy units, showed some evidence of mesophase formation but no detectable crystalline melting transitions. Polymer **6**, with 21% hexoxy groups, was completely amorphous. In addition, DSC thermal transitions detected above the glass transition temperature occurred at lower temperatures as the hexoxy content increased. The glass transition temperatures (T_g) were near −70 °C for most of these polymers. Thus, no significant decrease in the T_g was found below that of poly[bis(trifluoroethoxy)phosphazene] except for polymer **6** ($T_g = -76$ °C). Thus, it requires 11% of the hexoxy substituent to reduce the T_g by only 10 °C. An interesting aspect of this polymer system is the growth of a second transition just below the mesophase transition. The new transition increases in size relative to the mesophase transition with increasing incorporation of the hexoxy side group but disappears completely at 21% incorporation of the hexoxy side group.

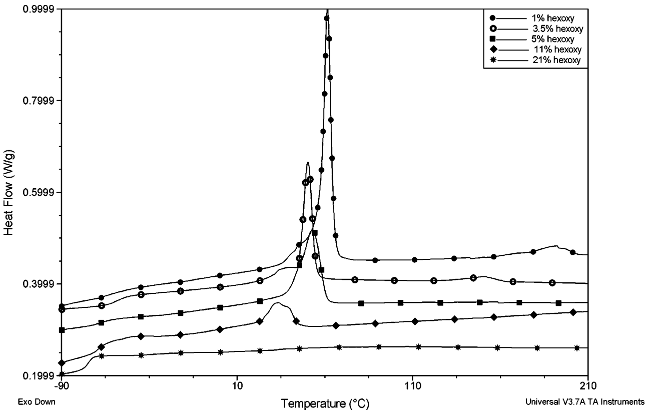


Figure 1. DSC curves for polymers **2**−**6**.

Limiting oxygen index (LOI) combustion measurements were also obtained for polymers **2**−**6**.[9] All the LOI values obtained were 26, which is also the value for poly[bis(trifluoroethoxy)phosphazene].[10] Thus, the incorporation of 1−21% of the hexoxy substituent does not increase the flammability of the materials. This is interesting because the polyphosphazene with only hexoxy substituents has an LOI value of 18. However, on a weight basis, even the 21 mol % hexoxy polymer is dominated by the influence of fluorine, which amounts to ∼37% of the weight of the material.

The percentage of hexoxy groups that allows rubbery elasticity without excessive swelling in organic solvents is in the region of 10%, and these materials may be useful as low-T_g elastomers and vibration damping materials. A wider range of compositions (10% or higher hexoxy units) may be useful as elastomers in aqueous environments, and possible applications as biomedical materials are foreseen.

Experimental Section

With the exception of the following descriptions, the techniques and materials were as described previously.[1,7] As a general procedure, polymer **1** (∼10 g) was dissolved in THF (∼1 L) in a 3 L round-bottomed flask equipped with a mechanical stirrer. Sodium hexoxide solutions were prepared by the addition of 1-hexanol (obtained from Aldrich, dried over CaH_2, and distilled before use) to slurries of NaH (95%) in THF (100−200 mL) with heating (∼50 °C) for 48 h. The sodium hexoxide solution was added to the polymer solution, and the mixture was stirred for 48 h at 25 °C. Sodium 2,2,2-trifluoroethoxide was prepared via slow addition of 2,2,2-trifluoroethanol (Halocarbon Products) to a slurry of NaH (95%) in THF (100−500 mL) with stirring for 1 h. The sodium fluoroalkoxide solution was then added to the main reaction mixture, which was then stirred for 24 h at 25 °C. The mixture was concentrated by removal of THF via a rotary evaporator, and the solids were precipitated into acidic water (pH ∼ 4). The acidity of the precipitant solution was to avoid the presence of a high-pH aqueous medium generated by excess, unreacted alkoxide. The polymers were then rinsed with triply deionized water, air-dried overnight, dissolved in THF, and again precipitated into triply deionized water. This was followed by two precipitations from THF into hexane. The products were dried for 2 days in a vacuum oven at 65 °C. Typical yields were about 60−70%.

Representative example; polymer **4**: The reagent amounts used were 1-hexanol (1.85 g, 18.1 mmol), NaH (0.41 g, 17.2 mmol), 2,2,2-trifluoroethanol (19.8 g, 197.9 mmol, NaH (4.46 g, 186 mmol), and poly(dichlorophosphazene) (10.0 g, 86.2 mmol). ^{31}P and ^{1}H NMR data; polymer **4**: ^{1}H NMR (d_6-acetone): δ = 4.5 (mlt, 4H, $OC\mathit{H}_2CF_3$), 4.0 (mlt, 4H, $OC\mathit{H}_2CH_2CH_2CH_2CH_2CH_3$), 1.7 (mlt, 4H, $OCH_2C\mathit{H}_2CH_2CH_2CH_2CH_3$), 1.4 (mlt, 12H, $OCH_2CH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$), 0.9 (mlt, 6H, $OCH_2CH_2CH_2CH_2CH_2C\mathit{H}_3$). ^{31}P NMR (d_6-acetone): δ = −6.3, −5 (singlet, broad).

Specific reagent quantities for polymers **2**, **3**, **5**, and **6**. Polymer **2**; $(NPCl_2)_n$ (**1**) 10 g, $C_6H_{13}OH$ 0.9 g, NaH (95%) 0.218 g, CF_3CH_2OH 19.8 g, NaH (95%) 5.01 g: Polymer **3**; $(NPCl_2)_n$ 10 g, $C_6H_{13}OH$ 1.8 g, NaH (95%) 0.436 g, CF_3CH_2OH 21.73 g, NaH (95%) 5.23 g: Polymer **5**; $(NPCl_2)_n$ 10 g, $C_6H_{13}OH$ 2.77 g, NaH (95%) 0.653 g, CF_3CH_2OH 19.1 g, NaH (95%) 4.57 g: Polymer **6**; $(NPCl_2)_n$ 10 g, $C_6H_{13}OH$ 4.8 g, NaH (95%) 1.09 g, CF_3CH_2OH 18 g, NaH (95%) 4.36 g.

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References and Notes

(1) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; Wiley-Interscience: Hoboken, NJ, 2003; pp 145−158, 435−436, 439−451, 656−660.
(2) Rose, S. H. *J. Polym. Sci., Ser. B* **1968**, *6*, 837−839.
(3) Tate, D. P. *J. Polym. Sci., Polym. Symp.* **1974**, *48*, 33−45.
(4) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Sci.* **1975**, *15*, 321−338.
(5) Kolich, C. H.; Klobukar, W. D.; Books, J. T. U.S. Patent 4945139, 1990.
(6) Maher, A. E; Ambler, C. M.; Powell, E. S.; Allcock, H. R. *J. Appl. Polym. Sci.*, **2004**, *92*, 2569−2576.
(7) Allcock, H. R.; Maher, A. E.; Ambler, C. M. *Macromolecules* **2003**, *36*, 5566−5572.
(8) Hindersinn, R. R. In *Fire and Polymers: Hazards Identification and Prevention*; Nelson, G. L., Ed.; ACS Symposium Series 425; American Chemical Society: Washington, DC, 1990; pp 91−92.
(9) Oxygen Index Test ASTM D 2863.
(10) An LOI value of 20 indicates that the polymer will burn in air. Values above 20 mean that atmospheres with oxygen concentrations above 20% are required to support combustion.

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