

# Polymers with Sulfur(VI)–Nitrogen–Phosphorus Backbones: Synthesis, Characterization, and Properties of Fluoroalkoxy-Substituted Poly(thionylphosphazenes)

Derek P. Gates, Andrew R. McWilliams, and Ian Manners\*

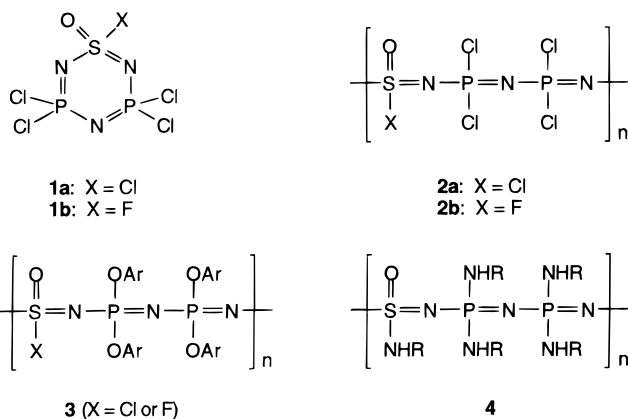
Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

Received October 23, 1997; Revised Manuscript Received March 5, 1998

**ABSTRACT:** Reaction of the halogenated poly(thionylphosphazene)  $[\text{NSOCl}(\text{NPCI}_2)_2]_n$  (**2a**), which possesses a novel S(VI)–N–P backbone, with 2, 3, and 4 equiv of  $\text{Na}[\text{OCH}_2\text{CF}_3]$ , followed by excess  $^n\text{BuNH}_2$ , afforded mixed-substituent poly[alkoxy(amino)thionylphosphazenes]  $[\text{NSO}(\text{NH}^n\text{Bu})(\text{NPR}_2)_2]_n$  (**6**) (**a**,  $R = 51\% \text{OCH}_2\text{CF}_3$ ,  $49\% \text{NH}^n\text{Bu}$ ; **b**,  $R = 76\% \text{OCH}_2\text{CF}_3$ ,  $24\% \text{NH}^n\text{Bu}$ ; **c**,  $R = 95\% \text{OCH}_2\text{CF}_3$ ,  $5\% \text{NH}^n\text{Bu}$ ) in which the polymers were regioselectively substituted with trifluoroethoxy substituents only at phosphorus and not at sulfur. The resulting moisture stable polymers were structurally characterized by  $^{31}\text{P}$ ,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectroscopy. Molecular weights were in the range  $M_w = 3.3 \times 10^4$  to  $1.4 \times 10^5$  and  $M_n = 1.9 \times 10^4$  to  $8.2 \times 10^4$  according to GPC analysis in THF versus polystyrene standards. The thermal transition behavior was investigated by DSC, glass transition temperatures ( $T_g$ 's) ranged from  $-30$  to  $-14$   $^\circ\text{C}$ , and no melt transitions were detected. Analysis of these new polymers by TGA showed that they were stable to weight loss up to ca.  $250$   $^\circ\text{C}$  under nitrogen at a heating rate of  $10$   $^\circ\text{C}/\text{min}$ .

## Introduction

Well-characterized, high molecular weight polymers based on inorganic elements are relatively rare but are attracting considerable attention because of their unique properties and potential applications.<sup>1,2</sup> We have previously reported that cyclic thionylphosphazenes **1a** and **1b** undergo facile thermal ring-opening polymerization



(ROP) to yield poly(thionylphosphazenes), **2a** and **2b**, a new class of macromolecules with a sulfur(VI)–nitrogen–phosphorus backbone.<sup>3–6</sup> These polymers can be regarded as hybrids of the well-known polyphosphazenes,  $[\text{N}=\text{PR}_2]_n$ ,<sup>7</sup> and poly(oxothiazenes),  $[\text{N}=\text{S}(\text{O})\text{R}]_n$ .<sup>8</sup> The perchlorinated ring-opened polymers, **2a** and **2b**, are moisture sensitive; however, substitution with sodium aryloxides,  $\text{Na}[\text{OAr}]$ , or primary amines,  $\text{RNH}_2$ , yields air-stable poly(thionylphosphazenes) (**3** and **4**).<sup>9,10</sup> We have shown that poly(thionylphosphazenes) show interesting differences from polyphosphazenes and poly(oxothiazenes) in terms of polymer morphology, thermal transition behavior, reactivity patterns, and the types of polymer structures accessible.<sup>11</sup> Interestingly, the reactions of **2a** and **2b** with aryloxides proceed regiose-

lectively at the phosphorus centers, leaving the sulfur–halogen bonds intact, whereas the reactions of **2a** with amines substitute both the phosphorus– and sulfur–halogen bonds.<sup>9,10</sup>

We have recently been exploring the properties and applications of poly(thionylphosphazenes) and have found that polymer **4** ( $R = ^n\text{Bu}$ ) represents an excellent matrix for phosphorescent pressure-sensing composite materials.<sup>12,13</sup> This is due, in part, to the unusual combination of low  $T_g$  ( $-17$   $^\circ\text{C}$ ), lack of crystallinity, high permeability to oxygen, and the polar structure, which helps disperse the luminophore. This provided us with motivation to develop routes to poly(thionylphosphazenes) with alkoxy side groups, which would be expected to furnish other polymers with lower  $T_g$ 's and also might be useful for sensing applications. Here we report the synthesis and characterization of the first well-characterized poly[(alkoxy)thionylphosphazenes].

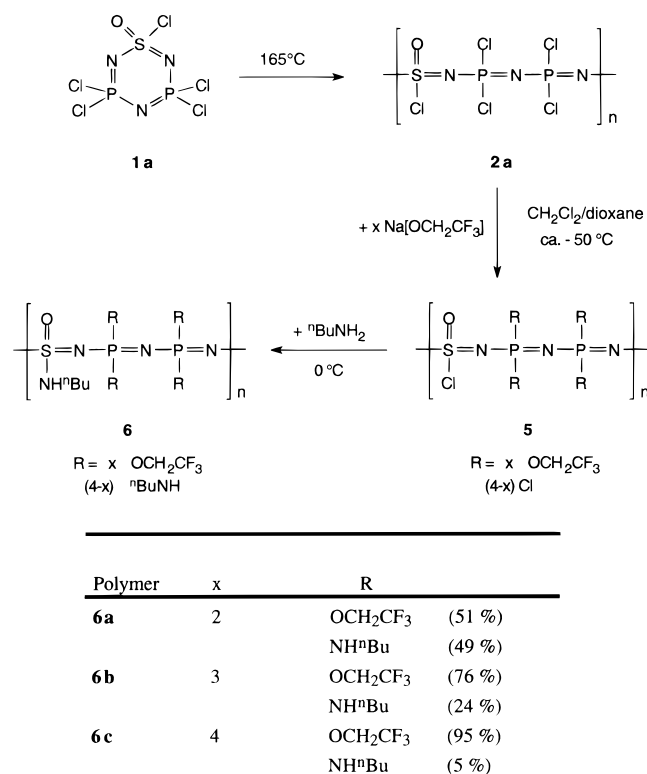
## Results and Discussion

The reactions of cyclic model compounds with nucleophiles have been invaluable in the elucidation of the substitution pathways for polyphosphazenes.<sup>14</sup> We have recently reported that when cyclic thionylphosphazenes, **1a** and **1b**, are treated with sodium alkoxides or aryloxides, substitution proceeds regioselectively, initially at phosphorus and subsequently at sulfur.<sup>15</sup> Previous studies have shown that reactions of poly(thionylphosphazene) **2a** with an excess of sodium alkoxide results in degradation of the polymer backbone.<sup>11,16</sup> Our model studies suggest that the synthesis of alkoxy-substituted poly(thionylphosphazenes) should be possible, and this paper reports the first examples of poly(thionylphosphazenes) with high loadings of trifluoroethoxide (tfe). Trifluoroethoxide was chosen as the reactive nucleophile for the substitution reactions in this study because of the low basicity of this species, which led us to expect minimization of the degree of cleavage of the S(VI)–N–P polymer backbone.

Table 1. NMR Spectral Data for Polymers 6a–c in CDCl<sub>3</sub>

	<sup>31</sup> P (ppm)	<sup>19</sup> F (ppm)	<sup>13</sup> C (ppm)	<sup>1</sup> H (ppm)
<b>6a</b>	–9.5 [P(tfe) <sub>2</sub> ] –0.2 [P(tfe)(NHBu)] 1.6 [P(NHBu) <sub>2</sub> ]	–75 (br)	13.7 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] and [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	0.9 (br, s, CH <sub>3</sub> )
			20.1 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] and [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	1.3 (br, m, CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )
			31.3 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	2.9 (br, s, PNHCH <sub>2</sub> )
			33.6 [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	3.0 (br, s, SNHCH <sub>2</sub> )
			40.5 [P(NHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) (OCH <sub>2</sub> CF <sub>3</sub> )]	3.7 (br, s, PNH)
			40.9 [P(NHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ]	4.3 (br, s, POCH <sub>2</sub> CF <sub>3</sub> )
			43.5 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	4.9 (br, s, SNH)
			63.5 [br, m, POCH <sub>2</sub> CF <sub>3</sub> ]	
			122 [br, m, POCH <sub>2</sub> CF <sub>3</sub> ]	
			13.4 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] and [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	0.9 (br, s, CH <sub>3</sub> )
			20.0 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] and [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	1.4 (br, m, CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )
			31.0 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	2.9 (br, s, PNHCH <sub>2</sub> )
			33.4 [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	3.0 (br, s, SNHCH <sub>2</sub> )
<b>6b</b>	–9.3 [P(tfe) <sub>2</sub> ] –0.2 [P(tfe)(NHBu)] 1.8 [P(NHBu) <sub>2</sub> ]	–76 (br)	13.4 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] and [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	0.9 (br, s, CH <sub>3</sub> )
			20.0 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] and [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	1.4 (br, m, CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )
			31.0 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	2.9 (br, s, PNHCH <sub>2</sub> )
			33.4 [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	3.0 (br, s, SNHCH <sub>2</sub> )
			40.9 [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	3.6 (br, s, PNH)
			43.5 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	4.3 (br, s, POCH <sub>2</sub> CF <sub>3</sub> )
			63.6 [br, m, POCH <sub>2</sub> CF <sub>3</sub> ]	5.1 (br, s, SNH)
			122.6 [q, POCH <sub>2</sub> CF <sub>3</sub> , <sup>1</sup> J <sub>CF</sub> = 280 Hz]	
			13.2 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] and [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	0.9 (br, s, CH <sub>3</sub> )
			19.8 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] and [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	1.5 (br, m, CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )
			30.9 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	3.0 (br, s, NHCH <sub>2</sub> )
			33.4 [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	4.3 (br, s, POCH <sub>2</sub> CF <sub>3</sub> )
			41.0 [PNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	5.0 (br, s, SNH)
<b>6c</b>	–9.5 [P(tfe) <sub>2</sub> ] –1 to 4 (br, PNHBU)]	–76 (br)	43.6 [SNHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ]	
			63.7 [q, POCH <sub>2</sub> CF <sub>3</sub> , <sup>2</sup> J <sub>CF</sub> = 37 Hz]	
			122.4 [q, POCH <sub>2</sub> CF <sub>3</sub> , <sup>1</sup> J <sub>CF</sub> = 278 Hz]	

Scheme 1



**Synthesis and Characterization of Poly[alkoxy(amino)thionylphosphazenes].** Hydrolytically stable poly(thionylphosphazenes) were prepared by the slow addition of 2–4 equiv of Na[OCH<sub>2</sub>CF<sub>3</sub>] in a dioxane/CH<sub>2</sub>Cl<sub>2</sub> mixture to **2a** in the same solvent system at ca. –50 °C (Scheme 1).<sup>16</sup> After warming to 0 °C and stirring for ca. 1 h, excess <sup>n</sup>BuNH<sub>2</sub> was added to substitute any remaining halogen sites, and the reaction mixture was

Table 2. Elemental Analysis for **6c**

	% C	% H	% N	% Cl
calcd	24.17	3.20	9.54	0.00
found	24.62	3.25	10.35	0.43

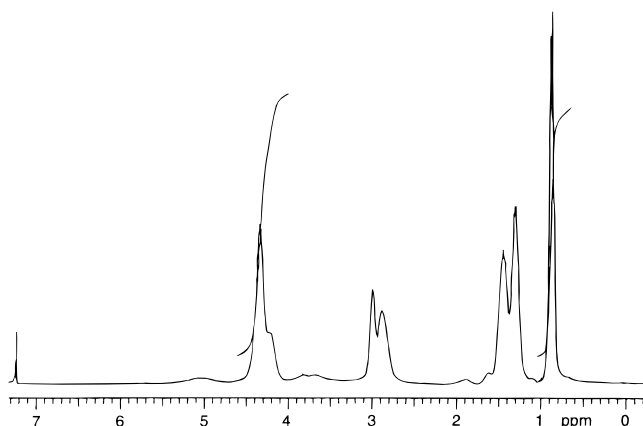
Table 3. Molecular Weight and Thermal Analysis for Polymers 6a–c

polymer	GPC <i>M<sub>w</sub></i> (PDI)	<i>T<sub>g</sub></i> (°C)
<b>6a</b>	140 000 (1.7)	–14
<b>6b</b>	33 000 (1.7)	–20
<b>6c</b>	39 000 (1.4)	–30

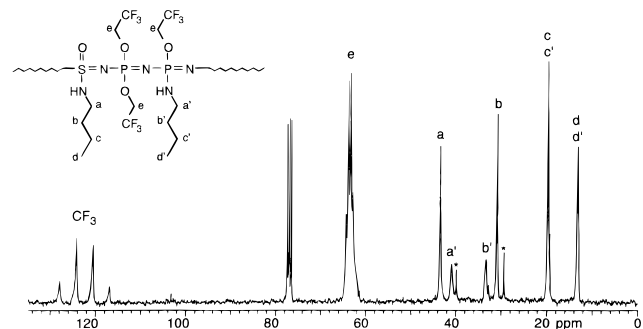
warmed to room temperature and stirred for ca. 12 h. The light-yellow gummy materials, obtained after purification by precipitation techniques, were soluble in polar organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, THF, and dioxane. The NMR spectroscopic data for polymers **6a–c** are presented in Table 1. Molecular weights were estimated by gel permeation chromatography (GPC) using polystyrene standards for calibration and are given in Table 3.

The <sup>1</sup>H NMR spectrum of **6b** is shown in Figure 1, and the relative amount of each side group present in the polymer structure was determined by integration of the methyl resonance (NHBu) at ca. 0.9 ppm, and the OCH<sub>2</sub>CF<sub>3</sub> resonance at ca. 4.3 ppm. These peaks were chosen due to their separation from the other often overlapping resonances, and the results were found to be in close agreement with those expected on the basis of the equivalents of Na[OCH<sub>2</sub>CF<sub>3</sub>] (x) added to **1a**.

The <sup>31</sup>P NMR spectra showed peaks consistent with P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (ca. –9.5 ppm), P(OCH<sub>2</sub>CF<sub>3</sub>)(NHBu) (ca. –0.2 ppm), and P(NHBu)<sub>2</sub> (ca. 1.7 ppm)<sup>17</sup> environments, and the ratio of these peaks was consistent with the trifluoroethoxy loading expected. In addition, elemental analysis on **6c** (Table 2) was in good agreement with the assigned structure. The residual chlorine detected may be due to incomplete substitution, or more



**Figure 1.** 300 MHz  $^1\text{H}$  NMR spectrum of **6b** in  $\text{CDCl}_3$ .

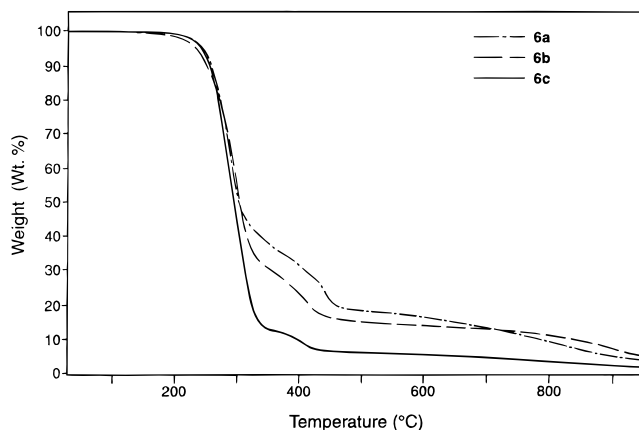


**Figure 2.** 300 MHz  $^{13}\text{C}$  NMR spectrum of **6c** in  $\text{CDCl}_3$ . The structure shown is not the repeating unit, as a  $\text{P}(\text{NHBU})$  group only occurs ca. 5% of the time. \*Unassigned.

likely some polymeric ammonium salts formed from the acid–base reaction of the  $-\text{NHBu}$  side group with  $\text{HCl}$  formed as a result of amino substitution.

To gain more information about the polymer microstructure in these mixed-substituent polymers,  $^{13}\text{C}$  NMR spectra were recorded. The spectrum of polymer **6c** is shown in Figure 2, and the high degree of trifluoroethoxy loading is clearly reflected by the intense quartets, due to the  $\text{CH}_2$  (e) and  $\text{CF}_3$  groups at ca. 63.5 and ca. 122 ppm, respectively. Only one resonance for each is observed, whereas two would be expected if both S- and P-bonded  $[\text{OCH}_2\text{CF}_3]$  groups were present. This suggests that the substitution of **2a** with  $\text{Na}[\text{OCH}_2\text{CF}_3]$  proceeds regioselectively at phosphorus and that no substitution at sulfur is observed. Further evidence for this comes from comparison of the relative intensities of the sulfur–amino methylene resonances (a and b) and the phosphorus–amino methylene resonances ( $a'$  and  $b'$ ), which were assigned by comparison with **4** ( $\text{R} = n\text{Bu}$ ).<sup>10</sup> The resonances a and b are much more intense, which is consistent with the high loading with trifluoroethoxide ( $\text{R} \approx 95\% \text{OCH}_2\text{CF}_3$ ) on phosphorus; thus only low-intensity peaks are observed for  $a'$  and  $b'$ . The ratio of sulfur- and phosphorus-substituted butylamino peaks ( $a:a'$  and  $b:b'$ ) decreases as the loading of trifluoroethoxide is decreased in polymers **2b** and **2a**.

**Thermal Transition Behavior of the Poly[alkoxy(amino)thionylphosphazenes].** To gain insight to the factors influencing the conformational flexibility of poly[alkoxy(amino)thionylphosphazenes], the thermal transition behavior of polymers **6a–c** was studied by differential scanning calorimetry (DSC). The glass transition temperatures ( $T_g$ 's) are listed in Table 3, and as with all the poly(thionylphosphazenes) synthesized to date, no melting transitions ( $T_m$ 's) were detected. This



**Figure 3.** Thermogravimetric analysis of poly[alkoxy(amino)thionylphosphazenes] (heating rate  $10\text{ }^\circ\text{C/min}$ ).

indicated that the polymers are amorphous which is consistent with the transparent nature of the materials. Upon an increase of the loading of trifluoroethoxide from **6a–c**, the  $T_g$  decreased from  $-14$  to  $-30\text{ }^\circ\text{C}$ . This is expected since the  $T_g$  for the butylamino polymer **4** ( $\text{R} = n\text{BuNH}$ ) is  $-17\text{ }^\circ\text{C}$ , and lower glass transition temperatures are observed for polyphosphazenes with trifluoroethoxy side groups,  $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$  ( $T_g = -66\text{ }^\circ\text{C}$ ),<sup>18</sup> than with butylamino side groups,  $[\text{NP}(\text{NH}^n\text{Bu})_2]_n$  ( $T_g = 8\text{ }^\circ\text{C}$ ).<sup>19</sup>

**Thermal Stability of Poly[alkoxy(amino)thionylphosphazenes].** The thermal stability of polymers **6a–c** was determined by thermogravimetric analysis (TGA), and traces are shown in Figure 3. For each polymer a substantial weight loss took place at ca.  $250\text{ }^\circ\text{C}$ , which is similar to that observed for polymers **4** with amine side groups.<sup>10</sup> As the loading of trifluoroethoxy side groups was increased, from **6a** to **6c**, this weight loss was found to be greater with ceramic yields after this first step of ca. 40% for **6a**, 35% for **6b**, and 15% for **6c**. This larger weight loss as trifluoroethoxy loading is increased might be partially attributed to the larger mass of the side chain in the trifluoroethoxy derivatives (for  $\text{CH}_2\text{CF}_3$ ,  $\text{FW} = 84.0\text{ g/mol}$ ; for  $n\text{Bu}$ ,  $\text{FW} = 57.1\text{ g/mol}$ ), as these are probably among the first fragments to be lost. A second weight loss followed at ca.  $350\text{--}400\text{ }^\circ\text{C}$ , at which point a further 20% was lost for **6a** and **6b** and 5% for **6c**. This might be attributed to the loss of the  $\text{NHBu}$  groups. At  $950\text{ }^\circ\text{C}$ , only 5–10% of the initial mass remained.

## Summary

A series of poly[fluoroalkoxy(amino)thionylphosphazenes] were prepared by reaction of the perhalogenated poly(thionylphosphazene) **2a** with  $\text{Na}[\text{OCH}_2\text{CF}_3]$  in various ratios followed by substitution with  $\text{BuNH}_2$  to ensure complete halogen substitution. The substitution was found to proceed regioselectively with reaction of the alkoxide only at phosphorus, and subsequent substitution of the remaining  $\text{P–Cl}$  and  $\text{S(O)–Cl}$  bonds with butylamine. The polymers synthesized were found to have the lowest  $T_g$ 's determined to date for hydrolytically stable poly(thionylphosphazenes), and the materials prepared were stable to weight loss up to  $250\text{ }^\circ\text{C}$ . Evaluation of these polymers as components of phosphorescent pressure-sensing composites is underway, and the results will be reported in due course.

## Experimental Section

Reagents,  $n$ -butylamine (Aldrich), and  $\text{NaH}$  (95%, Aldrich) were used without further purification; 2,2,2-trifluoroethanol

(Aldrich) was distilled from  $\text{CaSO}_4$  prior to use. The cyclic thionylphosphazene, **1a**, was prepared by literature procedures<sup>20</sup> and was purified by recrystallization from hexanes and vacuum sublimation (40–60 °C,  $1 \times 10^{-3}$  mmHg). Solvents were dried according to standard methods. All manipulations of air-sensitive reagents were performed under a nitrogen atmosphere in an Innovative Technologies glovebox or using standard Schlenk line techniques. Workup of the polymers was carried out in the air using reagent grade solvents.

<sup>31</sup>P NMR spectra (121.4 MHz) were referenced externally to 85%  $\text{H}_3\text{PO}_4$ , <sup>13</sup>C NMR spectra (75.4 MHz) were referenced to deuterated solvent, <sup>1</sup>H NMR spectra (300.0 MHz) were referenced to residual protonated solvent, <sup>19</sup>F NMR spectra (282.3 MHz) were referenced externally to  $\text{CFCl}_3/\text{CDCl}_3$ , and all were recorded on a Varian Gemini 300 spectrometer. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6K injector, Ultrastaygel columns with a pore size of  $10^3$  and  $10^5$  Å, and a Waters 410 differential refractometer. A flow rate of 1.0 mL/min was used, and samples were dissolved in a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Polystyrene standards were used for calibration purposes. The thermal behavior was studied using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a TAC7 instrument controller. Thermograms were calibrated with the melting transitions of heptane and indium and were obtained at a heating rate of 10 °C/min. The thermal stability was studied using a Perkin-Elmer TGA-7 thermal gravimetric analyzer equipped with a TAC-7 instrument controller. Thermograms were calibrated with the magnetic transitions of Nicoseal and Perkalloy and were obtained at a heating rate of 10 °C/min. Elemental analysis was performed by Quantitative Technologies Inc., Whitehouse, NJ.

**Synthesis of 2a.** Monomer **1** (2.00 g, 6.1 mmol) was polymerized and the product isolated by precipitation from  $\text{CH}_2\text{Cl}_2$  with hexanes following the standard procedure.<sup>10</sup> A yield of about 75–90% was obtained for polymer **2a**.

**General Procedure for the Substitution of 2a: Synthesis of 6c.**  $\text{Na}[\text{OCH}_2\text{CF}_3]$  was prepared from the reaction of  $\text{HOCH}_2\text{CF}_3$  (1.7 mL, 23 mmol) with  $\text{NaH}$  (0.56 g, 23 mmol) in dioxane (ca. 150 mL) and  $\text{CH}_2\text{Cl}_2$  (ca. 75 mL). The  $\text{Na}[\text{OCH}_2\text{CF}_3]$  solution was added dropwise over 7 h to a slush of **2a** (6.1 mmol) in dioxane (ca. 100 mL) and  $\text{CH}_2\text{Cl}_2$  (ca. 250 mL), and the reaction temperature was maintained between –50 and –70 °C. After the addition was complete, the reaction mixture was warmed to 0 °C, and a fine white precipitate was observed.  $^n\text{BuNH}_2$  (3.0 mL, 30 mmol) was then added and the reaction mixture was allowed to warm to ambient temperature and stirred for an additional 12 h. The white precipitate was filtered off, and the solvent was removed from the filtrate, leaving a yellow gummy material. The polymeric product was purified by redissolution in dioxane (ca. 10 mL), dropwise addition into water (three times), redissolution in  $\text{CH}_2\text{Cl}_2$  (ca. 10 mL), and precipitation into hexanes (two times). For **6c**: yield = 0.99 g (26%). For **6a**: yield = 0.90 g (26%). For **6b**: yield = 0.59 g (16%).

**Acknowledgment.** This work was funded by the Ontario Centre for Materials Research (OCMR). D.G. would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Graduate Fellowship (1993–97), A.M. also thanks NSERC for a Graduate Fellowship (1996–1998) and I.M. is grateful

to the Alfred P. Sloan Foundation for a Research Fellowship (1994–98), NSERC for an E. W. R. Steacie Fellowship (1997–1998), and the University of Toronto for a McLean Fellowship (1997). We also thank Tim Peckham and Dr. Xiao-Hua Liu for help with the DSC studies.

## References and Notes

- (1) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Toronto, 1992.
- (2) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602.
- (3) Sulfur(IV)–nitrogen–phosphorus polymers were first prepared in 1990, but these materials are rather sensitive to hydrolysis: (a) Dodge, J. A.; Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1990**, *112*, 1268. (b) Allcock, H. R.; Dodge, J. A.; Manners, I. *Macromolecules* **1993**, *26*, 11.
- (4) (a) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044. (b) Gates, D. P.; Edwards, M.; Liable-Sands, L. M.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **1998**, *120*, 3249.
- (5) Liang, M.; Manners, I. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 613.
- (6) Jaeger, R.; Lagowski, J. B.; Manners, I.; Vancso, G. J. *Macromolecules* **1995**, *28*, 539.
- (7) (a) Allcock, H. R. *Chem. Eng. News* **1985**, *63* (11), 22. (b) Allcock, H. R. *J. Inorg. Organomet. Polym.* **1992**, *2*, 197. (c) *Inorganic and Organometallic Polymers*; Zeldin, M.; Wynne, K. J.; Allcock, H. R., Eds.; American Chemical Society: Washington, 1988; Chapters, 19–25. (d) Allcock, H. R.; Krause, W. E. *Macromolecules* **1997**, *30*, 5683. (e) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1996**, *29*, 7740. (f) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541. (g) Montague, R. A.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1990**, *112*, 6721.
- (8) (a) Roy, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 1530. (b) Roy, A. K.; Burns, G. T.; Lie, G. C.; Grigoros, S. *J. Am. Chem. Soc.* **1993**, *115*, 2604.
- (9) Ni, Y.; Stammer, A.; Liang, M.; Massey, J.; Vancso, G. J.; Manners, I. *Macromolecules* **1992**, *25*, 7119.
- (10) Ni, Y.; Park, P.; Liang, M.; Massey, J.; Waddling, C.; Manners, I. *Macromolecules* **1996**, *29*, 3401.
- (11) Manners, I. *Coord. Chem. Rev.* **1994**, *137*, 109.
- (12) (a) Pang, Z.; Gu, X.; Yekta, A.; Masoumi, Z.; Coll, J. B.; Winnik, M. A.; Manners, I. *Adv. Mater.* **1996**, *8*, 768. (b) Gates, D. P.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1997**, 2525.
- (13) Masoumi, Z.; Stoeva, V.; Yekta, A.; Pang, Z.; Manners, I.; Winnik, M. A. *Chem. Phys. Lett.* **1996**, *261*, 551.
- (14) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
- (15) Gates, D. P.; Park, P.; Liang, M.; Edwards, M.; Angelakos, C.; Liable-Sands, L. M.; Rheingold, A. L.; Manners, I. *Inorg. Chem.* **1996**, *35*, 4301.
- (16) Attempts to produce a polymer with 100% loading of trifluorothiooxide via the reaction of **2a** with 5 equiv of  $\text{Na}[\text{OCH}_2\text{CF}_3]$  led to backbone cleavage, and the product detected by <sup>31</sup>P NMR was the six-membered ring  $[\text{NSO}(\text{OCH}_2\text{CF}_3)\{\text{NP}(\text{OCH}_2\text{CF}_3)_2\}_2]$  (see ref 15).
- (17) The <sup>31</sup>P NMR spectrum for poly[(butylamino)thionylphosphazene], **4** (R = <sup>*n*</sup>Bu), exhibits two peaks at 1.6 and 1.9 ppm, which have been attributed to the atactic nature of the polymer structure. See ref 10.
- (18) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315.
- (19) Allcock, H. R.; Cook, W. J.; Mack, D. P. *Inorg. Chem.* **1972**, *11*, 2584.
- (20) Suzuki, D.; Akagi, H.; Matsumura, K. *Synth. Commun.* **1983**, *369*.

MA971562E