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Synthesis, Glass Transition Behavior, and Solution Characterization of Poly[(aryloxy)thionylphosphazenes] with Halogen Substituents at Sulfur

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ABSTRACT: The cyclic thionylphosphazenes $[(NSOX)(NPCl_2)_2]$ (**1a**, X = Cl; **1b**, X = F) undergo thermal ring-opening polymerization to yield the hydrolytically sensitive, elastomeric poly(thionylphosphazenes) $[(NSOX)(NPCl_2)_2]_n$ (**2a**, X = Cl, **2b**, X = F). The reaction of these polymers with several different sodium aryloxides Na[OAr] yielded the moisture-stable poly[(aryloxy)thionylphosphazenes] $[(NSOX)(NP(OAr)_2)_2]_n$ (**3a**–**6a**, X = Cl; **3b** and **4b**, X = F) in which the sulfur–halogen bonds are retained. These new polymers were structurally characterized by ^{31}P, ^{1}H, ^{13}C, and (where appropriate) ^{19}F NMR spectroscopy, IR spectroscopy, and elemental analysis. Molecular weights of the aryloxy-substituted polymers **3a**–**6a**, **3b**, and **4b** were estimated by gel permeation chromatography and in one case (**4a**) by light scattering. The glass transition behavior of the polymers was investigated by differential scanning calorimetry. Glass transition temperatures of the poly(thionylphosphazenes) were in the range −56 to +55 °C. The solution behavior of $[(NSOX)(NP(OAr)_2)_2]_n$ (**4a**, X = Cl, OAr = OC_6H_4Ph-*p*) was investigated by low-angle laser light scattering and dynamic light scattering which yielded an absolute value of $\bar{M}_w$ = 64 000 and an effective hydrodynamic radius, $R_{h,eff}$, of 5.9 nm in THF at 22 °C.

Introduction

Polymers which contain inorganic elements as part of the main-chain structure are of considerable interest because of their unusual properties and potential applications.[1-8] As part of our program to develop routes to new classes of inorganic[3] and organometallic[4] macromolecules, we recently reported the synthesis of the first examples of poly(thionylphosphazenes) which possess backbones composed of sulfur(VI), nitrogen, and phosphorus atoms.[3a] These polymers represent a further class of polyheterophosphazenes[5-7] which are polymers formally derived from the well-studied "classical" polyphosphazenes, $[N{=}PR_2]_n$,[8] via the replacement of skeletal phosphorus atoms by atoms of another main-group element or transition metal.

The first, well-characterized polymers with sulfur–nitrogen–phosphorus backbones, poly(thiophosphazenes), were reported in 1990.[6] These species contained skeletal three-coordinate sulfur(IV) atoms in the polymer main chain. However, the initial polymers prepared were found to be sensitive to moisture unless very bulky side group substituents such as *o*-phenylphenoxy were present.[6] Bearing this in mind, we investigated the synthesis of polymers containing skeletal four-coordinate sulfur atoms in the +6 oxidation state for two main reasons. First, such moieties are present in very stable organic polymers such as poly(ether sulfones).[9] And second, small molecule species containing rings of sulfur(VI), nitrogen, and phosphorus atoms, which we have termed cyclic thionylphosphazenes, have been well-studied and the ring skeleton present in these species has generally been found to be stable and robust.[10]

In this paper we describe in detail the synthesis and properties of a variety of poly(thionylphosphazenes) with the main emphasis on species with aryloxy groups bonded to phosphorus and halogen groups attached to sulfur.

Experimental Section

Materials and Equipment. Phosphorus pentachloride (98%), sulfamide (99%), hexamethyldisilazane (98%), silver difluoride (98%), sodium, and the phenols were obtained from Aldrich and were used as received except in the case of the latter which were sublimed or distilled under reduced pressure before use. The cyclic thionylphosphazenes $[(NSOX)(NPCl_2)_2]$, X = Cl[11] or F,[12] were prepared by literature procedures and were purified by high-vacuum sublimation (40 °C, 0.05 mmHg). All synthetic experiments were performed under a nitrogen atmosphere by using a Vacuum Atmospheres glovebox or standard Schlenk line techniques. Solvents were dried according to standard methods.

The $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a Varian XL-300 or a XL-400 spectrometer operating at 121.4 and 161.9 MHz, respectively. The ^{1}H and ^{13}C NMR spectra were obtained with a Varian XR-200 spectrometer operating at 200.0 and 50.3 MHz, respectively. Chemical shifts are reported relative to $SiMe_4$ (^{1}H or ^{13}C), $CFCl_3$ (^{19}F), or to external H_3PO_4/D_2O (^{31}P). Fourier transform infrared spectra were obtained with the use of a Nicolet 5-DX spectrometer from samples of the polymers cast as thin films on KBr disks. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6K injector, Ultrastyragel columns with a pore size between 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. A Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a TAC 7 instrument controller was used to study the thermal behavior. The thermograms were calibrated with the melting transitions of decane and indium and were obtained at a heating rate of 10 °C/min. Elemental analyses were performed either by Canadian Microanalytical Service Ltd., Delta, BC, Canada, or by Galbraith Laboratories, Knoxville, TN.

Static light scattering experiments were carried out by utilizing the low-angle laser light scattering (LALLS) technique, using a Chromatix KMX-6 instrument at a wavelength of 632.8 nm and a scattering angle of 6–7°. Measurements were carried out at room temperature (22 °C) using a metal cell 4.93 mm in length. Each solution was filtered a minimum of four times through a Sartorius regenerated cellulose membrane filter with 0.2-μm average pore size before injection into the sample cell. The value of the refractive index increment d*n*/d*c* of the polymer solutions was obtained by using a Chromatix KMX-16 differential refractometer operating at a wavelength of 632.8 nm. The instrument was calibrated with NaCl solutions.

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Dynamic light scattering (DLS) measurements were performed by utilizing the photon correlation spectroscopy (PCS) technique.[13] The experimental setup includes a Brookhaven laser light scattering goniometer system, a Brookhaven BI 2030-AT correlator, and a Lexel Excel 3000 Ar-ion laser. DLS experiments were carried out at a wavelength of 514.5 nm at room temperature (22 °C), using scattering angles of both 60 and 90°. The samples were filtered in the same manner as described for the LALLS experiments.

Prior to LALLS and DLS measurements the UV–vis spectrum of the polymer was checked for possible absorption at the two wavelengths used in the light-scattering experiments. In the UV–vis spectrum two unresolved peaks were obtained centered at 252 and 272 nm, respectively. The 632.8 and 514.5-nm wavelengths utilized in LALLS and DLS were well remote from the characteristic absorption of the polymer.

Synthesis of $[(NSOCl)(NPCl_2)_2]_n$ (2a). The cyclic monomer $(NSOCl)(NPCl_2)_2$ (2.00 g, 6.07 mmol) was polymerized in an evacuated, sealed Pyrex tube at 165 °C for 4 h. The tube was rocked continuously during polymerization to ensure agitation of the contents. A marked increase in viscosity was observed as the molten material changed from colorless to light yellow. The polymeric material was dissolved in CH_2Cl_2 (10 mL) and transferred via cannula to a stirred solution of hexanes (100 mL). The resulting suspension was allowed to stir for 20 min, and the mother liquors were then decanted. The colorless, adhesive, gummy product was washed with diethyl ether and was then dried in vacuo. The yield was 1.55 g (78%).

Synthesis of $[(NSOF)(NPCl_2)_2]_n$ (2b). The same procedure described for **2a** was followed except that a higher polymerization temperature for **1b** (180 °C) was employed over a period of 4 h. Using 0.70 g of **1b**, polymer **2b** was obtained as a colorless gum. Yield: 0.49 g (70%).

General Procedure for the Preparation of $[(NSOCl)(NP(OAr)_2)_2]_n$ (3a–6a). A similar procedure was used for the synthesis of all of the polymers **3a–6a**, and a general procedure is therefore given with the synthesis of **4a** as the example.

Sodium *p*-phenylphenoxide was prepared via the reaction of excess sodium metal with *p*-phenylphenol in dioxane followed by an overnight reflux. The solution was filtered to remove excess sodium and the solvent was removed to yield the product as a white powder which was subsequently stored in the glovebox. The other sodium aryloxides were prepared similarly.[14]

To a stirred solution of polymer **2a** (0.81 g, 2.4 mmol) in 50 mL of THF at 25 °C was added slowly a solution of sodium *p*-phenylphenoxide (3.78 g, 19.7 mmol) in 200 mL of dioxane via cannula. A white precipitate formed immediately and the reaction was allowed to proceed for 12 h at room temperature. The solution was filtered through a frit (which was washed with an additional 100 mL of CH_2Cl_2), and the filtrate was concentrated to about one-fourth its volume under vacuum. The polymeric product was obtained by dropwise addition into water (twice) and hexane (twice) before drying in vacuo. Yield of **4a**: 1.40 g (66%). The yields of polymers **3a**, **5a**, and **6a** were 55–70%.

Polymers **3a** and **6a** were obtained as colorless gums whereas **4a** and **5a** were white powders. All of the polymers **3a–6a** appear indefinitely stable to the atmosphere, and no decomposition or molecular weight decline was detected by ^{31}P NMR or GPC after several months exposure to air. In addition, no hydrolysis was detected in solution by ^{31}P NMR or GPC after 1 month when a sample of **3a** was dissolved in a solution of 10% water in dioxane.

General Procedure for the Preparation of $[(NSOF)(NP(OAr)_2)_2]_n$ (3b and 4b). The procedure described for **3a–6a** was followed using **2b** instead of **2a** to give **3b** and **4b** in 55–65% yields.

Polymer **3b** was obtained as a colorless gum, and **4b**, as a white powder. Both **3b** and **4b** appear indefinitely stable to the atmosphere. In addition, no hydrolysis was detected in solution by ^{31}P NMR or GPC after 1 month when a sample of **3b** was dissolved in a solution of 10% water in dioxane.

Light-Scattering Measurements for $[(NSOX)(NP(OAr)_2)_2]_n$ (X = Cl, OAr = OC_6H_4Ph-*p*) (4a). Static light scattering experiments in the low-angle regime were used to determine the weight-average molecular weight $\bar{M}_w$ and the second virial coefficient A_2 of a sample of **4a**. The values of $\bar{M}_w$ were obtained from the Rayleigh–Debye relationship, in the limit of low scattering angles, θ:[15]

$$Kc/R_\theta = 1/\bar{M}_w + 2A_2c \qquad (1)$$

where c is the concentration of the polymer, R_θ is the measured Rayleigh ratio, A_2 is the second virial coefficient, and K is an optical constant defined as

$$K = [4\pi^2n^2/(N_0\lambda_0^4)](dn/dc)^2 \qquad (2)$$

where n is the refractive index of the solvent, λ_0 is the wavelength of the laser light in vacuum, N_0 is the Avogadro number, and dn/dc is the refractive index increment of the polymer solution. Refractive index increment measurements were performed at six different concentrations in THF at 22 °C, and a value of $dn/dc = 0.208 \pm 0.001$ mL/g was obtained.

Translational diffusion coefficients, hydrodynamic coil size, and friction for polymer **4a** were studied by dynamic light scattering (DLS) measurements. The time autocorrelation function of the scattered light obtained in DLS experiments was analyzed in terms of cumulants.[16] The value of the first cumulant, Γ, was determined from a cumulant expansion series truncated at the quartic term. The magnitude of Γ at infinite dilution is related to the *z*-average translational diffusion coefficient of the macomolecular center-of-mass $\langle D\rangle_{z,0}$ which, in turn, can be used to calculate the average Stokes effective hydrodynamic radius, $\bar{R}_{h,eff}$ through the following relationships:

$$\lim_{c\to 0} (\Gamma/\mathbf{q}) = \langle D\rangle_{z,0} = kT/(6\pi\eta\bar{R}_{h,eff}) \qquad (3)$$

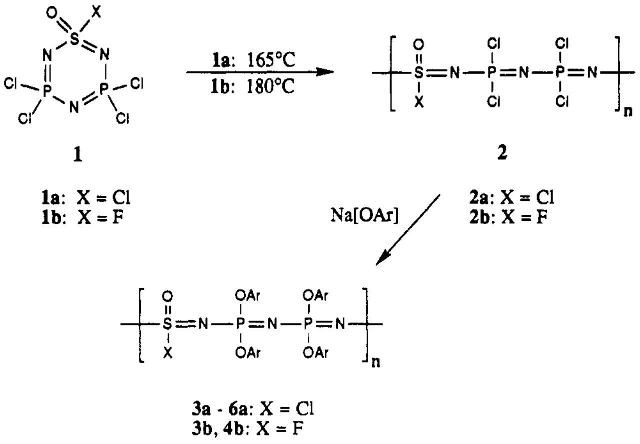
where $\mathbf{q}$ is the scattering vector defined as $|\mathbf{q}| = (4\pi n/\lambda_0)\sin(\theta/2)$, k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent.

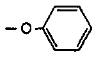
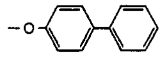
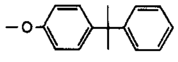
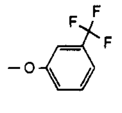
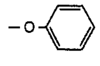
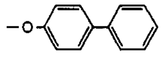
Results and Discussion

Synthesis and Properties of $(NSOCl)(NPCl_2)_2$ (1a). The cyclic thionylphosphazene $(NSOCl)(NPCl_2)_2$ (**1a**) was first prepared in 1972 by two different low-yield routes. van de Grampel and co-workers reported the synthesis of small quantities of this species via the vacuum thermolysis of $Cl_3P{=}N{-}PCl_2{=}N{-}SO_2Cl$.[17] In the same year, Glemser et al. reported a 3 + 3 cyclocondensation procedure to prepare **1a** which involved the reaction of sulfamide $SO_2(NH_2)_2$ with the salt $[Cl_3P{=}N{=}PCl_3][PCl_6]$ (yield 12%).[18] A much improved route to **1a** has since been described by Suzuki et al. which starts with sulfamide and PCl_5 and involves a 5 + 1 cyclocondensation reaction of $(Cl_3P{=}N)_2SO_2$ with $HN(SiMe_3)_2$ as the key ring-forming step.[11] Overall yields of **1a** using this procedure are 40–75%, and this method was therefore used for the work described in this paper. The cyclic thionylphosphazene **1a** is a white, sublimable, crystalline material which is only slightly sensitive to moisture in the solid state and can be easily handled in air. In the past 20 years the chemistry of this species has been studied quite extensively, particularly with respect to nucleophilic substitution reactions.[10] However, prior to our preliminary communication in 1991,[3a] no attempts to polymerize **1a** via ring-opening methods had been reported.

Thermal Ring-Opening Polymerization of $(NSOCl)(NPCl_2)_2$ (1a). When a pure sample of the cyclic thionylphosphazene **1a** was heated at 165 °C for 4 h in an evacuated, sealed Pyrex tube, a gradual increase in viscosity was observed. After this period the tube contents were virtually immobile. The reaction products dissolved slowly but completely in polar sovents such as CH_2Cl_2 or dioxane. However, continued heating at 165 °C or the use of more elevated temperatures afforded a polymeric product which swelled but would not dissolve in the same solvents. This behavior suggested that the product was cross-linked. Similar observations have been noted for the thermal ring-opening polymerization of the "classical" cyclic phosphazene $[NPCl_2]_3$.[1c,8b] Analysis of solutions of the product

Scheme I



	X	OAr
3a	Cl	
4a	Cl	
5a	Cl	
6a	Cl	
3b	F	
4b	F	

mixture in dioxane by ^{31}P NMR showed the presence of unreacted cyclic thionylphosphazene monomer (ca. 20%, δ = 26.5 ppm) and a new singlet resonance at −10.0 ppm assigned to the polymer **2a**. Similar shifts to high field have been noted in the ^{31}P NMR spectra for the polymerization of $[NPCl_2]_3$, the cyclocarbophosphazene $(NCCl)(NPCl_2)_2$, and the cyclic thiophosphazene $(NSCl)(NPCl_2)_2$.[5,6] Polymer **2a** can be isolated as a pale yellow, hydrolytically sensitive gum by precipitation from CH_2Cl_2 into dry hexanes. Although the IR spectrum of **2a** showed bands which could be assigned to S=O, P=N, and S=N vibrations, the characterization of hydrolytically stable derivatives provided the most convincing evidence for the proposed structure.

Synthesis and Structural Characterization of the Poly[(aryloxy)thionylphosphazenes] $[(NSOCl)(NP(OAr)_2)_2]_n$ (3a–6a). In order to prepare hydrolytically stable derivatives of polymer **2a** the reactions of this species with sodium aryloxides possessing different substituents attached to the aromatic nucleus were studied. These reactions proceeded to completion within 24 h at room temperature to yield colorless gums (**3a** and **6a**) or white powders (**4a** and **5a**) (Scheme I). The polymer products are soluble in polar organic solvents such as CH_2Cl_2, THF, or dioxane and were structurally characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy (Table I), elemental analysis (Table II), and IR spectroscopy (Table III). The molecular weights of the aryloxy-substituted polymers were estimated by gel permeation chromatography (GPC) using polystyrene standards for column calibration (Table II), and in one case (**4a**) an absolute value of the weight-average molecular weight ($\bar{M}_w$) was determined by static light scattering. The glass transition behavior of the polymers was investigated by differential scanning calorimetry (DSC) (Table II).

Characterization of polymers **3a–6a** indicated that the reaction of **2a** with sodium aryloxides involved replacement of the chlorine atoms only at phosphorus and that the sulfur–halogen bonds were retained (Scheme I). The assignment of a structure which implied regiospecific replacement of the halogen atoms was made after considering several pieces of evidence. First, the elemental analysis data (C, H, N, and Cl) for the polymers **3a–6a** were consistent with the presence of a single chlorine atom per repeat unit as a side group substituent. Second, the ^{31}P NMR spectra of **3a–6a** comprised single, singlet resonances significantly high field shifted by ca. 10 ppm compared to that of **2a** (δ = −10.0 ppm). This indicated that the phosphorus nuclei in **3a–6a** were equivalent and that substitution of the chlorine atoms at phosphorus had occurred. Third, the ^{13}C NMR spectra of **3a–6a** indicated the presence of a single environment for the aryloxy side groups. This is illustrated for polymer **4a** in Figure 1 where one set of ^{13}C NMR resonances for the *p*-phenylphenoxy side groups is evident. By contrast, poly(carbophosphazenes) with aryloxy substituents at both carbon and phosphorus show two sets of ^{13}C NMR aryloxy group resonances.[5]

The regiospecific substitution pattern detected for polymer **2a** was also found to occur when the cyclic monomer **1a** was treated with sodium aryloxides. For example, treatment of **1a** with sodium phenoxide, Na[OPh], at room temperature yielded $(NSOCl)[NP(OPh)_2]_2$.[19] Remarkably, the regiospecific nucleophilic substitution detected for **2a** involving the replacement of the chlorine atoms bonded to phosphorus rather than those at sulfur is exactly opposite to that detected for the sulfur(IV) analogues, poly(thiophosphazenes), where nucleophilic substitution takes place preferentially at the sulfur atom.[6] This can be attributed to the relatively low reactivity of S^{VI}–Cl bonds to nucleophilic halogen replacement compared to P–Cl bonds. By contrast, S^{IV}–Cl bonds are more reactive than the latter. In addition, the regiospecific substitution behavior of **2a** with aryloxy nucleophiles contrasts with the behavior of the classical polyphosphazene $[NPCl_2]_n$ under similar conditions. Thus, in general, when the latter is reacted with sodium aryloxides, *all* of the halogen side group substituents are replaced to give the poly[(aryloxy)phosphazenes] $[NP(OAr)_2]_n$.[8c,20]

Other noteworthy features of the characterization data for **3a–6a** included the IR spectra which showed characteristic absorptions for P=N skeletal vibrations and S=O, P—O, and C—O side group vibrations (Table III).[17] However, the skeletal S=N vibrations, which were readily assigned in the cases of **2a** and **2b**, were obscured by vibrations associated with the aryloxy side groups. Gel permeation chromatography yielded estimated weight-average molecular weights ($\bar{M}_w$) of 38 000–140 000 relative to polystyrene standards, and the measured polydispersities of 1.2–2.7 indicated that the molecular weight distributions were quite narrow. The absolute value of $\bar{M}_w$ for **4a** determined by light scattering was found to be 64 000 (see below).

All of the polymers **3a–6a** appear stable to hydrolysis both in the solid state and in solution. For example, no hydrolysis or molecular weight decline was detected by ^{31}P NMR or GPC in solution after 1 month when a sample of **3a** was dissolved in a solution of 10% water in dioxane.

Table I
NMR Spectral Data for Polymers 2a–6a and 2b–4b

polymer	^{31}P, ppm[a]	^{13}C, ppm[b]	^{1}H, ppm[b]	^{19}F, ppm[b]
2a	−10.0			
2b	−8.6			72.3
3a	−21.5	121.1 (*o*-Ph), 125.2 (*p*-Ph), 129.5 (*m*-Ph), 150.6 (ipso Ph), all s	7.0 (br, m)	
4a	−20.9	121.3 (*o*-Ph), 126.9 (*m*-Ph′), 127.2 (*p*-Ph′), 128.0 (*o*-Ph′), 128.8 (*m*-Ph), 138.1 (*p*-Ph), 139.9 (ipso Ph′), 149.9 (ipso Ph), all s[c]	7.1 (m)	
5a	−21.0	30.6 (Me), 42.3 (CMe$_2$), 120.7 (*o*-Ph), 125.7 (*p*-Ph′), 126.7 (*m*-Ph), 127.8 (*o*-Ph′), 128.1 (*m*-Ph′), 147.5 (*p*-Ph), 148.4 (ipso Ph), 150.5 (ipso Ph′), all s[c]	1.3 (s), 6.7 (m), 7.1 (m)	
6a	−21.0	117.8 (6-Ph), 122.7 (2-Ph), 123.2 (q, $^1J_{CF}$ = 273.7 Hz, CF$_3$), 124.0 (4-Ph), 130.5 (5-Ph), 132.4 (q, $^2J_{CF}$ = 33.4 Hz, 3-Ph), 150.1 (ipso Ph)	7.1 (m)	
3b	−20.3	121.3 (*o*-Ph), 125.5 (*p*-Ph), 129.5 (*m*-Ph), 150.6 (ipso Ph), all s	7.0 (m)	75.2
4b	−19.5	121.9 (*o*-Ph), 127.5 (*m*-Ph′), 127.7 (*p*-Ph′), 128.4 (*o*-Ph′), 129.4 (*m*-Ph), 138.7 (*p*-Ph), 140.5 (ipso Ph), 150.8 (ipso Ph′), all s[c]	7.1 (m)	75.2

[a] In CH$_2$Cl$_2$. [b] In CDCl$_3$. [c] Ph refers to the phenyl ring closest to the polymer backbone, Ph′ refers to the phenyl ring furthest from the polymer backbone.

Table II
Analytical and Glass Transition Data for Polymers 2a–6a and 2b–4b

polymers	GPC M_w, M_n	elem anal. calc/found		T_g, °C
2a				−46
2b				−56
3a	5.8 × 10^4, 4.0 × 10^4	C	51.48/51.70	10
		H	3.60/3.61	
		N	7.50/7.46	
		Cl	6.33/5.68	
4a	1.4 × 10^5, 5.1 × 10^4	C	66.70/66.38	55
		H	4.20/4.28	
		N	4.86/4.80	
		Cl	4.10/3.78	
5a	1.1 × 10^5, 6.3 × 10^4	C	69.80/67.47	43
		H	5.86/4.79	
		N	4.07/3.56	
		Cl	3.43/3.78	
6a	1.8 × 10^5, 1.5 × 10^5	C	40.43/40.26	−25
		H	1.94/2.03	
		N	5.05/5.00	
		Cl	4.26/5.09	
3b	3.8 × 10^4, 2.5 × 10^4	C	53.04/52.77	−15
		H	3.70/3.77	
		N	7.73/7.66	
		F	3.49/3.49	
4b	9.0 × 10^4, 5.8 × 10^4	C	68.00/67.40	48
		H	3.81/4.48	
		N	4.96/4.99	

Table III
Infrared Data for Polymers 2a–6a and 2b–4b

	selected IR bands (film), cm^{-1}
2a	1307 (vs, ν(S=O)), 1193 (vs, br, ν(P=N)), 1136 (vs, br, ν(S=O)), 733 (s, ν(S=N))
2b	1332 (vs, ν(S=O)), 1197 (vs, br, ν(P=N)), 1150 (vs, br, ν(S=O)), 820 (s, ν(S=N))
3a	1300 (s, ν(S=O)), 1194 (vs, br, ν(P=N)), 1161 (vs, ν(C—O)), 1137 (sh, ν(S=O)), 952 (vs, ν(P—O))
4a	1307 (s, ν(S=O)), 1203 (vs, br, ν(P=N)), 1165 (vs, br, ν(C—O)), 1148 (s, ν(S=O)), 967 (s, ν(P—O))
5a	1306 (s, ν(S=O)), 1203 (vs, br, ν(P=N)), 1168 (vs, br, ν(C—O)), 1149 (s, ν(S=O)), 971 (s, ν(P—O))
6a	1310 (s, ν(S=O)), 1191 (vs, br, ν(P=N)), 1168 (vs, br, ν(C—O)), 1144 (s, ν(S=O)), 970 (s, ν(P—O))
3b	1326 (s, ν(S=O)), 1197 (vs, br, ν(P=N)), 1187 (vs, ν(C—O)), 1160 (sh, ν(S=O)), 961 (vs, ν(P—O))
4b	1327 (s, ν(S=O)), 1199 (vs, br, ν(P=N)), 1186 (vs, ν(C—O)), 1166 (sh, ν(S=O)), 965 (vs, ν(P—O))

Synthesis and Thermal Ring-Opening Polymerization of (NSOF)(NPCl$_2$)$_2$ (1b). As the sulfur–chlorine bonds were found to remain intact in the reaction of **2a** with sodium aryloxides, we therefore investigated the polymerization of the fluorinated cyclic thionylphosphazene (NSOF)(NPCl$_2$)$_2$ (**1b**) with the aim of preparing stable poly(thionylphosphazenes) with fluorine atoms directly attached to the polymer backbone. Compound **1b** possesses physical properties similar to those of **1a** and is accessible via the reaction of the latter with AgF$_2$.[12] Compound **1b** was found to polymerize in the melt over 4 h at 180 °C, a slightly higher temperature than for **1a**. Polymer **2b** was isolated as a colorless, hydrolytically sensitive gum by a method similar to that used to isolate **2a**. The ^{31}P NMR spectrum of **2b** consisted of a singlet resonance at −8.6 ppm. The ^{19}F NMR spectrum of **2b** showed a singlet resonance at 72.3 ppm which is slightly shifted to low field compared to the triplet resonance of **1b** (δ = 75.9 ppm, $^3J_{PF}$ = 3 Hz). Additional characterization of **2b** was achieved by IR spectroscopy, which yielded spectra that showed strong absorptions characteristic[12] of S=O, S=N, and P=N vibrations (Table III).

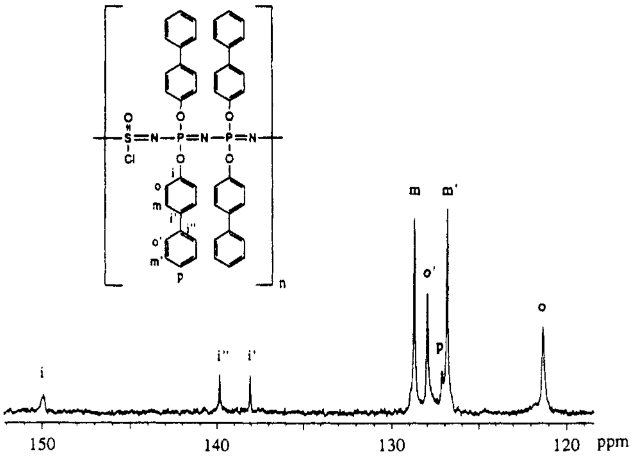


Figure 1. ^{13}C NMR spectrum of polymer **4a** (in CDCl$_3$).

Synthesis and Structural Characterization of the Fluorinated Poly[(aryloxy)thionylphosphazenes] [(NSOF)(NP(OAr)$_2$)$_2$]$_n$ (3b and 4b). In order to prepare moisture-stable products polymer **2b** was treated with sodium aryloxides in an manner analogous to that for **2a**. These reactions were carried out with sodium phenoxide and sodium *p*-phenylphenoxide (dioxane, 25 °C, 48 h) and yielded **3b** as a hydrolytically stable gum and **4b** as a white powder, respectively. Polymers **3b** and **4b** were characterized by multinuclear NMR techniques in a way similar to that of **3a**–**6a** except that ^{19}F NMR spectra were also obtained. Significantly, the latter spectra showed singlet resonances at 75.2 ppm. Combined with the other multinuclear NMR and elemental analysis data, this indicated that the halogen substitution on treatment of **2b** with aryloxides was regiospecific and that the fluorine substituents at sulfur were not replaced. A similar substitution pattern was detected when the cyclic species **1b** was treated with aryloxide nucleophiles.[19]

In a similar way to **3a**–**6a**, the fluorinated polymers **3b** and **4b** appear hydrolytically stable both in the solid state and in solution.

Glass Transition Behavior of $[(NSOX)(NPCl_2)_2]_n$ (2a, X = Cl; 2b, X = F). In order to investigate the conformational flexibility of the backbone present in poly(thionylphosphazenes), the glass transition behavior of the polymers **2a** and **2b** was investigated by DSC. Glass transitions (T_g's) were detected at −46 °C for **2a** and at −56 °C for **2b**. No evidence for melting transitions was found, which suggested that the polymers are amorphous. It is informative to compare the T_g values for **2a** and **2b** with those for related polymers. These values are higher than those for the classical polyphosphazenes $[N{=}PCl_2]_n$ (−63 °C) and $[N{=}PF_2]_n$ (−96 °C),[8b] which indicates that the presence of a N=S(O)X moiety in the place of a $N{=}PX_2$ unit leads to a decrease in skeletal flexibility. Additional evidence in favor of this conclusion was recently provided by Roy who reported the synthesis and isolation of the poly(oxothiazene) $[N{=}S(O)Me]_n$,[2a] which was found to possess a relatively high T_g value of 55–65 °C compared to that of $[N{=}PMe_2]_n$ (−46 °C).[8d] The most likely explanation for this effect is that the presence of the highly polar S=O groups increases intermolecular interactions which decreases the free volume present. Another possible explanation is that the skeletal N=S bonds possess a significantly higher conformational energy barrier than N=P bonds. However, this is unlikely as the $p\pi$–$d\pi$ nature of the π-bonding between nitrogen and sulfur would be expected to ensure good orbital overlap at all points of the conformational energy profile. This situation is similar to that for a N=P bond and a similar low conformational energy barrier would therefore be anticipated. Interestingly, the glass transition temperature of **2a** is significantly lower than that for the poly(carbophosphazene) $[(NCCl)(NPCl_2)_2]_n$ which has a T_g of −21 °C.[5b] This indicates that the decrease in conformational flexibility resulting from the replacement of a $N{=}PCl_2$ unit in a classical polyphosphazene by a N=S(O)Cl moiety is not as great as when the former is replaced by N=CCl. In the latter case the small size of the carbon atom probably leads to a decrease in free volume and an increase in the steric interactions between side groups, which tends to raise the T_g value. In addition, as carbon has no energetically accessible d orbitals the π-bonding between carbon and nitrogen involves $p\pi$–$p\pi$ orbital overlap. This would lead to a significantly higher activation energy for rotation compared to N=S and N=P bonds as π-overlap is only appreciable at two points of the bond twisting profile. The T_g of the fluorinated polymer **2b** (−56 °C) is lower than that of polymer **2a** (−46 °C) which has chlorine atoms at sulfur. This can be attributed to the smaller size and lower polarizability of a fluorine side group substituent compared to chlorine. Similar trends are observed with classical polyphosphazenes and organic polymers. For example, the T_g of $[N{=}PF_2]_n$ (−96 °C) is significantly lower than that of $[N{=}PCl_2]_n$ (−66 °C), and the T_g of poly(vinylidene fluoride) $[CH_2CF_2]_n$ (−39 °C) is lower than that of poly(vinylidene chloride) $[CH_2CCl_2]_n$ (−19 °C).[21]

Glass Transition Behavior of the Poly[(aryloxy)thionylphosphazenes] $[(NSOX)(NP(OAr)_2)_2]_n$ (3a–6a, X = Cl; 3b and 4b, X = F). In order to provide additional characterization and to gain further insight into the factors influencing the skeletal flexibility of poly(thionylphosphazenes), the glass transition behavior of the aryloxy polymers **3a**–**6a**, **3b**, and **4b** was studied by DSC. The T_g values for these polymers are listed in Table II. As expected, the replacement of the chlorine atoms at phosphorus in **2a** and **2b** by the bulkier aryloxy groups leads to a very significant increase in T_g. For the polymers with chlorine atoms at sulfur, the phenoxy polymer **3a** and the polymer **6a** with *m*-(trifluoromethyl)phenoxy side groups showed the lowest T_g values of 10 and −25 °C, respectively. As was the case with **2b** relative to **2a**, the fluorinated polymers **3b** and **4b** were found to possess lower T_g's than those of the analogous polymers with chlorine at sulfur, **3a** and **4a**. None of the polymers showed evidence for melting transitions which suggested that they are amorphous. This was confirmed for **4a** and **5a** by X-ray powder diffraction studies which gave diffractograms characteristic of amorphous materials. This contrasts with the situation for the analogous single-substituent classical poly[(aryloxy)phosphazenes] which are generally microcrystalline.[8c] Presumably, the presence of a sulfur(VI) atom bearing an oxygen and a chlorine substituent introduces sufficient asymmetry to the polymer structure to prevent side group stacking and crystallization. Higher T_g's were noted for poly(thionylphosphazenes) compared to classical polyphosphazenes for polymers **2a** and **2b** where halogen substituents are present. This was also found to be the case if relatively small aryloxy side groups are attached to phosphorus. For example, the T_g of **3a** is +10 °C, which is higher than that of poly(diphenoxyphosphazene), $[N{=}P(OPh)_2]_n$,[8c] which has a T_g of −6 °C. By contrast, with very bulky and rigid aryloxy side groups the T_g's of the poly(thionylphosphazenes) are similar to or even less than those of the analogous classical polyphosphazene with the same substituents at phosphorus. Thus, the T_g of **5a** (+43 °C) is only slightly greater than that of poly[(dicumylphenoxy)phosphazene] (+39 °C).[8c] Furthermore, the T_g of polymer **4a**, which possesses even bulkier and rigid *p*-phenylphenoxy side groups, is 55 °C and is dramatically *lower* than that of poly[(di-*p*-phenylphenoxy)phosphazene] (+93 °C).[8c] This suggests that two competing effects determine the T_g's of the poly(thionylphosphazenes) discussed in this paper relative to their classical polyphosphazene analogues. First, the presence of the highly polar S=O group tends to decrease skeletal flexibility relative to classical polyphosphazenes. Secondly, the smaller number of aryloxy substituents in poly[(aryloxy)thionylphosphazenes] (four per six atom repeat unit) compared to classical poly[(aryloxy)phosphazenes] (six per six atom repeat unit) tends to increase skeletal flexibility. With small substituents such as halogens or even small aryloxy groups, the first effect is the most significant and the poly(thionylphosphazene) has the higher T_g. By contrast, with bulky and rigid side groups such as *p*-phenylphenoxy, the second factor becomes dominant as the S=O groups are sterically shielded from one another and the poly(thionylphosphazene) has the lower T_g.

Light-Scattering Measurements for $[(NSOX)(NP(OAr)_2)_2]_n$ (4a, X = Cl, OAr = OC_6H_4Ph-*p*) in THF. In order to investigate the solution properties of poly(thionylphosphazenes) and to provide an absolute deter-

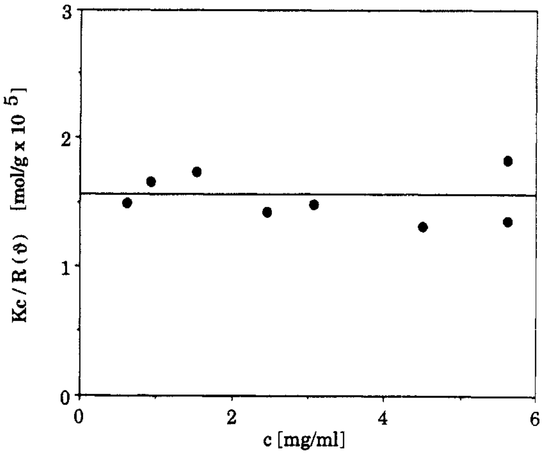


Figure 2. Low-angle laser light scattering results for polymer **4a**.

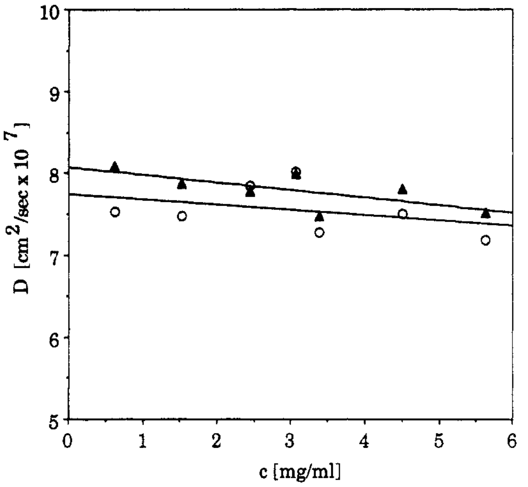


Figure 3. Translational diffusion coefficient as a function of solution concentration for polymer **4a** obtained from dynamic light scattering data. Scattering angles: open circles, 60°; filled triangles, 90°.

mination of molecular weight, low-angle laser light scattering (LALLS) and dynamic light scattering (DLS) studies were carried out on THF solutions of polymer **4a**, which was selected as a representative example.

Results of LALLS measurements for the polymer **4a** are shown in Figure 2 as a function of the solution concentration. Data plotted show no dependence on the solution concentration within the experimental error; i.e. the second virial coefficient of the polymer solution, A_2 in eq 2, is zero. This means that Θ conditions were utilized for the polymer in THF at 22 °C. The value of $\bar{M}_w$ was determined from the fitted intercept of the straight line in Figure 3 with the y-axis, and $\bar{M}_w = (6.4 \pm 0.5) \times 10^4$ was obtained.

Figure 2 shows the measured diffusion coefficient $\langle D \rangle_z$ as a function of polymer concentration for sample **4a** at two different scattering angles obtained in the DLS experiments. There was only a weak angular dependence of $\langle D \rangle_z$ observed, which is consistent with the molar mass and the Θ conditions.[22] Data plotted can be fitted by a straight line[23] according to the relationship

$$\langle D \rangle_z = \langle D \rangle_{z,0}(1 + k_D c) \qquad (4)$$

The slope k_D can be written as

$$k_D = 2A_2M - (k_s + \nu) \qquad (5)$$

where k_S is the frictional coefficient and ν is the partial specific volume of the polymer. The negative slope in Figure 2, which corresponds to a negative k_D value in eq 4 is due to the fact that A_2 in eq 5 is zero, as obtained from LALLS (Θ conditions). Thus, the concentration dependence of the diffusion coefficient is determined by the hydrodynamic friction which results in a negative value for k_D (see eq 5). A linear least squares fit for the data obtained at a 60° scattering angle resulted in a value for the diffusion coefficient $\langle D \rangle_{z,0}$ of 7.75×10^{-7} cm^2/s, which corresponds to an effective hydrodynamic radius $R_{h,eff}$ of 5.9 nm.

It is interesting to mention that GPC measurements yielded an effective value of $\bar{M}_w = 1.2 \times 10^5$ for the polymer using a GPC column calibrated against polystyrene standards. This "polystyrene-effective" molecular weight is roughly a factor of 2 larger than the true value obtained from LALLS. This difference can be easily understood by keeping in mind that the separation of GPC is based on the effective hydrodynamic size of the dissolved macromolecules.[24] In THF at 22 °C polymer **4a** forms a Θ solution (i.e. the macromolecular coils are compact) whereas THF is a good solvent for polystyrene under the same conditions (i.e. the polystyrene coils are swollen). The molecular weight of the polystyrene molecule with the average size that corresponds to the size of the molecules of polymer **4a** ($\bar{R}_{h,eff} = 5.9$ nm) in THF and at 22 °C can be calculated from the scaling equation between the hydrodynamic size and the molecular weight for monodisperse polystyrene. Using published data for this estimation,[25] we obtained a value of $\bar{M}_w = 4.7 \times 10^4$ for polystyrene with $\bar{R}_{h,eff} = 5.9$ nm, which is ca. 30% different from the true molecular weight of polymer **4a**. This 30% difference can be related with the polydispersity of polymer **4a** which was neglected in the comparison above. Thus, GPC overestimates the molecular weight of the poly[(aryloxy)thionylphosphazene] **4a** due to the differences in the coil sizes if polystyrene column calibration is used.

Conclusions

A series of poly[(aryloxy)thionylphosphazenes] with halogen substituents at sulfur have been synthesized and characterized. An investigation of these species has shown that the presence of skeletal sulfur(VI) atoms in the polymer backbone gives rise to interesting differences from classical polyphosphazenes in terms of material properties such as glass transition behavior and polymer morphology. In addition, poly(thionylphosphazenes) have been found to differ with respect to reactivity patterns and, consequently, the polymer structures that are accessible. The synthesis and properties of new poly(thionylphosphazene) derivatives are now under exploration and our results will be reported in the near future.

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Registry No. **1a** (homopolymer), 133551-00-5; **1b** (homopolymer), 138050-20-1.