Polymers with Sulfur(VI)−Nitrogen−Phosphorus Backbones: Synthesis, Characterization, and Properties of Poly[(dialkylamino)thionylphosphazenes]

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ABSTRACT: Aminolysis of the chlorinated poly(thionylphosphazene) $[NSOCl(NPCl_2)_2]_n$ (**2a**) with several secondary amines NHR_2 (diethylamine, piperidine, and pyrrolidine) yielded various hydrolytically stable poly[(amino)thionylphosphazenes] $[NSO(NR_2)\{NP(NR_2)_2\}_2]_n$ **6** (**a**, NR_2 = piperidine; **b**, NR_2 = pyrrolidine) in which chlorine atoms at both the phosphorus center and sulfur were replaced. In addition, treatment of **2a** with different equivalents of several secondary amines (diethylamine, piperidine, and pyrrolidine), followed by addition of excess of *n*-butylamine, lead to a series of mixed-substituent poly[(amino)thionylphosphazenes] $[NSO(NHR')\{NP(NR_2)_2\}_2]_n$ **7** (NHR′ = *n*-butylamine; **a**−**c**, NR_2 = diethylamine; **d**, **e**, NR_2 = piperidine; **f**, NR_2 = pyrrolidine). The new moisture stable polymers were characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy and elemental analysis. The molecular weights of the polymers **6a**,**6b** and **7a**−**7f** were in the range of $\bar{M}_w = 3.4 \times 10^4 - 1.1 \times 10^5$ and $\bar{M}_n = 3.1 \times 10^3 - 5.0 \times 10^4$ according to GPC analysis in THF versus polystyrene standards. The thermal transition behavior was investigated by means of DSC. Glass transition temperatures (T_g's) of the poly[(amino)thionylphosphazenes] **6a**,**6b** and **7a**−**7f** depend on the content of secondary amine versus primary amine and were in the range of −13 to +27 °C. No melt transitions were detected.

Introduction

Polymers based on inorganic elements are relatively rare but are attracting considerable attention due to their unusual properties and potential applications.[1,2] Although sulfur−nitrogen[3] and phosphorus−nitrogen polymers[4] represent interesting and well-studied examples of these inorganic materials, sulfur−nitrogen−phosphorus polymers have been prepared only recently.[5,6]

In 1991, we reported that cyclic thionylphosphazenes **1a** and **1b** (see Chart 1) undergo thermal ring-opening polymerization (ROP) to yield poly(thionylphosphazenes) **2a** and **2b**, a new class of inorganic polymers with a sulfur(VI)−nitrogen−phosphorus backbone.[6] In addition, we have recently shown that the ROP reaction occurs at ambient temperatures in the presence of Lewis acid initiators.[7] These polymers can be regarded as hybrids of poly(oxothiazenes) $[RS(O){=}N]_n$[8,9] and classical polyphosphazenes $[R_2P{=}N]_n$.[4] The perhalogenated ring-opened polymers **2a** and **2b** are moisture-sensitive. However, we have previously described in detail the synthesis and properties of air-stable poly(thionylphosphazenes) **3**, **4**, and **5**, substituted with sodium aryloxides Na[OAr],[10] sodium alkoxides $Na[OCH_2CF_3]$,[11] or primary amines RNH_2.[12] Poly(thionylphosphazenes) show interesting properties different from polyphosphazenes and poly(oxothiazenes) concerning polymer morphology, thermal transition behavior, reactivity patterns, and the types of polymer structures accessible.[13] In contrast to the reactions of **2a** and **2b** with aryloxides which proceeds regioselectively at the phosphorus centers, leaving the sulfur−halogen bonds intact, the reaction of **2a** with primary amines substitute both the phosphorus− and the sulfur−halogen bonds.[10,12] In the present paper we report comprehensive details of our studies of the reaction of the chlorinated polymer **2a** with secondary amines. Synthesis and characterization of the poly[(dialkylamino)thionylphosphazenes] are also described.

Results and Discussion

Allcock and co-workers have already described the substitution of poly(dichlorophosphazene) and poly[(pentachloro)carbophosphazene] with secondary amines. Besides the complete substitution of the perchlorinated polymers using secondary amines of low steric demand, a partial substitution of the polymers was observed, as well as a polymer degradation in the case of amines with high nucleophilicity.[14−16] In this paper we discuss the reactions of secondary amines with the high molecular weight poly(thionylphosphazene) **2a**. In particular, we describe the degree of substitution, address the issue of possible polymer degradation, and discuss the properties of primary and secondary amine mixed-substituent poly[(amino)thionylphosphazenes]. From our earlier studies on the aminolysis of the perchlorinated poly(thionylphosphazene) **2a** with primary amines, the following reactivity sequence $P(Cl)_2 > P(Cl, am) > S(O, Cl)$ (am = amino) was established.[12] In this work, it was of interest whether the aminolysis using secondary amines follows the same reactivity sequence.

Synthesis and Structural Characterization of the Poly[(amino)thionylphosphazenes] $[NSO(NR_2)\{NP(NR_2)_2\}_2]_n$ (6a and 6b). Hydrolytically stable poly(thionylphosphazene) derivatives were prepared by slow addition of cyclic secondary amines piperidine and pyrrolidine to a solution of **2a** in CH_2Cl_2 at 0 °C. After warming to room temperature and stirring for 24 h, any

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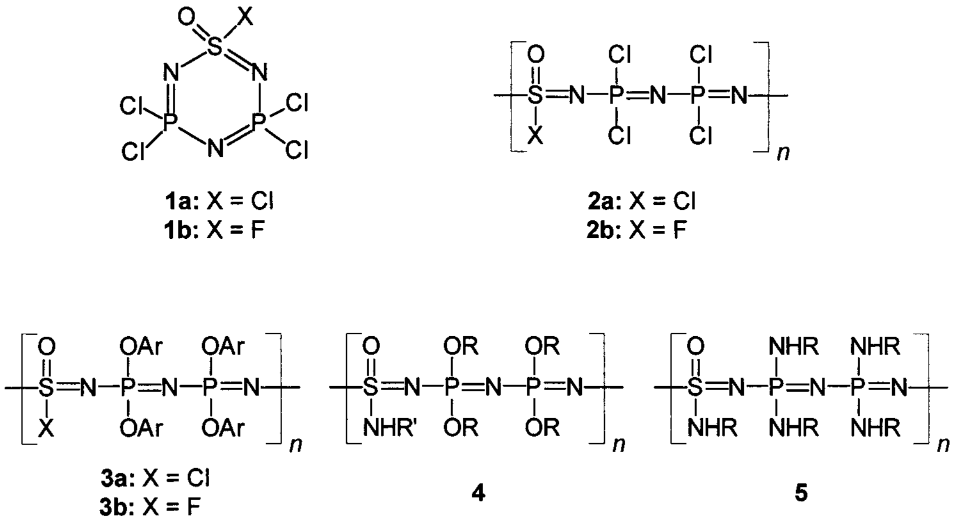
Chart 1



Scheme 1. Synthesis of Poly[(amino)thionylphosphazenes]

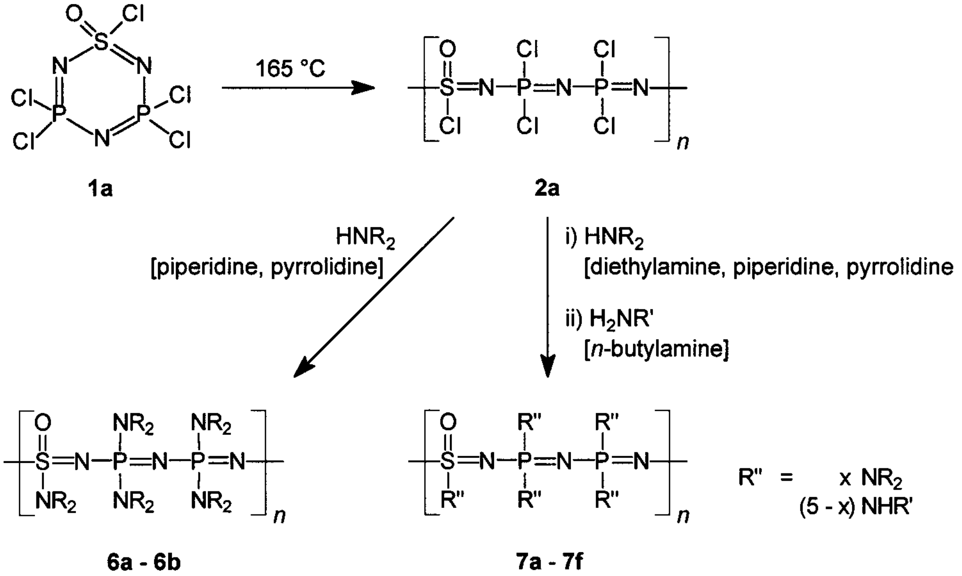


Table 1. Content of Primary and Secondary Amines in Poly[(amino)thionylphosphazenes]

polymer	NR$_2$	NHR′
6a	NC$_5$H$_{10}$ (100%)	
6b	NC$_4$H$_8$ (100%)	
7a	HNEt$_2$ (65%)	NH^{n}Bu (35%)
7b	HNEt$_2$ (57%)	NH^{n}Bu (43%)
7c	HNEt$_2$ (42%)	NH^{n}Bu (58%)
7d	NC$_5$H$_{10}$ (59%)	NH^{n}Bu (41%)
7e	NC$_5$H$_{10}$ (35%)	NH^{n}Bu (65%)
7f	NC$_4$H$_8$ (51%)	NH^{n}Bu (49%)

remaining chlorine atoms were substituted through the slow addition of of *n*-butylamine at 0 °C. The reaction mixture was warmed to room temperature and stirred for an additional 24 h to yield to the white glassy polymers **6a** and **6b** (Scheme 1 and Table 1) after purification by precipitation techniques. The polymeric products were soluble in polar organic solvents (such as CH$_2$Cl$_2$ and THF), as well as in dioxane. The ^{31}P, ^{13}C, and ^{1}H NMR spectroscopic and elemental analysis data for the poly[(amino)thionylphosphazenes] **6a** and **6b** are listed in Tables 2 and 3. The molecular weights and the thermal transition behavior of the polymers are given in Table 4.

Characterization of polymers **6a** and **6b** indicated that the reaction of **2a** with cyclic secondary amines resulted in replacement of all of the chlorine atoms at both phosphorus and sulfur (Scheme 1). The assignment of the structures of **6a** and **6b** was initially made from a consideration of the NMR data. The ^{1}H and ^{13}C NMR spectra of **6b** are shown in Figure 1 and Figure 2. From the NMR spectra it can be seen that no *n*-butylamine is substituted to the polymer chain. Thus, a complete substitution of **2a** with pyrrolidine can be assumed. As expected, the ^{13}C NMR spectra show four signals for the pyrrolidine substituents, attached to the sulfur and phosphorus centers.

The elemental analysis data (C, H, N, and Cl) for polymers **6a** and **6b** were consistent with the assigned structures. Small amounts of residual chlorine probably arise from the formation of pendant groups of the type $-NR_2H^+Cl^-$ where the basic poly[(amino)thionylphosphazene] competes with excess amine as an HCl acceptor. Similar behavior has been reported for the aminolysis of poly[(pentachloro)carbophosphazene][16] as well as of classical polyphosphazenes $[Cl_2P{=}N]_n$.[15]

Synthesis and Structural Characterization of the Mixed-Substituent Poly[(amino)thionylphos-

Table 2. NMR Spectral Data for Polymers 6a,6b and 7a−7f in $CDCl_3$

polymer	^{31}P (ppm)	^{13}C (ppm)	^{1}H (ppm)
6a	−3.6 (br)	24.3 [$\mathrm{S{-}NCH_2CH_2}\mathbf{CH_2}$] 25.2 [$\mathrm{P{-}NCH_2CH_2}\mathbf{CH_2}$] 25.8 [$\mathrm{S{-}NCH_2}\mathbf{CH_2}\mathrm{CH_2}$] 26.5 [$\mathrm{P{-}NCH_2}\mathbf{CH_2}\mathrm{CH_2}$] 45.8 [$\mathrm{P{-}N}\mathbf{CH_2}\mathrm{CH_2CH_2}$] 47.4 [$\mathrm{S{-}N}\mathbf{CH_2}\mathrm{CH_2CH_2}$]	1.44 [$\mathrm{P{-}NCH_2}\mathbf{CH_2CH_2}$] 1.59 [$\mathrm{S{-}NCH_2}\mathbf{CH_2CH_2}$] 3.05 [$\mathrm{P{-}N}\mathbf{CH_2}\mathrm{CH_2CH_2}$] 3.18 [$\mathrm{S{-}N}\mathbf{CH_2}\mathrm{CH_2CH_2}$]
6b	−6.5 (br)	25.2 [$\mathrm{S{-}NCH_2CH_2}$] 26.5 [$\mathrm{P{-}NCH_2CH_2}$] 46.6 [$\mathrm{P{-}N}\mathbf{CH_2}\mathrm{CH_2}$] 48.5 [$\mathrm{S{-}N}\mathbf{CH_2}\mathrm{CH_2}$]	1.70 [$\mathrm{P/S{-}NCH_2CH_2}$] 3.13 [$\mathrm{P/S{-}N}\mathbf{CH_2}\mathrm{CH_2}$] 3.22 [$\mathrm{P/S{-}N}\mathbf{CH_2}\mathrm{CH_2}$]
7a	−2.1 (br)	14.0 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] [$\mathrm{P{-}N(CH_2}\mathbf{CH_3}\mathrm{)_2}$] 20.4 [$\mathrm{P/S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 33.9 [$\mathrm{P/S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 39.3 [$\mathrm{P{-}N(}\mathbf{CH_2}\mathrm{CH_3)_2}$] 40.9 [$\mathrm{P/S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$]	0.87 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] 1.04 [$\mathrm{P{-}N(CH_2}\mathbf{CH_3}\mathrm{)_2}$] 1.33 [$\mathrm{P/S{-}NH{-}CH_2}\mathbf{CH_2CH_2}\mathrm{CH_3}$] 2.89 [$\mathrm{P/S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 3.10 [$\mathrm{P{-}N(}\mathbf{CH_2}\mathrm{CH_3)_2}$]
7b	0.3 (br)	14.0 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] [$\mathrm{P{-}N(CH_2}\mathbf{CH_3}\mathrm{)_2}$] 20.6 [$\mathrm{P/S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 33.8 [$\mathrm{P/S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 39.5 [$\mathrm{P{-}N(}\mathbf{CH_2}\mathrm{CH_3)_2}$] 40.6 [$\mathrm{P/S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$]	0.87 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] 1.06 [$\mathrm{P{-}N(CH_2}\mathbf{CH_3}\mathrm{)_2}$] 1.29 [$\mathrm{P/S{-}NH{-}CH_2}\mathbf{CH_2CH_2}\mathrm{CH_3}$] 2.85 [$\mathrm{P/S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 3.11 [$\mathrm{P{-}N(}\mathbf{CH_2}\mathrm{CH_3)_2}$]
7c	1.4 (br)	14.0 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] [$\mathrm{P{-}N(CH_2}\mathbf{CH_3}\mathrm{)_2}$] 20.3 [$\mathrm{P/S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 33.8 [$\mathrm{P/S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 39.3 [$\mathrm{P{-}N(}\mathbf{CH_2}\mathrm{CH_3)_2}$] 40.5 [$\mathrm{P/S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$]	0.87 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] 1.04 [$\mathrm{P{-}N(CH_2}\mathbf{CH_3}\mathrm{)_2}$] 1.28 [$\mathrm{P/S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 1.40 [$\mathrm{P/S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 2.84 [$\mathrm{P/S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 3.10 [$\mathrm{P{-}N(}\mathbf{CH_2}\mathrm{CH_3)_2}$]
7d	−0.2 (br)	13.9 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] 20.2 [$\mathrm{P{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 20.5 [$\mathrm{S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 25.0 [$\mathrm{P{-}NCH_2CH_2}\mathbf{CH_2}$] 26.3 [$\mathrm{P{-}NCH_2}\mathbf{CH_2}\mathrm{CH_2}$] 31.8 [$\mathrm{S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 33.9 [$\mathrm{P{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 40.6 [$\mathrm{P{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 43.0 [$\mathrm{S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 45.5 [$\mathrm{P{-}N}\mathbf{CH_2}\mathrm{CH_2CH_2}$] 47.6 [$\mathrm{S{-}N}\mathbf{CH_2}\mathrm{CH_2CH_2}$]	0.83 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] 1.26 [$\mathrm{P/S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 1.40 [$\mathrm{P/S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] [$\mathrm{P{-}NCH_2}\mathbf{CH_2CH_2}$] 2.80 [$\mathrm{P{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 3.00 [$\mathrm{S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] [$\mathrm{P{-}N}\mathbf{CH_2}\mathrm{CH_2CH_2}$]
7e	1.3 (br)	13.9 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] 20.2 [$\mathrm{P{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 20.4 [$\mathrm{S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 25.0 [$\mathrm{P{-}NCH_2CH_2}\mathbf{CH_2}$] 26.3 [$\mathrm{P{-}NCH_2}\mathbf{CH_2}\mathrm{CH_2}$] 31.8 [$\mathrm{S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 33.9 [$\mathrm{P{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 40.6 [$\mathrm{P{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 43.5 [$\mathrm{S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 45.3 [$\mathrm{P{-}N}\mathbf{CH_2}\mathrm{CH_2CH_2}$]	0.85 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] 1.28 [$\mathrm{P/S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 1.42 [$\mathrm{P/S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] [$\mathrm{P{-}NCH_2}\mathbf{CH_2CH_2}$] 2.79 [$\mathrm{P{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 3.01 [$\mathrm{S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] [$\mathrm{P{-}N}\mathbf{CH_2}\mathrm{CH_2CH_2}$]
7f	−1.1 (br)	14.0 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] 20.3 [$\mathrm{P{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 20.7 [$\mathrm{S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 26.5 [$\mathrm{P{-}NCH_2}\mathbf{CH_2}$] 31.8 [$\mathrm{S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 34.1 [$\mathrm{P{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 40.8 [$\mathrm{P{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 43.5 [$\mathrm{S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 46.6 [$\mathrm{P{-}N}\mathbf{CH_2}\mathrm{CH_2}$]	0.85 [$\mathrm{P/S{-}NH{-}CH_2CH_2CH_2}\mathbf{CH_3}$] 1.29 [$\mathrm{P/S{-}NH{-}CH_2CH_2}\mathbf{CH_2}\mathrm{CH_3}$] 1.40 [$\mathrm{P/S{-}NH{-}CH_2}\mathbf{CH_2}\mathrm{CH_2CH_3}$] 1.72 [$\mathrm{P{-}NCH_2}\mathbf{CH_2}$] 2.84 [$\mathrm{P{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 2.98 [$\mathrm{S{-}NH{-}}\mathbf{CH_2}\mathrm{CH_2CH_2CH_3}$] 3.17 [$\mathrm{P{-}N}\mathbf{CH_2}\mathrm{CH_2}$]

Table 3. Elemental Analysis for 6a and 6b

polymer		% C	% H	% N	% Cl
6a	calcd	52.43	8.80	19.57	0.00
	found	53.59	8.67	19.29	0.80
6b	calcd	47.80	8.02	22.30	0.00
	found	47.69	8.21	21.85	0.80

phazenes] [$NSO(NHR')\{NP(NR_2)_2\}_2]_n$ (7a−7f). Unlike the substitution of **2a** with cyclic secondary amines, we were unable to observe complete substitution of chlorine atoms by the sterically more demanding diethylamine. Indeed, treatment of **2a** with an excess (up to 4.5 equiv) of diethylamine resulted in only a partial substitution of the chlorine atoms. Hydrolytically stable mixed-substituent polymers were prepared by reacting partially substituted poly[(diethylamino)thionylphosphazenes] with the primary amine *n*-butylamine to yield **7a−7c**. In addition, for characterization purposes several mixed-substituent poly[(amino)thionylphosphazenes]

Table 4. GPC and Glass Transition Data for Polymers 6a−6b and 7a−7f

polymer	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_g (°C)
6a	42 800	13 800	3.1	27
6b	57 800	22 400	2.6	24
7a	52 400	27 100	1.9	1
7b	53 500	29 500	1.8	−9
7c	63 700	36 200	1.8	−13
7d	35 700	7 280	4.9	20
7e	113 700	49 900	2.3	6
7f	33 500	3 070	10.9	14

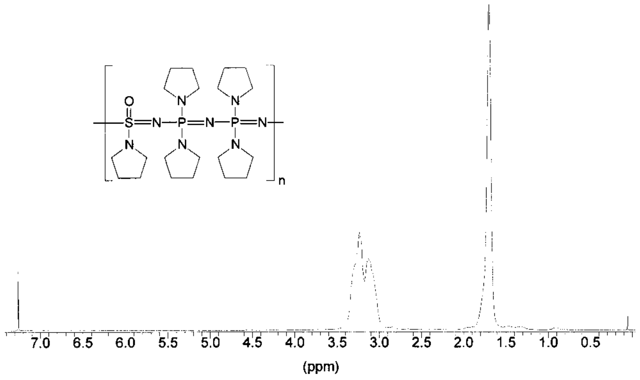


Figure 1. The 300 MHz ^{1}H NMR spectrum of polymer **6b** in $CDCl_3$.

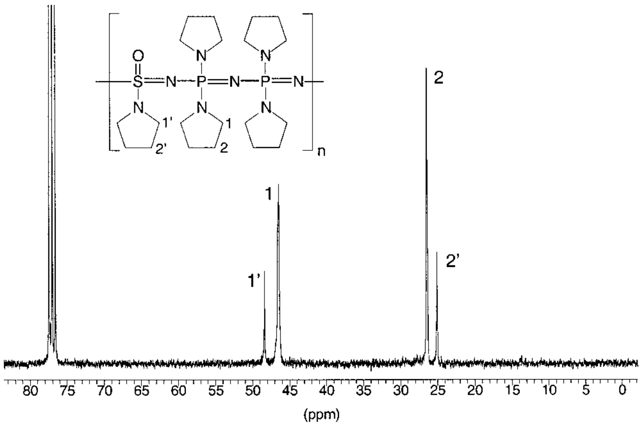


Figure 2. The 75.4 MHz ^{13}C NMR spectrum of polymer **6b** in $CDCl_3$.

7d−**7f** were prepared through an analogous synthetic approach. With these polymers, an analytical pathway was created by comparison of the NMR data of poly[(*n*-butylamino)thionylphosphazene][12] with the mixed-substituent polymers. The light-yellow elastomeric materials **7a**−**7c**, the white glassy polymer **7d**, and the colorless glassy materials **7e** and **7f** (Scheme 1 and Table 1) were obtained after purification by precipitation techniques. The polymeric products were soluble in polar organic solvents (such as CH_2Cl_2 and THF), as well as in dioxane. Interestingly, the diethylamine-substituted poly(thionylphosphazenes) **7a**−**7c** were also soluble in methanol. The polymer samples **7a**−**7f** were characterized by NMR (Table 2), GPC, and DSC (Table 4).

The contents of primary and secondary amines were calculated by integration of the ^{1}H NMR spectra and are listed in Table 1. In contrast to the nucleophilic substitution of poly(dichlorophosphazene)[14,15] with diethylamine, more than 50% of the chlorine atoms could be replaced. Apparently, the presence of an O=S(VI) moiety in the polymer backbone of **2a** provides more room for substitution with the sterically more demanding diethylamine. On the other hand, in contrast to the treatment of poly[(pentachloro)carbophosphazene][16] with diethylamine, a complete substitution of the polymer **2a** could not be observed, even when using a large excess of diethylamine.

From the reactions using different amounts of secondary amines followed by an excess of *n*-butylamine, it can be observed from the ^{1}H and ^{13}C NMR data that the chlorine atoms attached to the sulfur centers S(O, Cl) possess a higher reactivity than the single substituted phosphorus centers P(Cl, am). Thus, we found that aminolysis of the perchlorinated poly(thionylphosphazene) **2a** using secondary amines is following the reactivity sequence $P(Cl)_2 > S(O, Cl) > P(Cl, am)$ (am = amino). This effect was observed very clearly in the ^{13}C NMR spectra of poly[(piperidino)thionylphosphazene] (**6a**) and of the mixed-substituent polymers **7d** and **7e**. With a decreasing amount of piperidine substitution, the signal at $\delta = 47.4$ ppm (originating from the piperidine substituents) decreased, while the signal at $\delta = 43.5$ ppm (originating from the *n*-butylamine substituents) increased. For **7d** both signals can be observed in the ^{13}C NMR spectra, thus suggesting that both amines, piperidine and *n*-butylamine, are attached to the sulfur centers in the poly[(amino)thionylphosphazene].

Molecular Weight and Polymer Degradation of the Poly[(amino)thionylphosphazenes] 6a,6b and 7a−7f. The polymerization and depolymerization of classical phosphazenes are thought to be aspects of a common ring−polymer equilibration process.[17] Small sterically undemanding side groups will generally favor polymerization, while bulkier groups promote depolymerization. Similar observations were also made for the substitution of poly[(pentachloro)carbophosphazene] with secondary amines.[16] Thus, we expected to see some evidence for degradation of the polymer backbone during our attempts to isolate poly[(dialkylamino)thionylphosphazenes]. The molecular weights of polymers **6a**,**6b** and **7a**−**7f** vary from $\bar{M}_w = 3.4 \times 10^4$ to 1.1×10^5 and $\bar{M}_n = 3.1 \times 10^3$ to 5.0×10^4 according to GPC (see Table 4). Polymers prepared by nucleophilic substitution of **2a** using secondary amines of strong nucleophilicity, such as piperidine or pyrrolidine, possess high polydispersity indices ($\bar{M}_w/\bar{M}_n > 2$). It appears that attempts to substitute chlorine atoms in **2a** through use of strong nucleophilic amines lead to some degradation of the polymer backbone. Thus, substitution of **2a** with cyclic secondary amines is possible, but with cost of partial degradation of the polymer chain.

Thermal Transition Behavior of the Poly[(amino)thionylphosphazenes] 6a,6b and 7a−7f. To provide further characterization and to gain insight into the factors influencing the conformational flexibility of poly[(amino)thionylphosphazenes], the thermal transition behavior of polymers **6a**,**6b** and **7a**−**7f** was studied by differential scanning calorimetry (DSC). The glass transition temperatures (T_g's) for these polymers are listed in Table 4. As expected, the replacement of all chlorine atoms at the phosphorus and sulfur centers in **2a** by secondary amines leads to high T_g's of up to 27 °C (**6a**). The classical polyphosphazene with piperidine side groups possesses a lower T_g of 19 °C.[15]

Furthermore, the difference in the steric bulk of primary and secondary amines led to a strong influence on the chain flexibility. Mixed-substituent polymers **7a**−**7f** with secondary amines and *n*-butylamine possess T_g's from −13 to +20 °C. Upon an decrease of the diethylamine content from polymer **7a** to **7c**, the T_g decreased from 1 to −13 °C. As expected, the completely substituted poly[(*n*-butylamino)thionylphosphazene] possesses an even lower T_g of −16 °C.[12]

None of the poly[(amino)thionylphosphazenes] **6a**,**6b** or **7a**−**7f** showed evidence for a melting transition which leads to the conclusion that they are amorphous materials. This is consistent with a transparent nature of the investigated materials. The situation is similar for the analogous classical poly[(amino)phosphazenes] which are generally regarded as amorphous polymers.

Summary

A series of poly[(amino)thionylphosphazenes] have been synthesized by reaction of poly[(pentachloro)-thionylphosphazene] (**2a**) with different secondary amines in various ratios followed by substitution with *n*-butylamine to ensure a complete substitution of chlorine atoms. It was demonstrated that a complete substitution of poly[(pentachloro)thionylphosphazene] (**2a**) with secondary amines is possible, which yielded hydrolytically stable polymers, but with cost of partial degradation of the polymer chain. It was found that complete substitution is only possible using cyclic amines of lower steric demand. Furthermore, it was demonstrated that the preparation of moisture-stable, mixed amine-substituted polymers is possible using a less nucleophilic secondary amine such as diethylamine followed by reaction with a primary amine such as *n*-butylamine. In this case no degradation of the polymer backbone could be observed.

Experimental Section

All amines were obtained from Aldrich. Liquid amines were freshly distilled from calcium hydride before use. The cyclic thionylphosphazene **1a** was prepared by literature procedures[18] and was purified by recrystallization from hexanes and subsequent vacuum sublimation (40−60 °C, 1×10^{-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 air using reagent grade solvents.

^{31}P NMR spectra (121.4 MHz) were referenced externally to 85% H_3PO_4, ^{13}C NMR spectra (75.4 MHz) were referenced to deuterated solvent, ^{1}H NMR spectra (300.0 MHz) were referenced to residual protonated solvent, and all were recorded on a Varian Gemini 300 spectrometer. Molecular weights were obtained 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 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 Mettler-Toledo 821E differential scanning calorimeter. Thermograms were calibrated with the melting transition of indium and were obtained at a heating rate of 10 °C/min. Elemental analysis was performed by the “Mikroanalytisches Labor des Anorganisch Chemischen Instituts der Technischen Universität München”.

Synthesis of $[NSOCl(NPCl_2)_2]_n$ (2a). The cyclic monomer **1a** (1.00 g, 3.04 mmol) was polymerized and the product isolated by precipitation from CH_2Cl_2 with hexanes following literature procedures.[12] After drying under high vacuum a yield of about 80% was obtained for polymer **2a**.

General Procedure for the Preparation of $[NSO(NR_2)\{NP(NR_2)_2\}_2]_n$ (6a,6b). Polymers **6a** and **6b** were prepared by similar methods.

To a stirred solution of polymer **2a** (0.42 g, 1.3 mmol) in 20 mL of dry CH_2Cl_2 at 0 °C was added an excess of predried piperidine (3.0 mL, 30 mmol). A white precipitate formed immediately after the addition. The reaction solution was allowed to warm to room temperature. After 24 h, 3.0 mL (30 mmol) of *n*-butylamine was added at 0 °C. The reaction solution was stirred for 24 h at room temperature. The white precipitate was filtered off using a frit, and the filtrate was concentrated to about 10 mL. The polymeric product was obtained by dropwise addition into water (three times) and methanol (three times) before drying in vacuo. The yield of **6a**, a white glassy material, was 0.57 g (79%). Polymer **6b** was prepared by a similar method except that an excess of predried pyrrolidine (2.0 mL, 24 mmol) was added. The yield of the white glassy polymer **6b** was 0.55 g (87%). Characteristic data for **6a** and **6c** are given in Tables 1 and 2.

General Procedure for the Preparation of $[NSO(NHR')\{NP(NR_2)_2\}_2]_n$ (7a−7f). A similar procedure was used for the synthesis of all the polymers **7a**−**7f**; a general procedure is given for the synthesis of **7a** as a representative example.

To a stirred solution of polymer **2a** (0.42 g, 1.3 mmol) in 20 mL of dry CH_2Cl_2 at 0 °C was added an excess of predried diethylamine (3.0 mL, 29 mmol). A white precipitate formed immediately after the addition. The reaction solution was allowed to warm to room temperature. After 24 h, 3.0 mL (30 mmol) of *n*-butylamine was added at 0 °C. The reaction solution was stirred for 24 h at room temperature. The white precipitate was filtered off using a frit. The filtrate was concentrated to about 10 mL. The polymeric product was obtained by dropwise addition into water (five times) before drying in a vacuum. The yield of **7a**, a light-yellow elastomer, was 0.55 g (85%). Polymers **7b** and **7c** were prepared by a similar method except that 1.0 mL (9.7 mmol) and 0.7 mL (6.8 mmol) of predried diethylamine were added, respectively. The yield of the light-yellow elastomeric polymer **7b** was 0.54 g (84%) and of **6c** was 0.53 g (82%). Polymers **7d**−**7f** were prepared by a similar method except that 0.7 mL (7.0 mmol) and 0.3 mL (3.1 mmol) of predried piperidine and 0.3 mL (3.1 mmol) of predried pyrrolidine were added, respectively. The polymers were precipitated with water (three times) before precipitated with methanol (three times). The yields were 0.57 g (83%) for the white glassy polymer **7d** and 0.54 g (80%) and 0.25 g (39%) for the colorless glassy polymers **7e** and **7f**, respectively. Characterization data for **7a**−**7f** are given in Tables 1 and 2. Polymers **6a**,**6b** and **7a**−**7f** appear to be stable to the atmosphere, and no evidence of decomposition was detected by ^{31}P NMR or GPC.

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