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

Yizeng Ni, Peter Park, Mong Liang, Jason Massey, Chris Waddling, and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto M5S 1A1, Ontario, Canada

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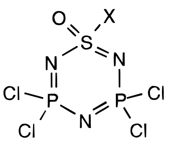
ABSTRACT: Aminolysis of the halogenated poly(thionylphosphazene) $[\mathrm{NSOCl(NPCl_2)_2}]_n$ (**2a**), which possesses a novel S(VI)−N−P backbone, with a series of primary amines $\mathrm{NH_2R}$ (R = Me, Et, ^{n}Pr, allyl, ^{n}Bu, ^{n}Hex, and Ph) afforded the hydrolytically stable poly[(amino)thionylphosphazenes] $[\mathrm{NSO(NHR)\text{-}\{NP(NHR)_2\}_2}]_n$ **4** (**a**, R = Me; **b**, R = Et; **c**, R = ^{n}Pr; **d**, R = allyl; **e**, R = ^{n}Bu; **f**, R = ^{n}Hex; **g**, R = Ph) in which both the chlorine substituents at the phosphorus center and at sulfur were replaced. Treatment of **2a** with a mixture of amines, $\mathrm{NH_2R}$ (R = allyl and ^{n}Bu), yielded a series of mixed substituent copolymers **5a**−**5c** of which **5a** and **5b** were thermally and UV cross-linkable. These new polymers were structurally characterized by ^{31}P, ^{1}H, and ^{13}C NMR and IR spectroscopy and by elemental analysis. The stereochemistry of the poly[(amino)thionylphosphazenes] was investigated by ^{31}P NMR which indicated the polymers are atactic. Molecular weights of the polymers **4a**−**4g** and **5a**−**5c** were in the range $M_w = 5.0 \times 10^3$ to 1.3×10^5, $M_n = 3.3 \times 10^3$ to 7.4×10^4 according to GPC analysis in THF versus polystyrene standards. An absolute value of $M_w = 1.0 \times 10^5$ was obtained by low-angle laser light scattering for **4e**, which was approximately double that obtained by GPC ($M_w = 4.9 \times 10^4$). The thermal transition behavior of the polymers was investigated by DSC. Glass transition temperatures (T_g's) of the poly[(amino)thionylphosphazenes] **4a**−**4g** and **5a**−**5c** were in the range of −40 to +82 °C. No melt transitions were detected and wide-angle X-ray scattering studies also indicated that poly[(amino)thionylphosphazenes] were amorphous. TGA analysis showed that the poly[(amino)thionylphosphazenes] were stable to weight loss up to 200−250 °C under nitrogen at a heating rate of 10 °C/min.

Introduction

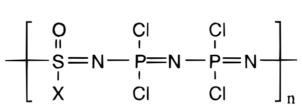
Macromolecules based on main group or transition elements are attracting considerable attention because of their unusual properties and potential applications.[1−4] Although sulfur−nitrogen[5] and phosphorus−nitrogen polymers[6] represent interesting and well-studied examples of these inorganic materials, sulfur−nitrogen−phosphorus polymers have been prepared only very recently.[7−14]

In 1991 we reported that cyclic thionylphosphazenes **1a** and **1b** undergo thermal ring-opening polymerization (ROP) to yield the poly(thionylphosphazenes) **2**, a new class of inorganic polymers with skeletal four-coordinate sulfur(VI), nitrogen, and phosphorus atoms.[10,11] These polymers[9−14] can be regarded as hybrids of poly(oxothiazenes) $[\mathrm{RS(O){=}N}]_n$[15−17] and classical polyphosphazenes $[\mathrm{R_2P{=}N}]_n$.[6]



1

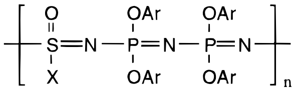
1a: X = Cl
1b: X = F



$$\left[\mathrm{S(O)(X){=}N{-}PCl_2{=}N{-}PCl_2{=}N}\right]_n$$

2

2a: X = Cl
2b: X = F



$$\left[\mathrm{S(O)(X){=}N{-}P(OAr)_2{=}N{-}P(OAr)_2{=}N}\right]_n$$

3

X = Cl or F

We have previously described in detail the synthesis and properties of poly(thionylphosphazenes) with aryloxy substituents *via* the reaction of **2a** or **2b** with sodium aryloxides Na[OAr].[10−12] These reactions proceeded regioselectively at the phosphorus centers to yield poly(thionylphosphazenes) **3** leaving the S(VI)−halogen bonds intact. In this paper we report full details of our studies of the reactions of the chlorinated polymer **2a** with primary amines. This leads to replacement of the halogen substituents at phosphorus and at sulfur. The synthesis, characterization, and cross-linking studies of poly[(allylamino)thionylphosphazenes] are also described.

Experimental Section

Materials and Equipment. All amines were obtained from Aldrich. Liquid amines were used after further distillation from potassium hydroxide. Gaseous amines were passed through drying tubes containing potassium hydroxide and freshly cut sodium metal. The cyclic thionylphosphazene **1a** was prepared by literature procedures[18] and was purified by recrystallization three times from hexanes at 50−70 °C and high vacuum sublimation twice at 45−55 °C, 0.008 mmHg. All syntheses were performed under a nitrogen atmosphere by using a Vacuum Atmospheres glovebox or standard Schlenk line techniques. Solvents were dried according to standard methods. Workup of the polymers was carried out in air. Dialysis experiments were performed in a Spectra/Por molecular porous membrane with the molecular weight cutoff at 3500.

The ^{31}P{^{1}H} NMR spectra were recorded on a Varian XL-300 spectrometer operating at 121.4 MHz. The ^{1}H and ^{13}C NMR spectra were obtained with a Varian XR-400 spectromter operating at 400.0 and 100.6 MHz and an XR-200 spectrometer operating at 200.0 and 50.3 MHz, respectively. Chemical shifts are reported relative to $\mathrm{SiMe_4}$ (^{1}H or ^{13}C) or to external $\mathrm{H_3PO_4/D_2O}$ (^{31}P). Fourier transform infrared spectra were obtained with the use of a Nicolet 550 spectrometer for thin films of polymers which were cast on NaCl disks from $\mathrm{CH_2Cl_2}$

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solution. 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 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. A Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a TAC 7/Unix 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. A Perkin-Elmer TGA-7/Unix thermal gravimetric analyzer equipped with a TAC-7 instrument controller was used to study the polymer thermal stability. Thermograms were calibrated with the magnetic transitions of Nicoseal and Perkalloy and were obtained at a heating rate of 10 °C/min under nitrogen. Wide-angle X-ray scattering data were obtained using a Siemens D5000 diffractometer employing Ni-filtered Cu Kα ($\lambda = 1.541\ 78$ Å) radiation. The samples were scanned at step widths of 0.02° with 1.0 s per step in the Bragg angle range 3−40°. Polymer films cast from THF solution were used for the X-ray studies. Elemental analyses were performed either by Canadian Microanalytical Service Ltd., Delta, B.C., Canada or by Quantitative Technologies Inc. P.O. Box 470, Salem Industrial Park, Bldg. 5, Whitehouse, NJ 08888. 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 (23 °C) using a metal cell 4.93 mm in length. Each solution was filtered twice through a Gelman Science arcodisk filter with a 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.

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 following the standard procedure.[12] After drying under high vacuum a general yield of about 55−65% was obtained for polymer **2a**.

General Procedure for the Preparation of $[NSO(NHR)\{NP(NHR)_2\}_2]_n$ (4a−4b). Polymers **4a** and **4b** were prepared by similar methods and details are therefore only given for **4a**.

Predried methylamine gas was bubbled through a stirred solution of polymer **2a** (0.50 g, 1.52 mol) dissolved in ca. 120 mL of CH_2Cl_2 at 0 °C. A white precipitate formed immediately after the addition. The reaction mixture became clear after ca. 5 min. Methylamine was allowed to bubble through for a further 5 min. The reaction solution was warmed to ambient temperature over 2 h. The solution was concentrated to ca. 20 mL and filtered through a filter frit.

Polymer **4a**, which was water soluble, was precipitated into hexanes three times followed by dialysis in H_2O for 3 days. The product was dried from a solution of CH_2Cl_2 under high vacuum for 24 h at ambient temperature. Yield of **4a**, a white powder: 0.22 g (49%).

For polymer **4b**, the purification was carried out by first redissolving the dried crude product in ca. 10 mL of THF and then precipitating into water three times followed by precipitating from CH_2Cl_2 into hexanes three times. The final product was dried under high vacuum for 24 h at ambient temperature. Yield of **4b**, a colorless elastomeric material: 0.41 g (62%).

General Procedure for the Preparation of $[NSO(NHR)\{NP(NHR)_2\}_2]_n$ (4c−4g). A similar procedure was used for the synthesis of polymers **4c**−**4g** and a general procedure is therefore given with the synthesis of **4e** as a representative example.

To a stirred solution of polymer **2a** (0.64 g, 1.95 mmol) in dry CH_2Cl_2 (100 mL) at 0 °C was added slowly 3.86 mL (39.0 mmol) of butylamine. A white precipitate formed immediately after the addition. The reaction solution was warmed to ambient temperature over a period of 2 h, and the reaction was allowed to proceed for 12 h at room temperature. The white precipitate was filtered, and the solvent was removed from the filtrate. The product was dried and redissolved in ca. 10 mL of THF. The polymeric product was obtained by dropwise addition into water (three times) and methanol (three times) before drying in vacuum for 24 h. Yield of **4e**, a colorless elastomer: 0.70 g (71%).

Except for the reaction with aniline, which took 48 h to complete at room temperature, all the reactions required 12 h for completion. The differences in the precipitations for each polymer were as follows: polymer **4f** was precipitated in the same fashion as polymer **4e.** Polymers **4c**, **4d**, and **4g** were precipitated from CH_2Cl_2 into hexanes instead of methanol three times. The yields of polymers were as follows: **4c**, colorless elastomer, 58%; **4d**, light yellow elastomer, 60%; **4f**, colorless elastomer, 64%; **4g**, white glassy material, 75%. Characterization data for **4a**−**4g** are given in Tables 1 and 2.

General Procedure for the Preparation of the Copolymers $[NSO(NHR')\{NP(NHR)_2\}_2]_n$ (5a−5c). A similar procedure was used for the synthesis of all of the polymers **5a**−**5c** and a general procedure is therefore given with the synthesis of **5a** as a representative example.

To a stirred solution of polymer **2a** (0.84 g, 2.5 mmol) in 200 mL of dry CH_2Cl_2 at 0 °C was added slowly 0.39 mL (5.1 mmol) of allylamine. A white precipitate formed immediately after the addition. After 1 h 2.51 mL (25.0 mmol) of butylamine was added at 0 °C. The reaction solution was warmed to ambient over a period of 2 h, and the reaction was allowed to proceed for 12 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 (twice) and methanol (three times) before drying in vacuum. The yield of **5a**, a colorless elastomer, was 0.80 g (69%). Polymers **5b** and **5c** were prepared by a similar method except that 1.5 and 1.0 equiv of allylamine were added, respectively. The yields of colorless elastomeric polymers **5b** and **5c** were 50−70%. Characterization data for **5a**−**5c** are given in Tables 1 and 2.

Polymers **4a**−**4c** and **4e-4g** appear indefinitely stable to the atmosphere, and no decomposition or molecular weight decline was detected by ^{31}P NMR or GPC after several months in THF solution containing 10% water.

Cross-Linking Studies of Polymers 4d and 5a−5c. The solubility of polymer **4d** and **5a**−**5c** in CH_2Cl_2 solution did not change when left in air over a few months, while films of **4d** and **5a** became insoluble but swellable in CH_2Cl_2 and THF after being left at room temperature in sunlight. A film of **5c** was irradiated for 24 h at 254 nm, only the surface became rigid and insoluble in THF and other conventional organic solvents. After further irradiation of the polymer film for 4 days at 50−60 °C, the color of the polymer film turned from light yellow to brownish. GPC results showed a broadening of the molecular weight distribution consistent with some decomposition of the polymer. In addition, thermal cross-linking studies at 120 °C for 3 days under air led to similar results. The cross-linking of thin film **5b** using UV irradiation and sunlight was carried out for 1 h and 7 days at room temperature, respectively.

Infrared Spectra of Polymers 4a−4g and 5a−5c. The infrared spectra of polymers **4a**−**4g** and **5a**−**5c** contained intense absorptions at 1420 and 1150−1180 cm^{-1}. These were assigned to S═O vibrations. Very intense C−N vibrations were present at 1080−1100 cm^{-1}, and a P═N vibration was also detected at 1220−1280 cm^{-1}. A characteristic S═N vibration was apparent at 730−780 cm^{-1}. For polymer **4d** and **5a**−**5c**, a very weak and sharp band for the C═C vibration of the allylamine side group was apparent at ca. 1650 cm^{-1}. Because of the low intensity of this band it was not possible to follow the cross-linking process by IR effectively.

Light Scattering Measurements for Polymer 4e. Static light scattering experiments in the low-angle regime were used to determine the weight average molecular weight M_w and the second virial coefficient A_2 of a sample of **4e**. The values of

Table 1. NMR Spectral Data for Polymers 4a−4g and 5a−5c

polymer	^{31}P, ppm	^{13}C, ppm[b]	^{1}H, ppm[b]
4a	5.09[a]	30.2 (SNHCH$_3$), 27.2 (PNHCH$_3$)	5.0 (br, s, SNH), 3.3 (br, s, PNH), 2.7 (br, s, SNHC*H*$_3$), 2.5 (br, s, PNHC*H*$_3$)
4b	1.03, 0.93[b]	38.4 (SNH*C*H$_2$CH$_3$), 35.5 (PNH*C*H$_2$CH$_3$), 17.0 (PNHCH$_2$*C*H$_3$), 14.6 (SNHCH$_2$*C*H$_3$)	5.1 (br, s, SNH), 3.4 (br, s, PNH), 3.1 (br, s, SNHC*H*$_2$), 2.9 (br, s, PNHC*H*$_2$), 1.1 (m, CH$_3$)
4c	1.82, 1.55[a]	46.0 (SNH*C*H$_2$CH$_2$CH$_3$), 43.2 (PNH*C*H$_2$CH$_2$CH$_3$), 25.3 (PNHCH$_2$*C*H$_2$CH$_3$), 23.2 (SNHCH$_2$*C*H$_2$CH$_3$), 12.0 (SNHCH$_2$CH$_2$*C*H$_3$), 11.8 (PNHCH$_2$CH$_2$*C*H$_3$)	5.1 (br, s, SNH), 3.4 (br, s, PNH), 3.0 (br, s, SNHC*H*$_2$), 2.8 (br, s, PNHC*H*$_2$), 1.5 (m, C*H*$_2$CH$_3$), 0.9 (m, CH$_3$)
4d	1.20, 1.10[b]	137.3 (PNHCH$_2$*C*H=CH$_2$), $^3J_{\mathrm{PC}} = 3.7$ Hz, $^5J_{\mathrm{PC}} = 2.2$ Hz,[e] 134.9 (SNHCH$_2$*C*H=CH$_2$), 116.4 (SNHCH$_2$CH=*C*H$_2$), 114.7 (PNHCH$_2$CH=*C*H$_2$), 46.5 (SNH*C*H$_2$CH=CH$_2$), 43.5 (PNH*C*H$_2$CH=CH$_2$), $^2J_{\mathrm{PC}} = 9.5$ Hz; $^4J_{\mathrm{PC}} = 2.9$ Hz[e]	5.8 (m, CH$_2$C*H*CH$_2$), 5.1 (m, CH$_2$CHC*H*$_2$), 3.6 (m, SNHC*H*$_2$), 3.4 (br, m, PNHC*H*$_2$)[d]
4e	1.90, 1.61[b]	43.5 (SNH*C*H$_2$CH$_2$CH$_2$CH$_3$), 40.7 (PNH*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.9 (PNHCH$_2$*C*H$_2$CH$_2$CH$_3$), 31.8 (SNHCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.5 (SNHCH$_2$CH$_2$*C*H$_2$CH$_3$), 20.3 (PNHCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.9 (SNHCH$_2$CH$_2$CH$_2$*C*H$_3$), and (PNHCH$_2$CH$_2$CH$_2$*C*H$_3$)	5.0 (br, s, SNH), 3.4 (br, s, PNH), 3.0 (br, s, SNHC*H*$_2$), 2.8 (br, s, PNHC*H*$_2$), 1.3 (br, m, C*H*$_2$C*H*$_2$CH$_3$), 0.8 (m, CH$_3$)
4f	1.78, 1.54[a]	44.4 (SNH*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 41.5 (PNH*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 32.4 (PNHCH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 32.4 (SNHCH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 32.3 (PNHCH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 30.2 (SNHCH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 27.7 (SNHCH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 27.5 (PNHCH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$), 23.2 (PNHCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$), and (SNHCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$), 14.3 (PNHCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), and (SNHCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$)	5.1 (br, s, SNH), 3.4 (br, s, PNH), 3.0 (br, s, SNHC*H*$_2$), 2.8 (br, s, PNHC*H*$_2$), 1.4 (br, m, C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.9 (m, CH$_3$)
4g	−18.69, −18.82[a]	140.4 (ipso-PhNP), 139.1 (ipso-PhNS), 129.7 (*m*-PhNP), 124.6 (*m*-PhNS), 122.2 (*p*-PhNP), 121.4 (*p*-PhNS), 120.3 (*o*-PhNS), 119.1 (*o*-PhNP)	6.9 (br, m, C$_6$H$_5$), 6.2 (br, s, SNH), 1.6 (br, s, PNH)
5a−5c	2.0 (br, m)[c]	137.5 (PNHCH$_2$*C*H=CH$_2$), 135.2 (SNHCH$_2$*C*H=CH$_2$), 116.0 (SNHCH$_2$CH=*C*H$_2$), 114.3 (PNHCH$_2$CH=*C*H$_2$), 46.5 (SNH*C*H$_2$CH=CH$_2$), 43.5 (PNH*C*H$_2$CH=CH$_2$) and (SNH*C*H$_2$CH$_2$CH$_2$CH$_3$), 40.7 (PNH*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.9 (PNHCH$_2$*C*H$_2$CH$_2$CH$_3$), 31.7 (SNHCH$_2$*C*H$_2$CH$_2$CH$_3$), 20.4 (SNHCH$_2$CH$_2$*C*H$_2$CH$_3$), 20.2 (PNHCH$_2$CH$_2$*C*H$_2$CH$_3$), 14.0 (SNHCH$_2$CH$_2$CH$_2$*C*H$_3$) and (PNHCH$_2$CH$_2$CH$_2$*C*H$_3$)	5.8 (m, CH$_2$C*H*=CH$_2$), 5.1 (m, CH$_2$CH=C*H*$_2$), 3.6 (br, s, PN*H*CH$_2$), 3.5 (br, s, PNHC*H*$_2$CH=CH$_2$), 3.0 (br, s, SNHC*H*$_2$CH$_2$CH$_2$CH$_3$), 2.8 (br, s, PNHC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.3 (br, m, C*H*$_2$C*H*$_2$CH$_3$), 0.8 (m, CH$_3$)[d]

[a] In CH$_2$Cl$_2$. [b] In CDCl$_3$. [c] In THF. [d] N*H*CH$_2$CH=CH$_2$ or N*H*CH$_2$CH$_2$CH$_2$CH$_3$ resonances were not identified due to overlap with other resonances. [e] Based on 100.6 MHz ^{13}C NMR spectrum.

M_{w} were obtained from the Rayleigh−Debye relationship, in the limit of low scattering angles, θ:[19]

$$Kc/R_\theta = 1/M_{\mathrm{w}} + 2A_2c \tag{1}$$

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

$$K = [4\pi^2n^2/(N_0\lambda_0{}^4)](\mathrm{d}n/\mathrm{d}c)^2 \tag{2}$$

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 five different concentrations in THF at 23 °C and a value of dn/dc = 0.0600 ± 0.0002 mL/g was obtained.

Results and Discussion

Van de Grampel and co-workers have previously reported that when the cyclic thionylphosphazene **1a** is treated with primary amines, substitution reactions take place at both the phosphorus and the sulfur centers.[20,21] The initial reaction occurs at phosphorus by either a geminal or a nongeminal substitution pathway depending on the amine, solvent, and degree of substitution. The substitution reactions were proposed to proceed *via* an S$_{\mathrm{N}}$2 mechanism at phosphorus with the formation of a five-coordinate intermediate, and *via* an S$_{\mathrm{N}}$1 type process at the sulfur center.[20,21] Aminolysis by primary amines was found to follow the reactivity sequence P(Cl$_2$) > P(Cl, Am) > S(O, Cl) (Am = amino). If considerable steric hindrance was present, as with secondary amines such as diethylamine and piperidine, the reverse sequence S(O, Cl) > P(Cl, Am) was observed.

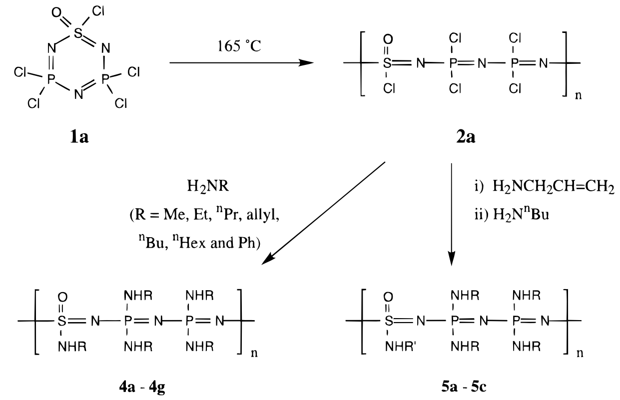
We found previously that the poly(thionylphosphazenes) **2a** and **2b** react with aryloxides exclusively at phosphorus.[10−12] On the basis of the studies of van de Grampel, different substitution patterns might be anticipated for the analogous reactions with amines. In this paper we report the reactions of primary amines with the high molecular weight poly(thionylphosphazene) **2a**.

Synthesis and Structural Characterization of the Poly[(amino)thionylphosphazenes] [NSO(NHR){NP(NHR)$_2$}$_2$]$_n$ (4a−4g). Hydrolytically stable derivatives were prepared by reacting **2a** with a variety of different primary amines. Due to the difficulty of separating the small molecule and cyclic oligomeric byproducts from the polymer in the final precipitation step, pure polymer **2a** was used for the substitution reactions. The reactions proceeded to completion by ^{31}P NMR over 12−48 h at 0−25 °C to yield the colorless glassy material **4a**, the colorless elastomeric materials **4b**, **4c**, **4e**, and **4f**, the light-yellow elastomeric material **4d**, and the white glassy polymer **4g** (Scheme 1). The polymeric products were soluble in polar organic solvents such as CH$_2$Cl$_2$, THF, or dioxane. Interestingly,

Table 2. Analytical and Glass Transition Data for Polymers 4a−4g and 5a−5c

polymers	GPC M_w, M_n	elem anal.	calc/found	T_g (°C)
4a	5.0×10^3, 3.3×10^3	C	19.9/18.8	22
		H	6.7/6.5	
		N	37.1/33.3	
		Cl	0/1.6	
4b	3.7×10^4, 1.6×10^4	C	32.2/31.2	4
		H	8.1/8.1	
		N	30.1/29.2	
		Cl	0/1.4	
4c	4.9×10^4, 2.6×10^4	C	40.7/40.4	6
		H	9.1/8.8	
		N	25.3/25.0	
		Cl	0/0.2	
4d	7.1×10^4, 2.9×10^4	C	41.7/40.5	−40 to −18
		H	7.0/6.8	
		N	25.9/25.1	
		Cl	0/1.2	
4e	4.9×10^4, 2.4×10^4	C	46.9/46.3	−16
		H	9.8/9.6	
		N	21.9/21.8	
		Cl	0/0.9	
4f	7.1×10^4, 3.7×10^4	C	55.2/54.9	−18
		H	10.8/10.4	
		N	17.2/16.8	
		Cl	0/1.2	
4g	1.3×10^5, 7.4×10^4	C	58.8/56.8	82
		H	4.9/4.3	
		N	18.3/18.8	
		Cl	0/1.0	
5a	8.3×10^4, 2.7×10^4			−19
5b	9.6×10^4, 4.8×10^4	C	44.8/44.7	−17
		H	8.9/8.7	
		N	22.8/23.2	
		Cl	0/0.8	
5c	5.4×10^4, 3.0×10^4			−14

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



Polymer	NHR	NHR'
4a	NHMe	
4b	NHEt	
4c	NH^{n}Pr	
4d	$NHCH_2CH{=}CH_2$	
4e	NH^{n}Bu	
4f	NH^{n}Hex	
4g	NHPh	
5a	46 % NH^{n}Bu 54 % $NHCH_2CH{=}CH_2$	NH^{n}Bu
5b	62 % NH^{n}Bu 38 % $NHCH_2CH{=}CH_2$	NH^{n}Bu
5c	72 % NH^{n}Bu 28 % $NHCH_2CH{=}CH_2$	NH^{n}Bu

Table 3. TGA Data for Polymers 4a−4g and 5a−5c (Temperature °C)

polymer	T_{10}[a]	T_{50}[a]	polymer	T_{10}[a]	T_{50}[a]
4a	280	570	**4f**	230	310
4b	230	360	**4g**	280	680
4c	230	350	**5a**	230	370
4d	250	620	**5b**	230	370
4e	240	350	**5c**	270	340

[a] T_{10} and T_{50} correspond to the temperatures at which the polymer sample has lost 10% and 50%, respectively, of its initial mass.

poly[(methylamino)thionylphosphazene] (**4a**) was also soluble in H_2O. The ^{31}P, ^{1}H, and ^{13}C NMR spectroscopic and elemental analysis data for polymers **4a**−**4g** are listed in Table 1 and 2.[22] The molecular weights for the poly[(amino)thionylphosphazenes] were estimated by gel permeation chromatography (GPC) using polystyrene standards for column calibration (Table 2) and in one case, **4e**, by low-angle laser light scattering (see below).[23] The thermal transition behavior of the polymers was investigated by differential scanning calorimetry (DSC) (Table 2). Thermal stability to weight loss was probed by thermogravimetric analysis (TGA) (Table 3).

Characterization of polymers **4a**−**4g** indicated that the reaction of **2** with amines involved replacement of all of the chlorine atoms at both phosphorus and sulfur (Scheme 1). The assignment of the structures of **4a**−**4g** was initially made from a consideration of the NMR data. The ^{13}C NMR spectra of **4a**−**4g** indicated the presence of two environments for the amine groups. This is illustrated for polymer **4e** in Figure 1 where two resonances were detected for each set of nonequivalent carbon atoms present in the butylamine side groups close to the polymer backbone. This observation is consistent with the ^{13}C NMR of aryloxy-substituted poly(carbophosphazenes) and poly(thiophosphazenes) where two sets of carbon resonances were also detected for the substituents on phosphorus and on carbon or sulfur, respectively.[7,8,24,25]

By contrast, poly[(aryloxy)thionylphosphazenes] with aryloxy substituents only at phosphorus showed one set of resonances for each aryloxy group.[10−12] The elemental analysis data (C, H, N, and Cl) for the polymers **4a**−**4g** were consistent with the assigned structures. Small amounts of residual chlorine probably arise from the formation of polymeric ammonium salts of the type $RR'NH_2^+Cl^-$ where the basic poly[(amino)thionylphosphazene] competes with excess amine as an HCl acceptor. Similar behavior has been reported during the aminolysis of poly[(halogeno)carbophosphazenes][26] as well as the classical polyphosphazene $[Cl_2P{=}N]_n$.[27] The ^{31}P NMR spectra showed resonances at a significantly lower field (ca. 11−15 ppm) for **4a**−**4f** compared to polymer **2a** and at a higher field (ca. 8 ppm) for polymer **4g** (Table 1). The infrared spectra of polymers **4a**−**4g** contained strong absorptions for secondary amine N−H stretching vibrations and S=O, C−N, P=N, and S=N vibrations. For polymer **4d**, a C=C vibration of the allylamine side group was also detected.

In contrast to the reaction of **2a** with amines, regioselective nucleophilic substitution of **2a** and **2b** is detected for the corresponding reaction with aryloxides where the sulfur−halogen bonds are left unsubstituted. It therefore appears that primary amines show stronger nucleophilicity with respect to substitution at the sulfur(VI) center.

^{31}P NMR Spectra of 4a−4g: Evidence for Atactic Stereochemistry. The chlorinated polymer **2a** and the

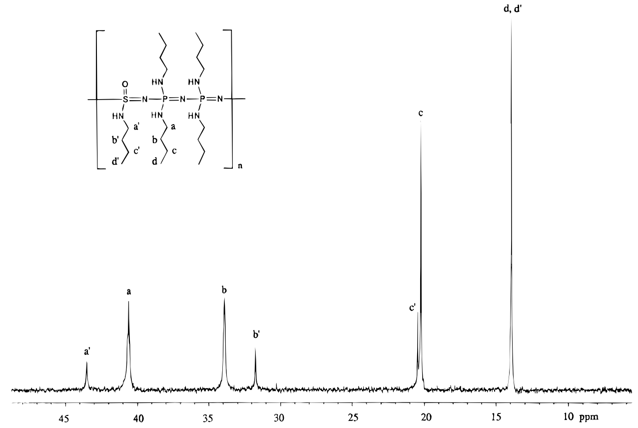


Figure 1. 100.6 MHz ^{13}C NMR of polymer **4e** in $CDCl_3$.

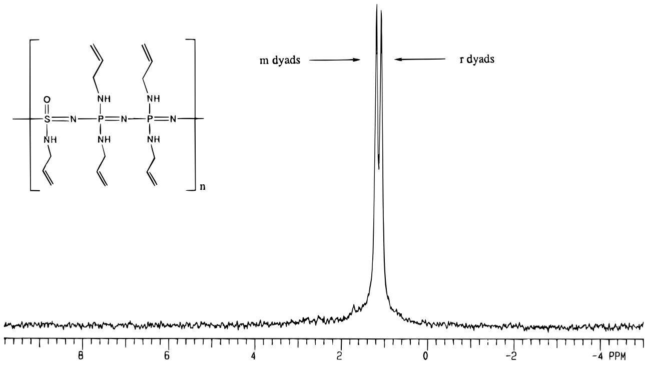


Figure 2. 121.4 MHz ^{31}P NMR of polymer **4d** in CH_2Cl_2.

methylamine-substituted polymer **4a** showed a single singlet ^{31}P NMR resonance whereas polymers **4b-4g** all displayed two singlet resonances with a ca. 1:1 ratio (as shown in Figure 2 for polymer **4d**). Recent studies of cyclic S(VI)−N−P oligomers showed that cyclic thionylphosphazene 12-membered rings exist as *cis* or *trans* isomers depending on the orientation of the S=O bonds relative to one another.[14] In the linear polymer, a similar situation should exist and the S=O bonds should also possess a *cis* or *trans* configuration relative to their neighbors within each −S=N−P=N−P=N− repeat unit. One would expect that the phosphorus atom within a *cis* environment would possess a different ^{31}P NMR chemical shift in comparison to those in a *trans* environment. Thus, poly(thionylphosphazenes) which possess sulfur(VI) stereocenters should possess tacticity and three tacticity patterns might be present, as shown in Figure 3.[28] In theory, the ^{31}P NMR spectra for isotactic (all *cis*, ···mmm···) and syndiotactic (all *trans*, ···rrr···) poly(thionylphosphazenes) should each possess only a singlet resonance due to the equivalent environments for the phosphorus nuclei. Significantly, if the difference between the environments of the phosphorus nuclei in the *cis* and *trans* configurations (m and r diads) were large enough, different chemical shifts for these singlet resonances would be anticipated. Thus, atactic poly(thionylphosphazenes) with mixed *cis* and *trans* configurations might be expected to show two ^{31}P NMR resonances. The fully halogenated polymers **2a** and **2b**, the aryloxy-substituted polymers **3** with halogen atoms at sulfur, and **4a** with methylamino substituents at sulfur showed a singlet by ^{31}P NMR. This is probably because with a small halogen or methylamino substituent at sulfur, the difference between phosphorus environments in the *cis* or *trans* configurations (m and r diads) is probably too small to be detected by ^{31}P NMR.

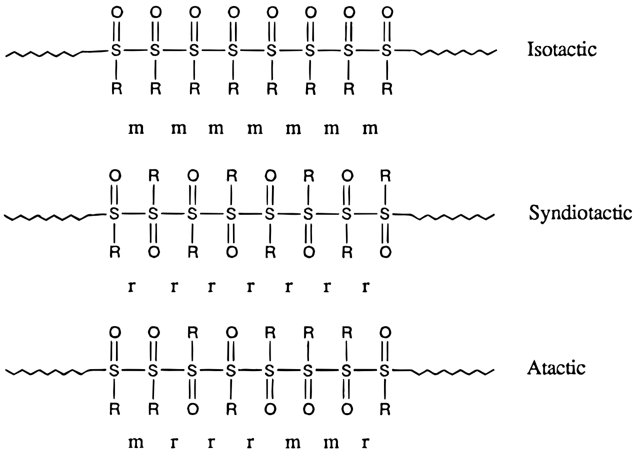


Figure 3. Possible tacticity patterns for poly(thionylphosphazenes) (where N and P fragments are omitted for clarity).

However, in the case of bulkier amines such as ethyl, propyl, or even larger substituents, polymers **4b**−**4g** all showed two different phosphorus environments by ^{31}P NMR. We therefore have assigned an atactic stereochemistry to these materials. This is logical as the ring-opening process involved in the polymerization of **1a** is unlikely to be stereoselective and then the most plausible form of the product should thus possess repeat units with a random distribution of *cis* and *trans* configurations (m and r diads). The polymer product should presumably possess a ca. 1:1 ratio of *cis* and *trans* repeat units which is consistent with the observed ca. 1:1 ratio of the two singlet resonances present in the ^{31}P NMR spectra for polymers **4b**−**4g**. In addition, the two singlets were separated by 0.10−0.29 ppm (in CH_2Cl_2) with no general correlation between their separation and the stepwise increase of the length and bulkiness of the side groups. On the basis of studies of cyclic thionylphosphazene oligomers we tentatively assigned the resonance at lower field to the *cis* configuration (m diad) and the higher field resonance to *trans* (r diad) repeat units (see Figure 2).[14]

Thermal and UV-Induced Cross-Linking of 4d. Polymer **4d** with allylamine side groups was found to undergo rapid heat- or light-induced cross-linking in the solid state. Elastomeric films of **4d** became rigid and insoluble after being exposed to light over 12 h or UV light irradiation at 254 nm for 1 h at 25 °C under N_2, or upon heating to 200 °C for a few minutes under air or N_2. Cross-linked **4d** showed a significant increase and broadening of the glass transition temperature from −40 to ca. −16 °C. The cross-linking of the allylamine-substituted phosphazene trimer $[NP(NHCH_2CH{=}CH_2)_2]_3$ and tetramer $[NP(NHCH_2CH{=}CH_2)_2]_4$ and allylamine-containing polymer $[NPR_x(NHCH_2CH{=}CH_2)_y]_n$ ($x + y = 2$) has been recently studied by Allcock and coworkers.[29,30] Studies have shown that allyl-substituted polyphosphazenes can also be readily cross-linked by an electron beam or γ-radiation.

Synthesis, Characterization, and Cross-Linking Studies of the Mixed-Substituent Poly[(amino)thionylphosphazenes] $[NSO(NHR')\{NP(NHR)_2\}_2]_n$ (5a−5c). In order to prepare cross-linkable, rubbery poly(thionylphosphazenes], mixed-substituent poly[(amino)thionylphosphazenes] **5a**−**5c** were prepared as light yellow elastomeric products via the reaction of **2a** sequentially with allylamine and butylamine (Scheme 1). According to the integration of the ^{1}H NMR spectrum, elemental analysis, and the ^{13}C NMR spectrum

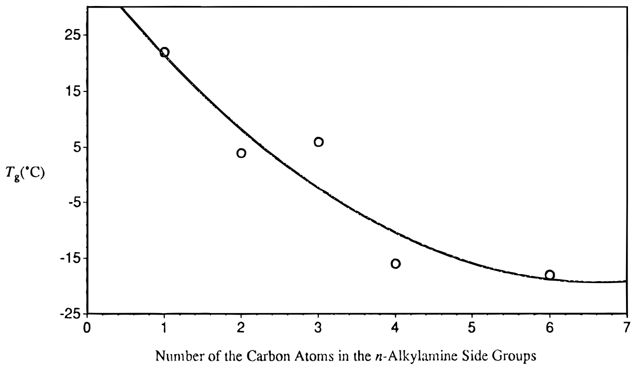


Figure 4. Plot of number of the carbon atoms in the *n*-alkylamine side groups vs the T_g (°C) of the corresponding poly[(amino)thionylphosphazenes].

of the product **5a**, the halogen atoms from ca. two P–Cl bonds in each polymer repeat unit were replaced by allylamino substituents and no substitution occurred at sulfur. A broad multiplet, shifted ca. 12 ppm to lower field compared to the case of polymer **2a**, was detected by ^{31}P NMR. The breadth of this resonance is attributed to the complex side group structure.

Polymer **5a** with ca. 2 allylamino substituents per repeat unit apparently cross-linked readily in the solid state upon exposure to sunlight at room temperature for 12 h. In contrast, polymer **5c** with only ca. 1 allylamine substituent per repeat unit was resistant to cross-linking even under prolonged UV irradiation. We then synthesized polymer **5b** with ca. 1.5 allylamino substituents per repeat unit. This particular polymer showed a modest cross-linking rate upon UV irradiation and the control of the cross-linking was much easier. A cross-linked polymer film of **5b** was then obtained by UV irradiation at 254 nm for 1 h or under sunlight for 7 days. The differences in the cross-linking behavior of **5a**–**5c** can be attributed to the free radical reactions of the allyl groups which are likely to be greatly influenced by steric effects. Thus, in polymer **5c**, the cross-linkable allylamino groups are probably effectively shielded from one another by the butylamine groups.

Thermal Transition Behavior of the Poly[(amino)thionylphosphazenes] 4a–4g and 5a–5c. In order to provide further characterization and to gain insight into the factors influencing the conformational flexibility of poly[(amino)thionylphosphazenes] the thermal transition behavior of the amino polymers **4a**–**4g** and **5a**–**5c** was studied by DSC. The T_g values for these polymers are listed in Table 2. As expected, the replacement of the chlorine atoms at phosphorus in **2a** by the bulkier amino groups such as aniline leads to a very significant increase in T_g from −46 to +82 °C. The un-cross-linked allylamino polymer **4d** had the lowest T_g of −40 °C. The *n*-HexNH, *n*-BuNH, *n*-PrNH, EtNH, and MeNH polymers possessed T_g's of −18, −16, +6, +4, and +22 °C, respectively (Table 2). In general, the longer the *n*-alkylamino side chain, the lower the glass transition temperature of the poly[(amino)thionylphosphazene] (Figure 4). This effect arises from the free volume increase derived from the presence of longer side groups which push the polymer chains further apart.

The classical polyphosphazene with methylamine side groups ([NP(NHMe)$_2$]$_n$) possesses a T_g of 14 °C.[31] This is lower than that of the corresponding poly[(amino)-thionylphosphazene] **4a** (T_g = 22 °C). In contrast, with bulkier side groups such as butylamine and aniline the polyphosphazene has a higher glass transition temperature than the analogous poly(thionylphosphazene) ([NP(NH^{n}Bu)$_2$]$_n$, T_g = 8 °C, [NP(NHPh)$_2$]$_n$, T_g = 91–105 °C).[31,32,33] However, the T_g values of the *n*-propylamine-substituted polyphosphazene ([NP(NH^{n}Pr)$_2$]$_n$, T_g = 4 °C) and the corresponding poly(thionylphosphazene) (T_g = 6 °C) are similar. As previously proposed for poly[(aryloxy)thionylphosphazenes],[12] two competing effects probably determine the T_g of poly[(amino)thionylphosphazenes] relative to their classical polyphosphazene analogues. First, the presence of the highly polar S=O group tends to decrease the skeletal flexibility relative to classical polyphosphazenes. Secondly, the smaller number of amino substituents in poly[(amino)thionylphosphazenes] (five per six skeletal atom repeat unit) compared to classical polyphosphazenes (six per six skeletal atom repeat unit) tends to increase the skeletal flexibility. With small substituents such as methylamine, the first effect is the most significant, resulting in a higher glass transition temperature for the poly[(amino)thionylphosphazene]. On the other hand, with bulkier side groups such as *n*-butyamine or aniline, the second effect is dominant as the S=O groups are sterically shielded from one another and the poly[(amino)thionylphosphazene] has the lower T_g. The two effects balance each other in the *n*-propylamino-substituted cases, and the polyphosphazene and the poly(thionylphosphazene) have similar T_g's.

Polymers **5a**–**5c** with mixed allylamine and *n*-butylamine substituents have T_g's of −14 to −19 °C, which is similar to that of the pure butylamino homopolymer **4e** and is much higher than the un-cross-linked allylamine-substituted polymer **4d** (−40 °C). On the basis of studies of poly(organophosphazenes), the presence of more than one type of side group leads to lower glass transition temperatures than either of the single-substituent polymers, due to the loss of symmetry and packing efficiency and the consequential increase in free volume.[1] This general rule does not appear to apply for these particular poly[(amino)thionylphosphazenes].

None of the polymers **4a**–**4g** or **5a**–**5c** showed evidence for a melting transition which suggested that they are amorphous. This was confirmed for **4b** and **4c** by X-ray powder diffraction studies which gave featureless diffractograms characteristic of amorphous materials. This is similar to the situation for the analogous classical poly[(amino)phosphazenes] which are generally regarded as amorphous polymers.[31] Also, in the case of poly[(aryloxy)thionylphosphazenes] **3**, the introduction of a sulfur(VI) atom bearing an oxygen and chlorine substituent introduces sufficient asymmetry to the polymer structure to also hinder side group stacking and crystallization.

Thermal Stability of Poly[(amino)thionylphosphazenes]. Thermogravimetric analysis data for polymers **4a**–**4g** and **5a**–**5c** are listed in Table 3, and selected TGA traces are shown in Figure 5. For polymers **4b**–**4c**, **4e**, **4f**, and **5a**–**5c**, a ca. 35% weight loss took place at ca. 250 °C followed by a second major weight loss at ca. 650 °C with ca. 30% of their original weight left after 650 °C. Above 800 °C, less than 10% of the original weight of these samples remained. Among all of the TGA traces, those of polymers bearing methylamino (**4a)**, anilino (**4g)**, and allylamino (**4d)** substituents showed significant differences in comparison to the others. For polymer **4a**, a weight loss of ca. 40% was detected from ca. 250 to 400 °C. The second major weight loss (relatively gradual) did not start until 600 °C, and at 940 °C 20% of the original weight still

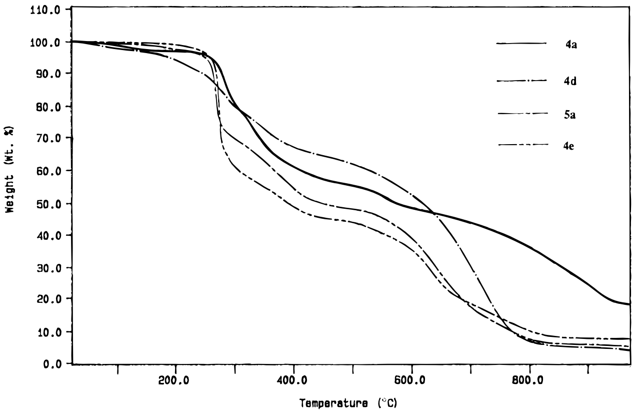


Figure 5. Thermogravimetric analysis of selected poly[(amino)thionylphosphazenes].

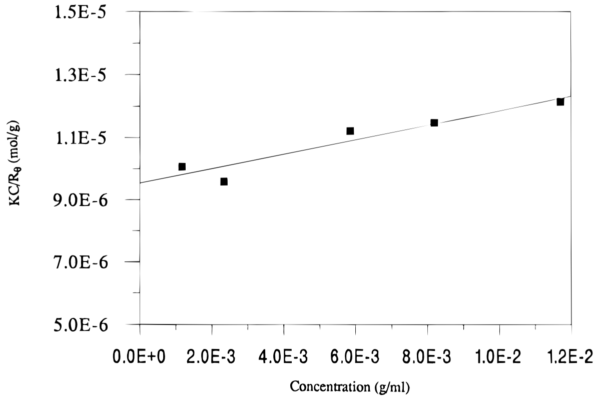


Figure 6. Low angle laser light scattering results for polymer **4e**.

remained. It is most likely that a cross-linking process was initiated at temperatures below 200 °C which led to stabilization to weight loss at higher temperatures. Polymer **4g** possessed a TGA trace similar to that of **4a** with the difference that only 13% of the original weight was still left at 940 °C. It seems the bulky anilino substituents increase the stability of the poly(thionylphosphazene) at moderate temperatures. Polymer **4d** suffered a gradual weight loss of ca. 40% from ca. 200 to ca. 400 °C and a second, significant weight loss (of ca. 45%) starting at ca. 600 °C and ending at 800 °C. A thermally-induced cross-linking process may have taken place which stabilized the polymer to weight loss from ca. 300 to 600 °C. This is also supported by the measurements of polymers **5a** and **5b** with 2 and 1.5 allylamine side groups per repeat unit, which showed a higher percentage of material left from 300 to 600 °C as compared to the butylamine-substituted polymer **4e**. Presumably, a similar thermally-induced cross-linking process takes place which leads to greater weight retention up to ca. 600 °C. However, ultimately, similar decomposition occurs above 650 °C, as shown in Figure 5 for the TGA traces of polymers **4e** and **5a**.

Light Scattering Measurements for Polymer 4e in THF. In order to investigate the solution properties of poly[(amino)thionylphosphazenes] and to provide an absolute determination of molecular weight, low-angle laser light scattering (LALLS) studies were carried out on THF solutions of polymer **4e**, which was selected as a representative example.

The results of LALLS measurements for polymer **4e** are shown in Figure 6 as a function of the solution concentration. The value of M_w was determined from the fitted intercept of the straight line in Figure 6 with the y-axis and was found to be $(1.05 \pm 0.03) \times 10^5$. There is a dramatic difference between the absolute M_w obtained from LALLS and that obtained from GPC measurements, $M_w = 4.9 \times 10^4$. GPC is a size-exclusion chromatographic technique and requires calibration with monodisperse fractions of known molecular weight to determine M_w.[34] Often a calibration curve for polystyrene is utilized even for polymers with very different structures. In this case, the molecular weight obtained by GPC is a relative quantity and is called the "polystyrene effective molecular weight". An absolute value for M_w can be obtained by GPC if the universal calibration technique is used[34] or if the column is calibrated with the polymer being studied. GPC separation is based on the effective hydrodynamic size, where the effective hydrodynamic size of a polystyrene random coil of a given M_w in a given solvent is not expected to be the same as a coil of a different polymer under the same conditions. Thus GPC underestimates the molecular weight of polymer **4e** due to the differences in the coil sizes if polystyrene column calibration is used. The second virial coefficient was determined from the fitted slope of the line in Figure 6, and a value of $A_2 = (1.1 \pm 0.2) \times 10^{-4}$ mol cm^{-2} g^{-2} was obtained. This suggested a favorable thermodynamic interaction between the polymer and the solvent.

Summary

A series of poly[(amino)thionylphosphazenes] have been synthesized and characterized. In contrast to the situation with aryloxide nucleophiles, substitution reactions of **2a** by primary amines replaced both the halogen substituents at phosphorus and at sulfur. Analysis of the poly[(amino)thionylphosphazenes], by ^{31}P NMR showed that these materials possess an atactic structure. The poly[(amino)thionylphosphazenes] were hydrolytically stable and the methylamino derivative **4a** is even soluble in water. In addition, poly[(amino)thionylphosphazenes] show thermal transition behavior different from that of the corresponding classical polyphosphazenes and in some cases possess greater free volume. Further studies of these and related materials are in progress, and our results will be reported in the near future.

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(22) Upon addition of a stronger base such as triethylamine as an HCl acceptor, the solution of polymer **2a** turned brown, and decomposition was evident by ^{31}P NMR and GPC analysis after reaction with butylamine. Thus all the aminolysis reactions were carried out without the addition of HCl acceptors other than the excess amine used for the substitution reaction.

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