Thionylphosphazene Monomers and Polymers—The Synthesis of Alternating Copolymers of Phosphazenes and Oxothiazenes**

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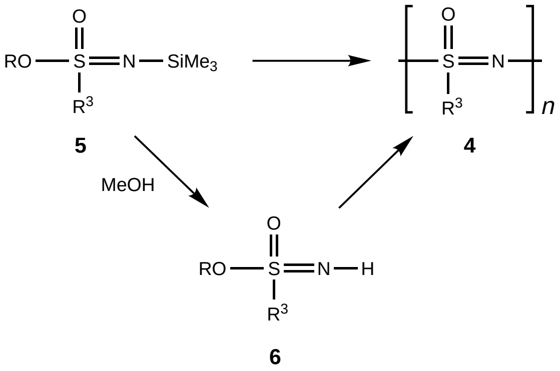
Inorganic polymers with a backbone of phosphorus, sulfur, and nitrogen atoms are a recent addition to the growing list of novel inorganic macromolecules.[1, 2] Polymers with sulfur(IV) centers in the backbone, the polythiophosphazenes, were first reported by Allcock et al. in 1990;[2a] whereas the more stable S^{VI}-based polymers, the polythionylphosphazenes (**1**), were prepared by Manners et al. in 1991.[2b] Application of the polythionylphosphazenes in phosphorescent oxygen sensors have recently been demonstrated.[3] One class of phosphorus-sulfur-nitrogen based polymers that have so far eluded researchers in this field are polymers in which the side groups are bound by P–C or S–C bonds. Herein we report the first synthesis of a polythionylphosphazene in which the substituents at phosphorus and sulfur are either alkyl or aryl groups.

Phosphazene polymers, $[P(R^1)(R^2){=}N]_n$ **2**, with alkyl or aryl side groups were first prepared in the mid-1980s[4] by the polymerization of a *N*-silylphosphoranimine, $RO{-}P(R^1)(R^2){=}N{-}SiMe_3$ (**3**) ($R = CH_2CF_3$ or Ar; R^1, R^2 = alkyl or aryl), with elimination of $ROSiMe_3$.[4b] Polymers (**2**) of well-defined molecular weight have recently been prepared by a living cationic polymerization.[5] Analogous sulfur-nitrogen based polymers, the polyoxothiazenes, $[S(O)(R^3){=}N]_n$ (**4**), can be prepared by the polymerization of an *N*-silylsulfonimidate, $RO{-}S(O)(R^3){=}N{-}SiMe_3$ (**5**), or a sulfonimine, $RO{-}S(O)(R^3){=}NH$ (**6**).[6]



Clearly, the preparation of polythionylphosphazenes with alkyl or aryl side groups can be envisaged by the copolymerization of *N*-silylphosphoranimines (**3**) and *N*-silylsulfonimidates (**5**). Unfortunately, heating mixtures of **3** and **5** at over 140 °C produces an inseparable mixture of oligomers of low molecular weight and cyclic compounds. However, if equimolar amounts of **3** and **5** are heated at between 80 and 140 °C, then a regioselective coupling of the two compounds can be accomplished. The reaction of **3b** ($R = CH_2CF_3$, $R^1 = Ph$, $R^2 = Me$) and **5b** ($R = CH_2CF_3$, $R^3 = Ph$) has been monitored by ^{31}P NMR spectroscopy. The spectra in C_6D_6 are collected in Figure 1 which shows that a slow decrease in the signal at $\delta = 20$ for **3b** is accompanied by the growth of two new singlets at $\delta = 39.6$ and 40.0. These peaks can be assigned to the formation of the new thionylphosphazene $CF_3CH_2O{-}P(Me)(Ph){=}N{-}S(O)(Ph){=}N{-}SiMe_3$ (**7b**). The presence of two signals of equal intensity can be attributed to the presence of equimolar amounts of two diastereomers, as **7b** contains both an asymmetric phosphorus and an asymmetric sulfur atom.

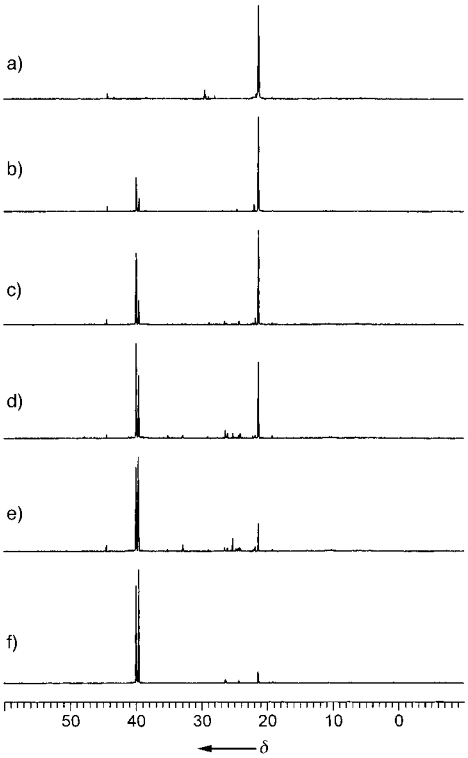


Figure 1. ^{31}P NMR spectra (101 MHz, C_6D_6) of the reaction between **3b** and **5b** when heated at 120 °C for a) 3, b) 9, c) 12, d) 18, and e) 21 days. f) ^{31}P NMR spectrum of **7b**, which was isolated by extraction of the reaction mixture with hexane.

A number of examples of these compounds **7a**–**7d** have been prepared and they are typically isolated by vacuum distillation in moderate yields as colorless liquids or crystalline solids at room temperature. The structures of these compounds have been fully characterized by spectroscopic and analytical techniques, and the solid-state structure of **7c** has been determined by *X*-ray crystallography (Figure 2).[7]

The single-crystal X-ray structure analysis of **7c** confirmed that the coupling reaction of **3** and **5** is highly regioselective and that it is the $SiMe_3$ group of the phosphoranimine and the trifluoroethoxy group of the sulfonimidate that is lost upon reaction. The selectivity of this reaction is determined by the greater nucleophilicity of the nitrogen atom of the phosphor-

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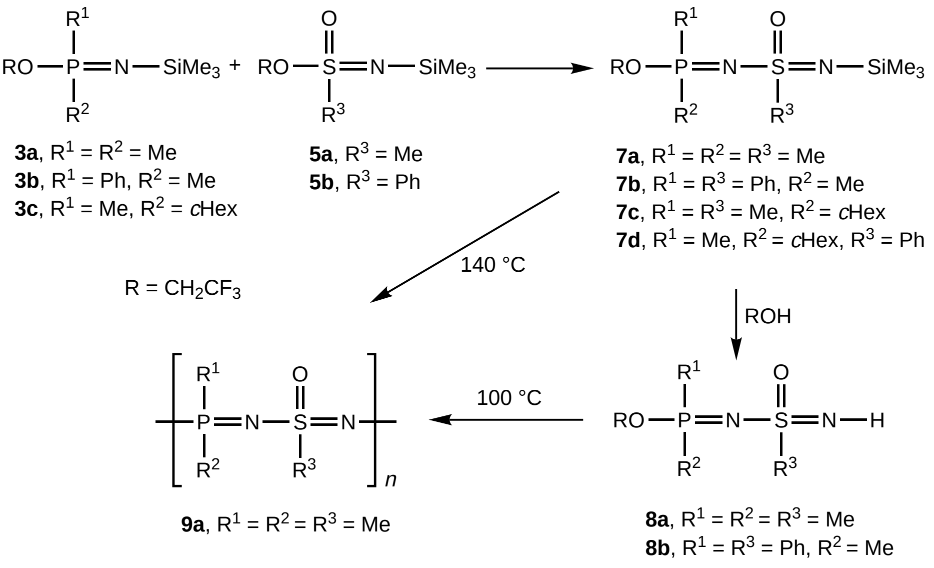

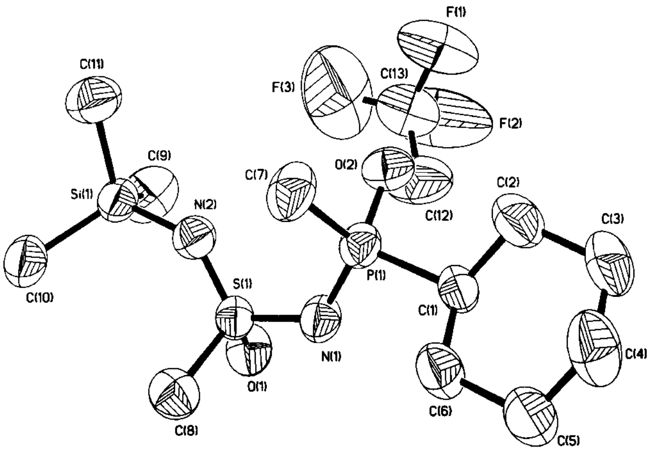

Figure 2. Solid-state structure of **7c**. Selected bond lengths [Å] and angles [°] (estimated standard deviations in parentheses): S(1)–O(1) 1.448(3), S(1)–N(2) 1.499(4), S(1)–N(1) 1.598(3), S(1)–C(8) 1.760(5), Si(1)–N(2) 1.712(4), Si(1)–C(9) 1.848(6), Si(1)–C(11) 1.850(5), Si(1)–C(10) 1.855(5), P(1)–N(1) 1.576(4), P(1)–O(2) 1.591(4), P(1)–C(7) 1.787(4), P(1)–C(1) 1.800(4), O(2)–C(12) 1.404(7), C(1)–C(6) 1.525(6), C(1)–C(2) 1.534(6), C(2)–C(3) 1.519(7), C(3)–C(4) 1.523(8), C(4)–C(5) 1.520(7), C(5)–C(6) 1.511(7); O(1)-S(1)-N(2) 118.8(2), O(1)-S(1)-N(1) 108.3(2), N(2)-S(1)-N(1) 110.4(2), O(1)-S(1)-C(8) 105.0(2), N(2)-S(1)-C(8) 110.5(2), N(1)-S(1)-C(8) 102.4(2), N(2)-Si(1)-C(9) 111.5(2), N(2)-Si(1)-C(11) 105.8(2), C(9)-Si(1)-C(11) 110.6(3), N(2)-Si(1)-C(10) 111.3(2), C(9)-Si(1)-C(10) 109.1(3), C(11)-Si(1)-C(10) 108.5(3), N(1)-P(1)-O(2) 115.4(2), N(1)-P(1)-C(7) 117.6(2), O(2)-P(1)-C(7) 100.1(2), N(1)-P(1)-C(1) 105.8(2), O(2)-P(1)-C(1) 107.4(2), C(7)-P(1)-C(1) 110.2(2), P(1)-N(1)-S(1) 126.8(2), S(1)-N(2)-Si(1) 130.5(2), C1(2)-O(2)-P(1) 122.6(3), C(6)-C(1)-C(2) 110.9(4), C(6)-C(1)-P(1) 112.1(3), C(2)-C(1)-P(1) 114.3(3), C(3)-C(2)-C(1) 110.7(4), C(2)-C(3)-C(4) 111.8(4), C(5)-C(4)-C(3) 110.4(4), C(6)-C(5)-C(4) 111.0(5), C(5)-C(6)-C(1) 111.7(4), O(2)-C(12)-C(13) 110.4(5).

animine over that of the nitrogen atom of the sulfonimidate. The geometry around sulfur and phosphorus in **7c** is pseudotetrahedral with bond angles varying from 102.4(2) to 118.8(2)° and 100.1(2) to 117.6(2)°, respectively. The N-S-N and P-N-S angles are 110.4(2)° and 126.8(2)°, which are consistent with similar N-S-N and P-N-S angles recorded for cyclic thionylphosphazenes.[8] The S–N bond lengths of **7c** are 1.499(4) and 1.598(3) Å, the P–N bond length is 1.576(4) Å. These values lie between those of single and double bonds but are more indicative of double- rather than single-bond character.[8]

The thionylphosphazenes **7a**–**7d** are highly reactive and were rapidly hydrolyzed on exposure to the atmosphere. Reaction of **7a** or **7b** with trifluoroethanol at room temperature resulted in replacement of the trimethylsilyl group with a proton to give the thionylphosphazenes $CF_3CH_2O{-}PMe(R^1){=}N{-}S(O)(R^3){=}N{-}H$ **8a** ($R^1 = R^3 = Me$) or **8b** ($R^1 = R^3 = Ph$), respectively. The functional groups of the thionylphosphazenes **7** and **8** are analogous to those of the oxothiazene monomers **5** and **6**, and as such may undergo polymerization in a similar fashion by elimination of $CF_3CH_2OSiMe_3$ or CF_3CH_2OH, respectively.[6] Initial polymerization studies on the permethyl-substituted thionylphosphazenes **7a** and **8a** suggest that this is indeed the case. Heating **7a** at 140 °C in a thick-walled evacuated ampoule resulted in an increase in viscosity of the tube contents and the formation of two liquid layers. After one week the tube was opened and a volatile component removed under vacuum. This was identified as $CF_3CH_2OSiMe_3$ by ^1H NMR spectroscopy. The solid contents of the polymerization tube were dissolved in CH_2Cl_2 and precipitated into stirred toluene. A white solid was recovered from the toluene which was redissolved in CH_2Cl_2 and reprecipitated into toluene. This process was repeated at least three times and the resulting white powder was finally dried under high vacuum at 50 °C overnight. The polymeric product was soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, and DMSO, and it was also very soluble in water. The polymer structure was assigned by spectroscopic and analytical techniques as $[PMe_2{=}N{-}S(O)Me{=}N]_n$ (**9a**), an alternating copolymer of dimethyl phosphazene and methyloxothiazene units. This is the first polythionylphosphazene with alkyl or aryl side groups and the first inorganic polymer with a repeating unit of one sulfur, one phosphorus, and two nitrogen atoms.

Polymerization of thionylphosphazene **8a** occurred rapidly on heating at 100 °C in a nitrogen-filled flask. The reaction was accelerated by decreasing the pressure to remove the trifluoroethanol produced on condensation. The reaction was complete within three to four hours and the polymer isolated from this reaction was essentially identical to that obtained on polymerization of **7a**. The molecular weight of polymer **9a** was estimated by gel permeation chromatography to be in the low thousands with an average degree of polymerization (DP) of around 30. The low molecular weight of **9a** explained the presence of small peaks in the ^{31}P NMR spectrum at $\delta = 59.2$, 24.2, 22.3, 21.7, 19.1 and 16.3 (Figure 3). These peaks were assigned to the polymer end groups, as analogous signals have been observed in the ^{31}P NMR spectrum of oligomeric $[NPCl_2]_n$ prepared by a cationic living polymerization.[5a]

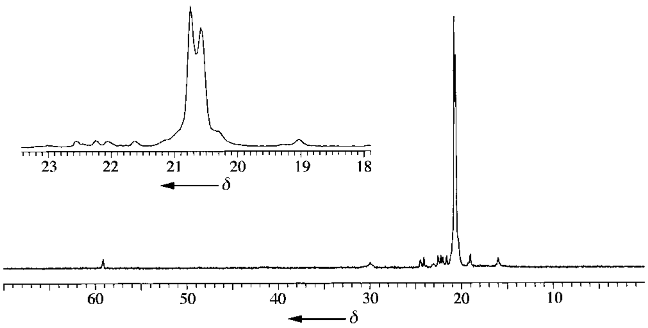

Figure 3. ^{31}P NMR spectra (162 MHz, $CDCl_3$) of **9a**. Insert: Expansion of the region $18 < \delta < 23$.

Identification of the polymer end groups and confirmation of the backbone structure was obtained by FAB mass spectrometry. Intense ions corresponding to $CF_3CH_2O[PMe_2{=}N{-}S(O)Me{=}N]_nH$ were detected up to the detection limit of the instrument (ca. 3800 Da). Integration of the polymer end groups in the ^{31}P and ^{1}H NMR spectra gave an absolute molecular weight (M_n) for **9a** of 8000 (DP = 53). The backbone structure of **9a** is an exact alternating copolymer of dimethylphosphazene and methyloxothiazene units. The phosphorus atoms are adjacent to sulfur atoms with either isotactic (a *meso* diad) or syndiotactic (a *rac* diad) placement of the two methyl groups. These phosphorus environments are inequivalent as two major peaks are detected in the ^{31}P NMR spectrum ($CDCl_3$) of **9a** at $\delta = 20.57$ and 20.74. The intensities of these signals are very similar indicating that the polymer backbone has equal amounts of *meso* and *rac* placements and hence is completely atactic. The atacticity was confirmed by the ^{1}H and ^{13}C NMR spectra of **9a** which showed three doublets in a 1:2:1 ratio for the methyl groups attached to phosphorus. The intense doublet is assigned to the equivalent methyl groups of the *rac* diad and the less intense doublets to the inequivalent methyl groups of the *meso* diad.[4b]

In summary, *N*-silylphosphoranimines **3** and *N*-silylsulfonimidates **5** can be regioselectively coupled to give *N*-silylthionylphosphazenes **7**. Initial studies show that the methyl-substituted derivatives **7a** and **8a** can be thermally polymerized to give an alternating copolymer of dimethylphosphazene and methyloxothiazene units. This polymer, **9a**, is the first polythionylphosphazene in which the side groups are bound by P–C and S–C bonds and the first inorganic polymer with a repeating unit of one sulfur, one phosphorus, and two nitrogen atoms.

Experimental Section

7: *N*-Silylphosphoranimine **3a** (5.05 g, 20 mmol) and *N*-silylsulfonimidate **5a** (5.06 g, 20 mmol) were heated in a round-bottomed flask at 140 °C for four days. The volatile products of the reaction were removed under vacuum and characterized by ^{1}H NMR spectroscopy as $CF_3CH_2OSiMe_3$. The liquid residue was extracted with toluene. The toluene was removed at reduced pressure and the resulting viscous brown oil was distilled (60 °C, 0.01 mmHg) to give a colorless liquid (**7a**) in 55 % yield (3.63 g, 11 mmol). Postive-ion FAB-MS: *m/z* (%): 324 (27) [M^+], 309 (100, [$M^+ - Me$]), 232 (65, [$M^+ - FSiMe_3$]), 225 (9, [$M^+ - CF_3CH_2O$]); ^{31}P NMR (101 MHz, C_6D_6): $\delta = 52.7$; ^{1}H NMR (250 MHz, C_6D_6): $\delta = 0.26$ (s, 6H; $SiMe_3$), 1.21, 1.26 (2d, $J_{P,H} = 11$ Hz, 6H; PMe), 2.80 (d, $^{4}J_{P,H} = 3$ Hz, 3H; SMe), 4.02, 4.48 (2ddq, $J_{H,H} = 9$ Hz, $J_{F,H} = 17$ Hz, $J_{P,H} = 4$ Hz, 2H; CH_2CF_3); ^{13}C NMR (63 MHz, C_6D_6): $\delta = 1.85$ (s, $SiMe_3$), 13.95, 15.45 (2d, $J_{P,C} = 25$ Hz; PMe), 49.46 (d, $^{3}J_{P,C} = 6$ Hz; SMe), 62.58 (dq, $J_{F,C} = 37$ Hz, $J_{P,C} = 6$ Hz; $\mathit{C}H_2CF_3$), 122.7 (dq, $J_{F,C} = 278$ Hz, $J_{P,C} = 10$ Hz; $CH_2\mathit{C}F_3$). Compounds **7b-7d** were prepared in a similar fashion and isolated by distillation in 39 % (140 °C, 0.03 mmHg), 35 % (104 °C, 0.02mmHg), and 45 % (162 °C, 0.01 mmHg) yield.

9a: Thionylphosphazene **7a** (7.08 g, 22 mmol) was sealed in an evacuated glass ampoule and heated to 140 °C for 16 days. The tube was opened and the volatile components removed under vacuum. These were identified as $CF_3CH_2OSiMe_3$ by ^{1}H NMR spectroscopy. The solid contents were dissolved in CH_2Cl_2 and precipitated into stirred toluene. A white solid was recovered from the toluene which was redissolved in CH_2Cl_2 and reprecipitated into toluene. This process was repeated at least three times, and the resulting white powder (1.02 g, 25 %) was finally dried under vacuum at 50 °C overnight. ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 20.57$, 20.74; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.68$ (d, $J_{P,H} = 14$ Hz, 3H; *meso*-PMe_2), 1.73 (d, $J_{P,H} = 14$ Hz, 6H; *rac*-PMe_2), 1.77 (d, $J_{P,H} = 14$ Hz, 3H; *meso*-PMe_2), 3.17 (s, 6H; SMe); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 18.44$ (d, $J_{P,C} = 84$ Hz; *meso*-PMe_2), 18.50 (d, $J_{P,C} = 90$ Hz; *rac*-PMe_2), 18.64 (d, $J_{P,C} = 95$ Hz; *meso*-PMe_2), 48.75 (s, SMe). Elemental analysis: calcd: C 23.68, H 5.92, N 18.42, S 21.05; found: C 23.24, H 6.03, N 16.24, S 21.72. Thionylphosphazene **8a** (6.28 g, 25 mmol) polymerizes on heating at 100 °C to give polymer **9a** (2.0 g, 25 %), identical to that prepared from **7a**.

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[7] Crystal data for **7c**: single crystals crystallize from toluene/hexane as colorless blocks; crystal dimensions $0.63 \times 0.44 \times 0.32$ mm, triclinic, space group $P\bar{1}$, $a = 10.224(2)$, $b = 10.371(2)$, $c = 10.739(2)$ Å, $\alpha = 100.51(2)$, $\beta = 100.38(2)$, $\gamma = 107.93(2)^\circ$, $U = 1030.7(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.265$ g cm^{-3}. Measuring range $3.5 < 2\theta < 45^\circ$, 3116 reflections measured, 1946 observed with $|F|/\sigma(|F|) > 4.0$. Refinement converged at a final $R = 0.0543$ ($wR_2 = 0.1520$) for all 2565 unique data, 208 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101046. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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