Synthesis and Metal Coordination of Thioether Containing Cyclo- and Poly(organophosphazenes)

URSULA DIEFENBACH,[1] ANGELA M. CANNON,[2] BRIGITTE E. STROMBURG,[1] DAVID L. OLMEIJER,[2] HARRY R. ALLCOCK[2]

[1] Fachbereich Chemie, Biologie, Pharmazie; Institut für Chemie, Anorganische und Analytische Chemie; Freie Universität Berlin, Fabeckstr. 34-36, 14195 Berlin, Germany

[2] Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

ABSTRACT: Several small molecule cyclotriphosphazenes and high polymeric poly(organophosphazenes) with methylthio groups (CH_3SR) have been synthesized: $[NP(OCH_2CH_2SCH_3)_2]_n$ ($n = 3$, **1**; $n = 15,000$, **5**); $[NP(OCH_2CH_2CH_2CH_2SCH_3)_2]_n$ ($n = 3$, **2**; $n = 15,000$, **6**); $[NP(OCH_2CH_2CH(SCH_3)CH_2CH_2CH_3)_2]_n$ ($n = 3$, **3**; $n = 15,000$, **7**); and $[NP(OCH_2C_6H_4SCH_3)_2]_n$ ($n = 3$, **4**; $n = 15,000$, **8**). Both series of compounds possess multiple thioether coordination sites for potential binding to metals. The methylthioethoxide substituent readily oxidizes to the sulfoxide derivatives in the presence of peroxides. All the phosphazenes were characterized by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy and elemental analysis, and the small molecule cyclotriphosphazenes were examined by mass spectrometry. Gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) were also employed to characterize the polymers. Metal complexation and extraction capabilities of both the small molecule and polymeric systems are described. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 650–661, 2000

Key words: synthesis; polyphosphazenes; metal coordination; thioether; GPC; DSC

INTRODUCTION

A need exists to develop coordination polymer systems that complex and remove metals.[1,2] Widespread applications for such materials are foreseen in areas as diverse as water pollution control, medicine, veterinary science, and extraction of precious metals.[2–4] A number of chelating ion exchangers are commercially available, including polyamines, aminophosphonic acid, and dithiocarbamic acid derivatized polymers. These are useful in waste water treatment, ocean mining of precious metals, and purification of mining effluent. Chelating ion exchangers operate under the same principles as classical ion exchangers. However, chelation of a transition metal is known to enhance the stability of the complex and, in some cases, results in greater ion selectivity.[5–7] Coordination to metals can also play a role in polymer to metal adhesion.

Metal-coordination polymers should have some or all of the following properties: (1) stability to synthetic and fabrication processes, (2) coordination or chelation ability unhindered by the polymer substrate, (3) strong metal binding, (4) selectivity, (5) capability of resin formation, and (6) recovery of metal and exchanger.[2] Ideally, a small molecule model system should also be available to

---

assist in the elucidation of complexation mechanisms at a fundamental level. Polymers that form very stable coordination complexes with metal ions are not useful as ion exchangers or extraction materials because the metals cannot easily be removed from the polymer substrate. However, stable macromolecular coordination compounds have been used as polymeric substrates for heterogeneous and homogeneous catalysis,[8–13] and as nucleation sites for inorganic crystals and metal nanoclusters,[13–15] and strong coordination could be important in adhesion.

Sulfur containing polymers are good candidates for coordination materials.[5,16,17] Replacement of one oxygen atom in crown ethers by a sulfur atom (soft base) results in increased complexation of silver ions and other metals (soft acids).[18–20] Poly(alkylenesulfides) have been synthesized, but they are unsuitable for metal complexation studies due to their insolubility and crystallinity.[21] Polymers that contain thioether functionality in the pendent groups are rare, and may provide more desirable properties. To our knowledge, the few side chain thioether-derivatized polymers synthesized to date have never been studied for their coordination abilities.[22–30] A few thioether-derivatized polystyrenes have been investigated for their use as polymeric supports to immobilize catalysts.[8,9]

Poly(organophosphazenes) have a backbone of alternating phosphorus and nitrogen atoms. The chemical and physical properties of these polymers can be altered by facile changes in the side group structure.[31–33] These changes are usually accomplished by replacement of the chlorine atoms in the macromolecular intermediate, poly(dichlorophosphazene) by organic side units. This macromolecular substitution process allows the polymer properties to be tailored over a wide range by the choice of the nucleophile employed.[34–37] The utilization of thioether-functionalized nucleophiles permits the incorporation of potential coordination sites. Phosphazene small molecule systems are also available for fundamental studies of the coordination chemistry involved in metal uptake processes and these serve as useful models for the behavior of the corresponding macromolecules.

The objective of this study was to synthesize cyclo- and polyphosphazenes with thioether side chains and to examine their physical and chemical properties. The new polymers are especially suited for the study of their chelation ability because they bear two side substituents per repeat

unit, which allows a chelating system to be formed from otherwise monodentate ligands. They might allow for the more facile release of the metal ions compared to crown thioethers, which form quite stable chelates with various metal ions such as silver(I) and mercury(II). Yet, not all organic noncyclic thioethers make good chelates.[17] There are some promising studies from Japan that use alkylthio and arylthio containing phosphazenes in silver halide photographic materials.[38,39]
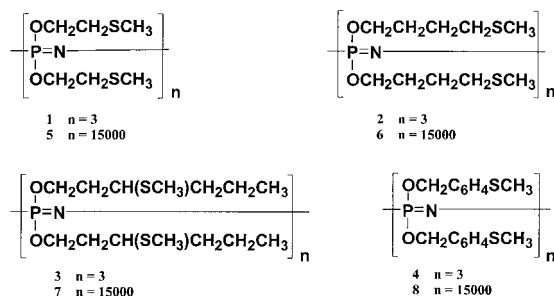

We describe here the following series of studies. Cyclo- and polyphosphazenes **1–8** (Chart 1) containing a variety of methylthio side groups were synthesized, purified, and characterized by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy and elemental analysis. In addition, the small molecule cyclotriphosphazenes were examined by mass spectrometry. The polymers were further characterized by differential scanning calorimetry and gel permeation chromatography. Metal complexation of mercury(II) was studied in the cyclotriphosphazene systems **1–3**. Complexes of **1** with silver(I) and cadmium(II) were also examined. The first results of ion uptake and selectivity for mercury(II), cadmium(II), and silver(I) on pendent thioether-derivatized polymers **5–7** are reported.

RESULTS AND DISCUSSION

Synthesis of Cyclotriphosphazenes

Heavy metal complexation is difficult to understand on a macromolecular basis. Therefore, the synthesis and metal binding of small molecule model compounds is useful to generate information about metal uptake that may occur in the corresponding polymeric system. The new cyclotriphosphazenes [NP(OCH$_2$CH$_2$SCH$_3$)$_2$]$_3$, **1**; [NP(OCH$_2$CH$_2$CH$_2$CH$_2$SCH$_3$)$_2$]$_3$, **2**; [NP(OCH$_2$CH$_2$CH(SCH$_3$)CH$_2$CH$_2$CH$_3$)$_2$]$_3$, **3**; and [NP(OCH$_2$C$_6$H$_4$SCH$_3$)$_2$]$_3$, **4** (Scheme 1) were obtained by treatment of (NPCl$_2$)$_3$ with
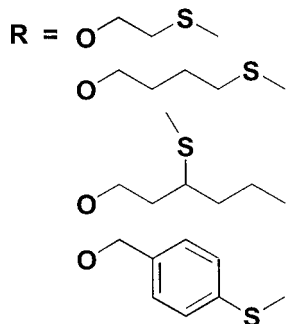
Scheme 1   Synthesis of methylthio containing phosphazenes.

Scheme 2   Formation of cyclotriphosphazene : HgI$_2$ complexes.

$NaOCH_2CH_2SCH_3$, $NaOCH_2CH_2CH_2CH_2SCH_3$, $NaOCH_2CH_2CH(SCH_3)CH_2CH_2CH_3$, or p-$NaOCH_2C_6H_4SCH_3$ in THF. Complete chlorine replacement was indicated by the respective singlet resonances at 17.8, 18.2, 18.4, and 17.3 ppm in the ^{31}P-NMR spectra (Table I). Trimers **1–3** were isolated as clear, yellow, oils through liquid–liquid extraction with methylene chloride. Trimer **4** is a sweet smelling, white powder. Both the ^{1}H- and ^{13}C-NMR spectra confirm the proposed structures. Integration of the ^{1}H-

NMR signals further supported the conclusions that the substituents are the respective thioether derivatives. The molecular ion peaks in the mass spectra correlate with each of the hexasubstituted cyclotriphosphazenes (Table I).

Trimers **1–3** are soluble in a variety of organic solvents, including ethers, acetone, ethyl acetate, most alcohols, chlorinated and aromatic solvents. Hexa-2-methylthioethoxycyclotriphosphazene, **1**, dissolves in methanol and is partially soluble in diethyl ether. Trimer **3** is also soluble in hexane. Hexa-4-methylthiobenzoxycyclotriphosphazene, **4**, only dissolves in chlorinated and aromatic solvents. Attempts to obtain single crystals of the species **1–4** yielded oils (**1–3**) in the cases of derivatives with very flexible side groups, and thin platelets for compound **4** with the more rigid substituent.

Complexation of Trimers

Complexation of cyclotriphosphazenes **1–3** was attempted using 1 : 1, 1 : 3, and 1 : 6 ratios of trimer : mercury iodide (Scheme 2). Addition of the dissolved linear thioether derivatized cyclotriphosphazenes, **1** and **2**, to the mercury salt solutions resulted in the immediate formation of a

Table I   Characterization Data of Hexasubstituted Cyclotriphophazenes, 1–4

Trimers	1		2		3		4	
E.A.	Theor.	Act.	Theor.	Act.	Theor.	Act.	Theor.	Act.
%C	31.71	30.71	42.38	40.84	49.53	47.36	54.68	54.87
%H	6.21	6.00	7.83	7.18	8.91	8.44	5.16	5.16
%N	6.16	6.75	4.94	5.31	4.13	3.85	3.99	4.05
%S	28.22	26.70	22.63	21.17	18.89	17.61	18.25	18.07
^{31}P-NMR	17.8 ppm		18.2 ppm		18.4 ppm		17.3 ppm	
^{1}H-NMR	4.1, 2.8, & 2.1 ppm I–2:2:3		3.8, 2.3, 1.9, and 1.6 ppm I–2:2:3:4		4.1, 2.7, 2.0, 1.9, 1.8, 1.5 and 1.5, and 0.9 ppm I–2:1:3:1:1:4:3		7.2, 4.9, and 2.4 ppm I–4:2:3	
^{13}C-NMR	65.0, 33.6, and 15.8 ppm		65.2, 33.5, 29.0, 25.1, and 15.3 ppm		63.7, 42.6, 36.6, 35.7, 19.9, 13.9, and 12.3 ppm		138.4, 136.0, 128.1, 126.4, 67.2, and 15.7 ppm	
Mass	681 amu		849 amu		1,017 amu		1,053 amu	
FAB MS	682.3 amu		850.3 amu		1,018.3 amu		1,054.3 amu	

^{a}Not measured.

white precipitate. The more concentrated mercury iodide solutions produced larger quantities of precipitate. In all cases, the precipitate dissolved after stirring or heating the solution to reflux.

No precipitation occurred with the branched thioether derivatized cyclotriphosphazene **3**. This lack of an immediate precipitate formation for cyclotriphosphazene **3** can be attributed to the fact that the thioether substituent is bonded to a secondary carbon atom and is, therefore, sterically hindered. This would prevent the formation of coordination polymers and networks. In addition, the complexes might remain in solution because of solubilization by the large aliphatic substituents.

The reaction mixtures were heated to reflux in absolute ethanol for 1 h under argon. The solutions were cooled and placed in vials to allow slow evaporation of the solvent. Mercury complexes were obtained as bright yellow gums or microcrystals with speckles of red solid (HgI_2) and/or a pale yellow oil (starting trimers), depending on the complexation ratio. Attempted recrystallization of the crude products from several solvents did not yield crystals suitable for X-ray crystal structure analysis but gave pure bright yellow oils. Each of the products was characterized by elemental analysis.

The elemental analysis results and the calculated theoretical elemental content for all the possible whole integer ratios of complexation are recorded in Table II. The complexation of HgI_2 by **1** in all three, 1 : 1, 1 : 3, and 1 : 6, ligand : metal reaction mixtures yielded a metal complex with a trimer : metal ratio of 1 : 3. Thus, chelation of the mercury atoms probably occurs by coordination of two geminal thioether groups. Hexa-2-methylthioethoxycyclotriphosphazene preferentially formed a 1 : 3 complex even with a high stoichiometric excess of either the ligand or the metal.

Trimer **2** reacted with three or six equivalents of mercury iodide to yield a complex with a ligand : metal ratio of 1 : 4. If only one equivalent of metal salt was employed, the product isolated contains almost the stochiometric ratio of one molecule of mercury iodide attached to one molecule of the cyclophosphazene **2**. Infrared spectra of **2** with n HgI_2 showed significant changes (1428 cm^{-1} shifted to 1418 cm^{-1} and fingerprint region below 900 cm^{-1}) compared to that of the free ligand **2**, and this suggested complex formation. However, the evidence is insufficient to allow the structures

of the unsymmetrical products with these unexpected ligand : metal ratios to be proposed.

Cyclotriphosphazene **3** is the only ligand studied which formed mercury complexes in which all six thioether donor groups appeared to be bonded to mercury atoms. A compound with a ligand : metal ratio of 1 : 6 was obtained in high yield by treatment of **3** with six equivalents of mercury iodide. Reactions with three equivalents of mercury(II) iodide yielded the stoichiometric product with three metal atoms attached to the ligand. The product mixture obtained in the reaction with one equivalent of metal salt showed an elemental content appropriate for ratios between 1 : 1–2.

The complex formation of cyclotriphosphazene **1** with silver(I) and cadmium(II) nitrates were also studied. Solutions of **1** in CH_2Cl_2 were added to one, three, and six equivalents, with each of the salts dissolved in acetonitrile. The silver reactions were kept in the dark and yielded slightly tinted, clear oils after 3 days of reaction. Only the 1 : 6 cadmium(II) nitrate sample separated as a suspended powder from solution after stirring for several days. The powder was isolated by centrifugation and the solid was decanted and washed with water. For the reaction mixtures of **1** with one and three equivalents of metal salt, the solvents were removed under reduced pressure, yielding oils. These samples were washed with methylene chloride and deionized water to remove excess trimer and cadmium(II) nitrate, respectively. All dried silver and cadmium complexes were off-white solids that were analyzed by elemental analysis (Table II).

The only well-defined complex obtained from these reactions was a 1 : 2 ligand : metal complex of **1** with silver(I) nitrate from a 1 : 1 reaction mixture. No well-defined products could be isolated from the reactions of **1** with three or six equivalents of silver nitrate. The ligand : metal ratios of the mixtures obtained are 1 : 3–4 and 1 : 4–5, respectively. Cadmium also did not form well-defined coordination compounds with **1** in any of the stoichiometric amounts examined. The elemental contents of the samples showed ratios of 1 : 2–3 for the product mixture obtained from one equivalent of cadmium salt and 1 : 4–5 with three equivalents of the metal salt. The mixture isolated from a 1 : 6 reaction yielded a complex containing a large excess of cadmium nitrate.

Because the reactions of **1** with silver and cadmium nitrate did not yield clearly defined products, and therefore, did not offer the prospect of

Table II Elemental Content, Calculated (Found), for Heavy Metal Complexes with Different Ratios of Trimer : Salt

Trimer : Salt	1 : 0	1 : 1	1 : 2	1 : 3	1 : 4	1 : 5	1 : 6
1 : HgI₂				(Obt. 1 : 1; 1 : 3; 1 : 6 React.)			
% C	31.71	19.03	13.59	10.57 (**10.60; 10.11; 10.64**)	8.65	7.32	6.34
% H	6.21	3.73	2.66	2.07 (**2.26; 2.09; 2.14**)	1.69	1.43	1.24
% N	6.16	3.70	2.64	2.05 (**2.20; 2.05; 2.06**)	1.68	1.42	1.23
% S	28.22	16.93	12.10	9.41 (**9.48; 9.15; 9.38**)	7.70	6.49	5.64
2 : HgI₂	(Obt. 1 : 1 React.)				(Obt. 1 : 3; 1 : 6 React.)		
% C	42.38 (**31.37**)	27.62	20.49	16.28	13.51 (**13.57; 13.88**)	11.54	10.07
% H	7.83 (**6.07**)	5.10	3.78	3.01	2.49 (**2.56; 2.63**)	2.13	1.86
% N	4.94 (**3.47**)	3.22	2.39	1.90	1.58 (**1.71; 1.78**)	1.35	1.17
% S	22.63 (**13.67**)	14.75	10.94	8.69	7.21 (**7.53; 7.59**)	6.16	5.38
3 : HgI₂		(Obt. 1 : 1 React.)	(Obt. 1 : 3 React.)				(Obt. 1 : 6 React)
% C	49.53	34.25 (**30.64**)	26.17 (**22.84**)	21.18	17.79	15.33	13.47 (**13.45**)
% H	8.91	6.16 (**5.50**)	4.71 (**4.11**)	3.81	3.20	2.76	2.42 (**2.51**)
% N	4.13	2.85 (**2.72**)	2.18 (**2.00**)	1.76	1.48	1.28	1.12 (**1.29**)
% S	18.89	13.10 (**11.32**)	9.98 (**8.67**)	8.08	6.78	5.85	5.14 (**5.14**)
1 : AgNO₃			(Obt. 1 : 1 React.)	(Obt. 1 : 3 React.)	(Obt. 1 : 6 React.)		
% C	31.71	25.38	21.16 (**21.44**)	18.15 (**17.32**)	15.88 (**15.37**)	14.12	12.71
% H	6.21	4.97	4.14 (**4.13**)	3.55 (**3.36**)	3.11 (**2.97**)	2.76	2.49
% N	6.16	6.58	6.86 (**6.53**)	7.05 (**7.18**)	7.20 (**7.30**)	7.32	7.41
% S	28.22	22.59	18.83 (**17.88**)	16.15 (**14.58**)	14.13 (**13.69**)	12.56	11.31
1 : Cd(NO₃)₂			(Obt. 1 : 1 React.)		(Obt. 1 : 3 React.)		(Obt. 1 : 6 React.)
% C	31.71	23.54	18.72 (**17.02**)	15.54	13.28 (**12.89**)	11.60	10.29 (**5.91**)
% H	6.21	4.61	3.67 (**3.87**)	3.04	2.60 (**2.98**)	2.27	2.02 (**2.64**)
% N	6.16	7.63	8.49 (**8.83**)	9.02	9.47 (**9.47**)	9.77	10.00 (**7.27**)
% S	28.22	20.95	16.66 (**14.83**)	13.83	11.82 (**10.88**)	10.32	9.16 (**3.05**)

Table III   Characterization Data of Poly(organophosphazenes), 5–8

Polymers	5		6		7		8	
E.A.	Theor.	Act.	Theor.	Act.	Theor.	Act.	Theor.	Act.
%C	31.72	31.35	42.38	41.75	49.53	48.81	54.68	54.58
%H	6.18	6.10	7.82	7.49	8.91	8.60	5.16	5.47
%N	6.16	6.21	4.94	5.14	4.13	4.28	3.99	3.82
%S	28.22	27.18	22.63	20.51	18.89	18.23	18.25	d
%Cl	Trace	a	Trace	1.67	Trace	0.49	Trace	0.44
				361 ppm[b]				
^{31}P-NMR	−7.4 ppm		−10.0 ppm		−8.2 ppm		−6.3 ppm	
^{1}H-NMR	4.1, 2.8, and 2.2 ppm I–2 : 2 : 3		3.9, 2.5, 2.1, and 1.7 ppm I–2 : 2 : 3 : 4		4.1, 2.6, 2.0, 1.9, 1.9, 1.5 & 1.4, and 0.9 ppm I–2 : 1 : 3 : 1 : 1 : 4 : 3		6.8, 4.7, and 2.3 ppm I–4 : 2 : 3	
^{13}C-NMR	65.0, 34.1, and 16.0 ppm		65.1, 34.1, 29.7, 25.6, and 15.6 ppm		63.6, 42.9, 36.8, 35.4, 20.0, 14.2, and 12.1 ppm		137.6, 134.0, 128.0, 126.0, 67.2, and 15.5 ppm	
T_g (°C)	−79		−98		−79		−5 and 113[d] (68[e])	
M_w [K]	226		614		1143		589	

[a]Chlorine content could not be measured.
[b]This value was obtained after further precipitations from commercial THF.
[c]Sulfur content was not measured.
[d]The transition temperature for rearrangement of the polymer from phosphazene to phosphazane.
[e]The T_g of the new rearranged polymer.

understanding the coordination chemistry involved, these small-molecule studies were not extended to the ligands **2** and **3**. Although we could not obtain single crystals suitable for crystal structure determination, the combinatorial studies described gave useful information about the tendencies of the complexing ability of the new multifunctional ligands **1–3**.

Preparation of Polymers

The new polyphosphazenes [NP(OCH$_2$CH$_2$SCH$_3$)$_2$]$_n$, **5**; [NP(OCH$_2$CH$_2$CH$_2$CH$_2$SCH$_3$)$_2$] $_n$, **6**; [NP(OCH$_2$-CH$_2$CH(SCH$_3$)CH$_2$CH$_2$CH$_3$)$_2$]$_n$, **7**; and [NP(OCH$_2$-C$_6$H$_4$SCH$_3$)$_2$]$_n$, **8** were obtained by treatment of (NPCl$_2$)$_n$ with NaOCH$_2$CH$_2$SCH$_3$, NaOCH$_2$-CH$_2$CH$_2$CH$_2$SCH$_3$, NaOCH$_2$CH$_2$CH(SCH$_3$)CH$_2$CH$_2$-CH$_3$, or p-NaOCH$_2$C$_6$H$_4$SCH$_3$ in THF (Scheme 1). Complete chlorine replacement was indicated by the respective singlet resonances at −7.4, −10.0, −8.2, and −6.3 ppm in the ^{31}P-NMR spectra. The polyphosphazenes were isolated through repeated precipitations from THF into water, ethanol, or hexane. Polymers **5–7** were tan, transparent elastomers, while **8** was a white, fibrous material. The proton and carbon shifts in the ^{1}H- and

^{13}C-NMR, as well as integration of the ^{1}H-NMR signals, supported the structure of the polymers. Elemental microanalysis detected less than 0.5% residual chlorine and this indicated complete replacement of the chlorine atoms. Characterization data are listed in Table III.

Oxidation of Thioether Substituents

Although, the synthesis of the polymers appeared straightforward, the purification proved quite challenging, especially in the case of polymer **5**. Several precipitations from freshly distilled THF caused the polymer to become less and less soluble. ^{1}H-NMR spectroscopy of the insoluble samples showed that this was caused by partial oxidation of the thioether groups to the sulfoxides (Fig. 1). The chemical shifts of the protons neighboring the sulfur atom could easily be distinguished. The spectrum of the thioether showed methyl proton shifts at 2.2 ppm and methylene proton shifts at 2.8 and 4.1 ppm. A spectrum of the polymer with partially oxidized side groups revealed both the thioether protons and a second set of substituent protons at 2.7, 3.0, 3.2, and 4.4 ppm for the sulfoxide species. The fourth signal

A

B
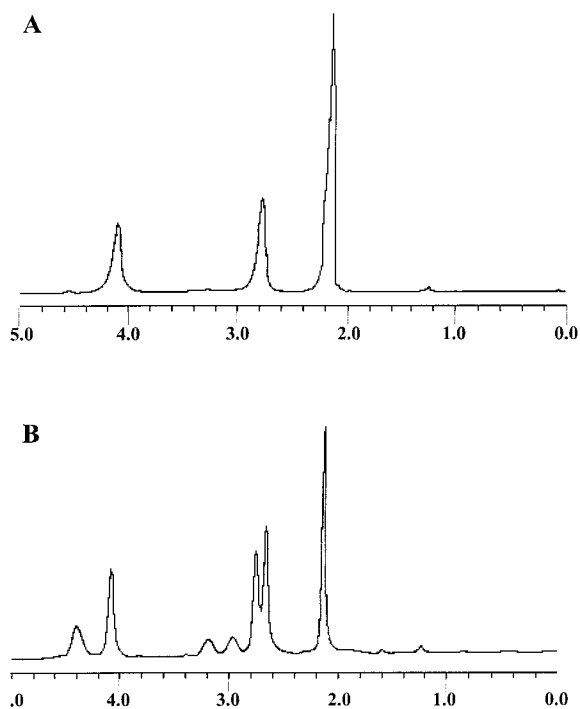
Figure 1   ^{1}H-NMR spectra of **5** during purification, (A) before and (B) after partial oxidation.

for the sulfoxide substituent was assigned to the methylene protons adjacent to the sulfur atoms, a signal that was split as a result of the chirality introduced at the sulfur atom by sulfoxide formation.

By contrast, the small molecule model **1** could easily be isolated without evidence of oxidation of the sulfur atom, even after months of exposure to the atmosphere.

However, the side groups of **1** were oxidized when peroxides were present in unstabilized THF. This confirmed the hypothesis that oxidation was a result of peroxide impurities in the distilled THF after exposure to light and air. The oxidation process[40] is much more dramatic during the purification of the polymers than with the small molecules. During polymer precipitation, a minute but significant amount of solvent is trapped in the bulk material. Peroxide formation can occur readily with THF, and further reactions with the polymer side groups are possible. No methods are available to isolate unoxidized polyphosphazenes from such mixtures. By contrast, partially oxidized small molecules can easily be separated from the unoxidized species by column chromatography or recrystallization.

A method to obtain polymer **5** without oxidation was to carry out the reaction in anhydrous

"stabilized" THF. The polymer was subsequently precipitated from stabilized THF, followed by precipitations from methylene chloride.

Polymers **6** and **7** were the least sensitive to oxidation. They did not oxidize when precipitated from distilled (unstabilized) THF. Polymer **8** decomposed over months, and more quickly at elevated temperatures above 80°C. This could be due to oxidation or a phosphazene/phosphazane rearrangement that is possible with benzyloxyphosphazenes (Scheme 3).

Thermal Transitions

The aliphatic thioether polymers **5–7** have glass transition temperatures (T_g) well below room temperature, specifically in the range of -98 to $-79°C$ (Table III). Polymer **8,** with the less flexible aromatic thioether groups, has a T_g of $-5°C$. These values indicate that the torsional mobility of the polymer is seriously hindered by the presence of the bulky aromatic substituent. A second transition temperature was detected only for polymer **8**. This transition at 113°C could reflect a thermal rearrangement of the phosphazene to a phosphazane (Scheme 3). Once the polymer was cycled above this transition temperature, the original T_g of $-5°C$ was no longer detected and a new glass transition temperature at 68°C appeared. The polymer also changed from a fibrous, white material to a powdery, bright yellow solid.

Ion Uptake, Capacity and Selectivity of Polymers 5–7

Preliminary studies of the ion uptake, capacity, and selectivity of polymers **5–7** were focussed on the behavior (1) of films and (2) of solutions when the polymers were exposed to mixtures of several heavy metal salt solutions.
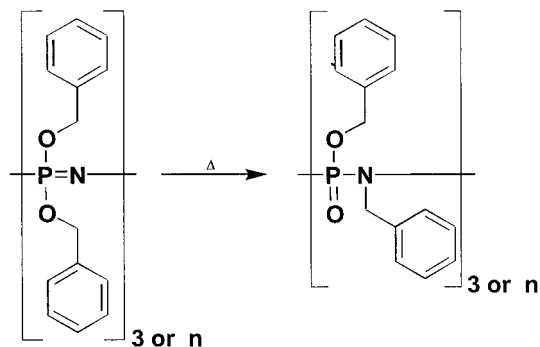
Scheme 3   Rearrangement of benzoxyphosphazenes.

Qualitative Studies of Polymer Films

Films of polymers **5–7** and poly(*bis*-hexoxyphosphazene), $[NP(OCH_2CH_2CH_2CH_2CH_2CH_3)_2]_n$, as a nonfunctional control material, were cast onto glass slides and dried. Each polymer was first studied for its stability in the various aqueous solutions. The pH values of the aqueous solutions were 3, 5, and 7. A solution of nitric acid (c = 0.001 mol/l) in THF/water 25/75% was also employed. The THF induced swelling at the surface of the films. No weight loss or gain was detected for any of these polymers in any of the solutions. The films were then immersed in aqueous solutions of silver nitrate, cadmium nitrate, mercury nitrate, and a mixture of the three (c = 0.1 mmol/l) for 48 h, washed with deionized water to remove all metal not absorbed or chelated on the surface, and dried. The characteristics of the metal-containing films varied from brittle, for most of polymer **5** films, to rubbery, for the poly(*bis*-hexoxyphosphazene) samples. The products were analyzed by X-ray microanalysis to determine qualitative ion uptake and selectivity.

First, it was necessary to determine the uptake capability of each polymer film for each metal from the various aqueous solutions. Poly(*bis*-hexoxyphosphazene) (the unfunctionalized phosphazene control) underwent metal uptake of Ag^+ ion only during exposure to light. This suggested that the process involved deposition of silver particles on the polymer. Although cadmium and mercury are less sensitive to photo effects, precautions were taken to eliminate exposure to light as an experimental factor. Films of polymers **5–7** absorbed silver from all the aqueous solutions studied. For the most part, cadmium was undetected or was barely detected at various pH values for films of poly(*bis*-methylthioethoxyphosphazene) (**5**) or at pH 5 for polymer **6**. Mercury was incorporated from solution by films of polymers **5** and **6**. However, poly(*bis*-methylthiohexoxyphosphazene) **7** was more selective in its absorption of mercury, which occurred from THF and from aqueous solutions at pH 7.

Films soaked in solutions of all three salts were studied to evaluate the selectivity of the polymers for the various metal ions. X-ray emission spectroscopy was used for analysis. Unfortunately, the X-ray emission of cadmium is hidden beneath the silver emission. For this reason, it was assumed from the single metal uptake studies that cadmium does not compete for coordination to the polymer films. Both silver and mercury were absorbed from all the solutions by films of **5** and **6**. Unfortunately, the relative selectivity could not be determined by this technique. However, films of polymer **7** were selective for silver from all solutions except at pH 7 where it also incorporated mercury ions.

## Quantitative Studies in Solution of Polymers 6 and 7

The ion uptake and selectivity of polyphosphazenes **6** and **7** in solution were studied quantitatively with the use of atomic absorption spectroscopy. Similar studies of pyridylalkylamino-substituted polyphosphazenes were reported previously.[41–43] Species **5** was not included in this study because of its low solubility and the brittle nature of products formed in the studies performed on the films of this polymer. Polymers **6** and **7** dissolved in THF/water were dialyzed against acidic solutions of mixed metal salts for 24 h at 25°C. The macromolecular metal complexes obtained were extremely stable, and the metals were removed from them only by complete destruction of the samples in concentrated acid. The molar quantities of each metal in the polymeric complexes are compared in Figure 2.

Polymers **6** and **7** have a significantly greater affinity for silver than for either mercury or cadmium. Poly(*bis*-4-methylthiobutoxyphosphazene) **6**, hardly forms complexes with cadmium, and the affinity of poly(*bis*-3-methylthiohexoxyphosphazene) **7** toward this metal is only slightly higher. Species **7** absorbs a slightly higher loading of metal ions. This is despite the lower sulfur content and the fact that it is more sterically hindered. However, this could be explained by the greater aliphatic character of the side substituent, which increases its solubility and also enhances the donor ability of the lone pairs at sulfur. In addition, the bulkiness of the side groups makes chelation/crosslinking significantly less favorable. This also explains the lack of precipitation of trimer **3** in the presence of HgI_2.

CONCLUSIONS

Phosphazenes **1–8** with methylthioether groups were synthesized: $[NP(OCH_2CH_2SCH_3)_2]_n$ (n = 3, **1**; n = 15,000, **5**); $[NP(OCH_2CH_2CH_2CH_2SCH_3)_2]_n$ (n = 3, **2**; n = 15,000, **6**); $[NP(OCH_2CH_2CH(SCH_3)CH_2CH_2CH_3)_2]_n$ (n = 3, **3**; n = 15,000, **7**); and $[NP(OCH_2C_6H_4SCH_3)_2]_n$ (n = 3, **4**; n
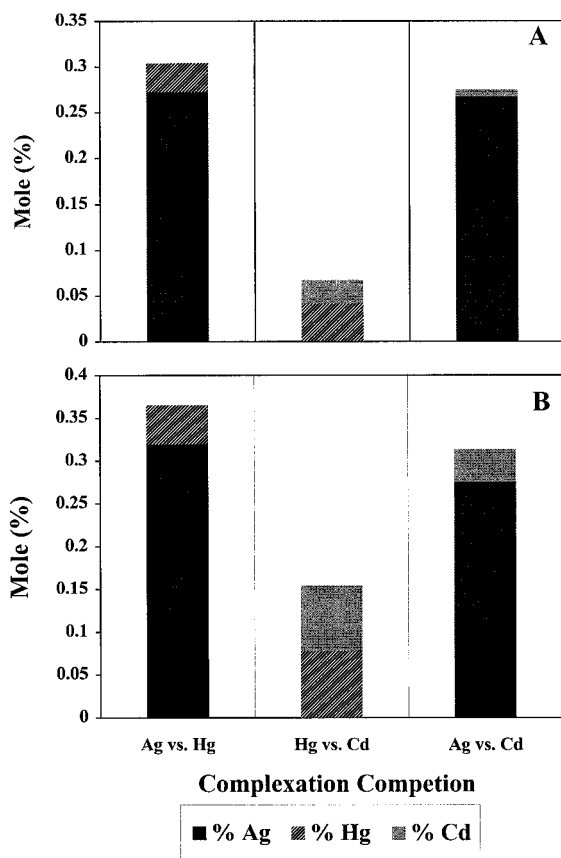
Figure 2 The metal contents obtained for each metal in the complexation competition between the various metals for solubilized polymers (A) **6** and (B) **7** corrected for the atomic weight of the metal.

= 15,000, **8**). They were characterized by various analytical techniques. Cyclotriphosphazenes **1–3** form metal complexes of different ratios with mercury iodide. Trimer **1** also reacted with silver(I) and cadmium(II) nitrates to yield product mixtures. The ligand : metal ratios of all these small molecule complexes were determined by elemental analysis. These studies underline the complexity of the complexation process and the fact that chelation by multiple thioether units is plausible but not necessary, such as in the case of $[\mathbf{3} * 6 \; HgI_2]$.

The methylthioethoxy substituted phosphazenes **1** and **5** were especially prone to oxidation by peroxides. Polymer **8** decomposes with time and/or rearranges at elevated temperatures.

Polymers **5–7** were investigated as films and in solution for selective uptake of metals. All of these had the highest affinity for silver. They also complexed mercury and cadmium in solution, but were significantly less effective ligands for these

metals. The stability of the macromolecular metal complexes suggests that these systems could be particularly useful as silver extractants or as polymer substrates for catalysis.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (Nippon Fine Chemical/Ethyl Corp.) was purified by recrystallization from heptane and by sublimation at 50°C (0.05 mmHg). Poly(dichlorophosphazene) (Ethyl Corp.) was used as received ~9.3 g per 100 mL of solution in cyclohexane. Sodium hydride (60% dispersion in mineral oil, Aldrich/Acros) was used as received. Tetrahydrofuran (THF) (Omnisolv), was dried over sodium benzophenone ketyl and was distilled under a nitrogen atmosphere. In some cases (specified), THF was used as received. The 2-(methylthio)ethanol, 4-(methylthio)butanol, and 3-(methylthio)-1-hexanol (Acros/Aldrich) were vacuum distilled and stored over 4 Å molecular sieves. 4-(Methylthio)benzyl alcohol was purified by sublimation. Mercury(II) iodide, silver(I) nitrate, cadmium(II) nitrate, and mercury(II) nitrate (Acros and Merck) were used as received. 6000–8000 MWCO dialysis membranes (Spectra/por) were used. The synthesis of cyclo- and polyphosphazenes were performed under an atmosphere of dry argon using standard Schlenk techniques.

Equipment

^1H-, ^{13}C-, and ^{31}P-NMR were recorded by the use of a Bruker WM-360 NMR spectrometer at 360, 90.27, and 146 MHz, respectively. ^{31}P chemical shifts are relative to 85% phosphoric acid as an external reference with positive shift values downfield from the reference. ^1H- and ^{13}C-NMR spectra were referenced to internal $CDCl_3$. Elemental microanalyses were obtained by the use of an Elementar Vario EL CHNS analyzer (Elementar Analysensyteme GmbH, Hanau). Molecular weights were estimated using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector and a Polymer Laboratories PL gel 10 μm column. The samples were eluted with a 0.1% by weight of tetra-n-butylammonium nitrate in THF (Omnisolv). The GPC column was calibrated with polystyrene standards (Waters). Glass transition tem-

peratures were obtained by differential scanning calorimetry on a Perkin-Elmer DSC-7 unit controlled by a PE7500 computer. Heating rates of 10–40°C/min. were used. A Shimadzu IR-435 infrared spectrometer was used for the IR spectroscopy. FAB (+) mass spectra were collected on a voyager DESTR spectrometer. The X-ray microanalysis/energy dispersive spectroscopy (EDS) was performed on a JEOL JSM 5400 scanning electron microscope (SEM) (JEOL, Peabody, MA) using PGT IMIX-PC software (Princeton, NJ). These sample were first carbon coated in a BAL-TEC SCD050 (TechnoTrade, Boston, MA) sputter coater. The silver and cadmium contents were determined using a Pye Unicam SP 9 atomic absorption spectrophotometer and mercury contents were obtained by the use of Thermo Jarell Ash IRIS/AP instruments.

Synthesis of Cyclotriphosphazenes 1–4

The synthesis of trimers **1–4** was carried out using similar procedures. The synthesis of trimer **1** is given as a typical example. Sodium hydride (3.97 g, 99.23 mmol) was suspended in THF (300 mL). 2-(Methylthio)ethanol (9.53 g, 103.5 mmol) was added dropwise. After the solution cleared, hexachlorocyclotriphosphazene (5.03 g, 14.4 mmol) was added and the reaction mixture was stirred at room temperature until the reaction was complete after 24–48 h. The solvent was then removed under reduced pressure. The crude product was separated from the salts by liquid/liquid extraction in CH_2Cl_2/water. The methylene chloride solution was dried over anhydrous $MgSO_4$ and filtered. The product was further purified by column chromatography with ethyl acetate on silica gel. Note: Cyclotriphosphazenes **2** and **3** required column chromatography with 1 : 1 diethyl ether/methylene chloride and diethyl ether, respectively, as the solvent systems. Trimer **4** was obtained as a powder after recrystallization from benzene : ethanol. Yields of 65–85% were obtained. All characterization data are given in Table I.

Complexation of Trimers 1–3 with Mercury(II) Iodide

Complexation of cyclotriphosphazenes **1–3** was attempted with 1 : 1, 1 : 3, and 1 : 6 molar ratios of approximately 0.5 g cyclotriphosphazene : mercury iodide in 50 mL of refluxing absolute ethanol for 1 h in an inert atmosphere. The mixtures were

cooled and placed in vials to allow slow evaporation and if possible to favor crystal growth. Viscous liquids to hard solids were obtained that ranged in color from yellow to red (plus small amounts of pale yellow oil from 1 : 1 reaction mixtures). The pale yellow oil was removed by washing with methylene chloride and characterized by ^{31}P- and ^{1}H-NMR. The spectra of the oils exactly matched those of the respective pure trimers. The red solid contained no phosphorus signal. Recrystallization attempts of the amorphous, yellow gums and solids were limited due to their insolubility. All products were analyzed by elemental analysis (Table II).

Complexation of Trimer 1 with Silver(I) and Cadmium(II) Nitrates

Complexation of cyclotriphosphazenes **1** was attempted in 1 : 1, 1 : 3, and 1 : 6 molar ratios of approximately 0.25 g cyclotriphosphazene with the respective ratios of silver nitrate and cadmium nitrate in 5 mL of 1 : 1 CH_2Cl_2/CH_3CN. The solutions were stirred for 3 days at room temperature. The silver reactions were carried out in complete darkness, and resulted in the separation of a slightly tinted clear gum from which the reaction solution was decanted. These gums had no thioether odor. ^{1}H- and ^{31}P-NMR spectra were obtained for the wet products. The ^{1}H-NMR spectra indicated chemical shifts at 4.1, 2.9, and 2.2 ppm, with integration of 2 : 2 : 3 as well as shifts for the residual solvents, CH_2Cl_2 and CH_3CN. The complexes dried to off-white solids. The products from the reactions with cadmium remained soluble for days. After evaporation of the solvents clear tan gums were obtained. The 1 : 6 product mixture contained powder mixed with the gum. The products were washed with methylene chloride to remove the uncomplexed trimer, and were then redissolved in acetonitrile. Deionized water was added to the acetonitrile to precipitate the complexes from solutions and leave excess cadmium(II) nitrate in solution. The 1 : 6 reactant ratio product was the only one that precipitated. This precipitate was centrifuged and separated from the solution. The product was washed with water, again centrifuged, and decanted to obtain an off-white powder. The ^{31}P-NMR spectrum indicated the presence of trimer **1**. The solvent was also evaporated from the 1 : 1 and 1 : 3 product mixtures. They were washed with deionized water and methylene chloride and dried to form off-white solids. All products were analyzed by elemental analysis once isolated (Table II).

Synthesis of Poly(organophosphazenes) 5–8

The syntheses of polymers **5–8** were carried out using similar procedures. The procedure for polymer **6** is given as a typical example. 4-(Methylthio)butanol (15.92 g, 132.4 mmol) was added dropwise to a suspension of sodium hydride (4.82 g, 120.4 mmol) in THF (800 mL). After the formation of sodium 4-(methylthio)butoxide was completed, a solution of poly(dichlorophosphazene) (50 mL, 40.1 mmol) was added slowly. The reaction mixture was then heated to reflux for 18–48 h, and was monitored daily by ^{31}P-NMR spectroscopy until the reaction was complete. The mixture was then cooled and concentrated under vacuum. Stabilized THF needed to be added to the solution of **5** to allow for purification without oxidation of the sulfur. Polymer **6** was isolated by precipitation into a 1 : 1 mixture of ethanol/water. Further preciptations were carried out to purify the polymer, once into water from THF (stabilized for **5**) and twice more from CH_2Cl_2 into 1 : 1 hexane ethanol. The polymer was then dried and characterized. All characterization data are given in Table III.

Stability of Polymer Films 5–7 in Aqueous Solutions

The stability of the polymer films to various aqueous solutions; pH 3, 5, 7, and 10 and nitric acid, c = 0.001 mol/l, 25/75 % THF/water; was determined by mass loss. The preweighed films were soaked for 48 h in the various aqueous solutions and then dried under vacuum. No change in mass was detected.

Qualitative Ion Uptake and Selectivity of Thin Films of Polymers 5–7 and Poly(*bis*-hexoxyphosphazene)

Thin films of films of polymers **5–7** and poly(*bis*-hexoxyphosphazene, $[NP(OCH_2CH_2CH_2CH_2CH_2CH_3)_2]_n$, as a control poyphosphazene, were cast from methylene chloride onto glass slides and were dried under vacuum. The films were soaked in solutions of $AgNO_3$, $Cd(NO_3)_2$, $Hg(NO_3)_2$ (c = 0.1 mmol/L, and in a mixture of all three at pH 3, 5, and 7, and nitric acid (c = 0.001 mol/L) 25/75% THF/water for 48 h, washed three times with deionized water to remove uncomplexed metal salts from the surface, and dried under vacuum. All solutions were kept in the dark to reduce effects of light exposure, especially for samples that contained silver.

The films were then prepared for characterization by X-ray microanalysis. A piece of each film was lifted from the glass and affixed to a stainless steel mount with carbon adhesive tabs, four to five samples per mount. The samples were then sputter coated with carbon and placed in the instrument for analysis. All data were collected using an accelerating voltage of 20 kV, a 30° take-off angle, and 500× magnification for 200 s.

Quantitative Ion Uptake and Selectivity of Polymers 6–7

For each experiment 50 mg of **6** (0.176 mmol) or **7** (0.147 mmol) were dissolved in 25 mg of THF. The solutions were contained within dialysis membranes. The samples were then reacted with THF solutions containing small amounts of HNO_3 and mixtures of $Hg(NO_3)_2$*H_2O/$AgNO_3$, $Hg(NO_3)_2$*H_2O/$Cd(NO_3)_2$*4 H_2O, and $Cd(NO_3)_2$*4 H_2O/$AgNO_3$, respectively [c(metal) = 0.001 mol/L, n(metal) = 4n(polymer), V = 1.4 L, pH = 3]. The reaction mixtures were stirred at room temperature for 24 h. During this period the polymeric metal complexes precipitated from solution. They were filtered off and rinsed with THF. To determine the metal contents by AAS (silver and cadmium) or ICP (mercury), 15 mg of each sample were completely dissolved/degraded in either concentrated HNO_3 or HNO_3/HCl mixtures for periods from days to weeks. Samples of polymer **6** contained 29.37 wt % Ag : 6.35 wt % Hg, 2.92 wt % Cd : 8.33 wt % Hg, and 0.92 wt % Cd : 28.79 wt % Ag. Polymer **7** samples measured to contain 34.43 wt % Ag : 9.96 wt % Hg, 8.63 wt % Cd : 15.52 wt % Hg, and 4.29 wt % Cd : 29.70 wt % Ag.

REFERENCES

1. Gash, A. E.; Spain, A. L.; Dysleski, L. M.; Flaschenriem, C. J.; Kalaveshi, A.; Dorhout, P. K.; Strauss, S. H. Environ Sci Technol 1998, 32, 1007.
2. Sahini, S. K.; Reedijk, J. Coord Chem Rev 1984, 59, 1.
3. Dorfner, K. Ion Exchangers; Walter de Gruyter: Berlin, 1991.

4. Slater, M. J. The Principles of Ion Exchange Technology; Butterworth-Heinemann Ltd.: Oxford, 1991.

5. Ciardelli, F.; Tsuchida, E.; Wöhrle, D. Macromolecule–Metal Complexes; Springer: New York, 1996.

6. Jones, M. M.; Pratt, T. H.; Brown, C. H. J Inorg Nucl Chem 1974, 36, 194.

7. Pratt, T. H.; Jones, M. M. J Inorg Nucl Chem 1975, 37, 2403.

8. Crosby, G. A. U.S. Pat. 3 928 293 (1975).

9. Hodge, P. Polymer-Supported Reagents; Hodge, P.; Sherrington, D. C., Eds.; John Wiley & Sons Ltd.: New York, 1980, p 83.

10. Jana, N. R.; Sau, T. K.; Pal, T. J Phys Chem B 1999, 103, 115.

11. Pittman, C. U., Jr. In Polymer-Supported Reactions in Organic Synthesis; Hodge, P.; Sherrington, D. C., Eds.; John Wiley & Sons Ltd.: New York, 1980, p. 249.

12. Pittman, C. U., Jr. In Comprehensive Organometallic Chemistry; Wilkinson, G., Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Elmsford, NY, 1982, p. 553.

13. Antonello, M.; Arnold, G. W.; Battaglin, G.; Bertoncello, R.; Cattaruzza, E.; Colombo, P.; Mattei, G.; Mazzoldi, P.; Trivillin, F. J Mater Chem 1998, 8, 457.

14. Grummt, U. W.; Geissler, M.; Drechsler, T.; Fuchs, H.; Staub, R. Agnew Chem Int Ed Engl 1998, 37, 3286.

15. Yanagihara, N.; Uchida, K.; Wakabayashi, M.; Uetake, Y.; Hara, T. Langmuir 1999, 15, 3038.

16. Mitchell, P. C. H.; Taylor, M. G. Polyhedron 1982, 1, 225.

17. Murray, S. G.; Hartley, F. R. Chem Rev 1981, 81, 365.

18. Blake, A. J.; Schröder, M. In Advances in Inorganic Chemistry; Sykes, A. G., Ed.; Academic Press: New York, 1990, vol. 35, p. 1.

19. Cooper, S. R. Acc Chem Res 1988, 21, 141.

20. Cooper, S. R.; Rawle, S. C. In Structure and Bonding; Springer Verlag: Berlin, 1990, p. 1, vol. 72.

21. Duda, A.; Penczek, S. In Encyclopedia of Polymer Science and Engineering; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwitz, J. I., Eds.; John Wiley & Sons: New York, 1989, p. 246, vol. 16.

22. Ameduri, B.; Bongiovanni, R.; Malucelli, G.; Pollicino, A.; Priola, A. J Polym Sci Part A Polym Chem 1999, 37, 77.

23. Charmas, W.; Podkoscielny, W.; Rudz, W. J Appl Polym Sci 1990, 39, 1623.

24. Davies, J. A.; Sood, A. Makromol Chem Rapid Commun 1983, 4, 777.

25. Lee, J. C.; Litt, M. H.; Rogers, C. E. J Polym Sci Part A Polym Chem 1998, 36, 793.

26. Lee, J. C.; Litt, M. H.; Rogers, C. E. J Polym Sci Part A Polym Chem 1998, 36, 495.

27. Ranucci, E.; Ferruti, P.; Volpe, C. D.; Migliaresi, C. Polymer 1994, 35, 5571.

28. Urankar, E. J.; Brehm, I.; Niu, Q. J.; Fréchet, J. M. J. Macromolecules 1997, 30, 1304.

29. Allcock, H. R.; Olmeijer, D. L. Macromolecules 1998, 31, 8036.

30. Allcock, H. R.; Napierala, M. E.; Olmeijer, D. L.; Best, S. A.; Merz, K. M., Macromolecules 1999, 32, 732.

31. Allcock, H. R. Chem Eng News 1985, 63, 22.

32. Allcock, H. R. Science 1992, 255, 1106.

33. Mark, E. J.; Allcock, H. R.; West, R. Inorganic Polymers; Prentice Hall Inc.: Englewood Cliffs, NJ, 1992.

34. Allcock, H. R.; Kugel, R. L. J Am Chem Soc 1965, 87, 4216.

35. Allcock, H. R.; Kugel, R. L. Inorg Chem 1966, 5, 1709.

36. Allcock, H. R. Phosphorus–Nitrogen Compounds. Cyclic, Linear, and High Polymeric Systems.; Academic Press: New York, 1972.

37. Diefenbach, U.; Allcock, H. R. Inorg Chem 1994, 33, 4562.

38. Hasegawa, T.; Fukuwatari, N.; Konica Co., Japan: Jpn. Kokai Tokkyo Koho, 1999.

39. Ishikawa, W.; Fukuwatari, N. ; Konica Co., Japan: Eur. Pat. Appl., 1999.

40. The oxidation products of these phosphazenes were further studied in ref. 29.

41. Diefenbach, U.; Kretschmann, M.; Stromburg, B. Phosphorus, Sulfur, Silicon 1997, 124/125, 143.

42. Diefenbach, U.; Bloy, M.; Stromburg, B. Phosphorus, Sulfur, Silicon, 1999, 144–146, 65.

43. Diefenbach, U. Multifunctionelle Cyclo-und Polyphosphazene; Wissenschaft und Technik Verlag: Berlin, Germany, 1999.