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Sulfur–nitrogen–phosphorus polymers

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CONTENTS

ABSTRACT

Macromolecules with backbones of sulfur, nitrogen and phosphorus atoms have only been successfully prepared in the last three years and the study of these materials represents a new and interesting area of research. In this article the synthesis and properties of the three currently known classes of sulfur–nitrogen–phosphorus polymers are reviewed. These include poly(thiophosphazenes) and poly(thiazylphosphazenes), which, in addition to nitrogen and phosphorus, possess skeletal three-coordinate sulfur(IV) and two-coordinate sulfur(III) atoms, respectively. Poly(thionylphosphazenes), which were discovered in 1991, appear to represent the most stable and diverse class of S–N–P polymers prepared to date and possess skeletal four-coordinate sulfur(VI), nitrogen and phosphorus atoms. Developments to date concerning this particular polymer system are also described in detail.

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1. INTRODUCTION

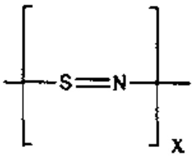
The synthesis and study of polymers with main chains constructed from atoms of main group elements or transition metals represents an active area of current research because of the unusual and attractive physical and chemical characteristics associated with these materials [1–9]. Indeed, well studied main group element-based polymers such as polyphosphazenes, polysilanes, and in particular polysiloxanes (silicones) have found a variety of commercial applications [1–5]. However, despite extensive efforts since the late 1950s, it is still the case that relatively few well characterized inorganic polymer systems have been reported and the construction of new types of polymer chains containing atoms of inorganic elements remains a substantial synthetic challenge.

Two of the most thoroughly studied and well known classes of inorganic polymers based on main group elements are poly(sulfur nitride) [10] and classical poly(organophosphazenes) [3,11], which possess backbones of alternating sulfur and nitrogen, and phosphorus and nitrogen atoms, respectively. In contrast, well characterized "hybrid" polymers with main chains of sulfur, nitrogen and phosphorus atoms, which would be expected to possess interesting combinations of properties, have only been prepared in the last three years. These recent advances have been facilitated by the prior development of a diverse range of structurally and chemically interesting molecular species based on S–N–P skeletons [12,13]. The purpose of the present review article is to survey developments to date in the field of sulfur–nitrogen–phosphorus polymers, a new area of inorganic polymer research.

2. SULFUR–NITROGEN AND PHOSPHORUS–NITROGEN POLYMERS

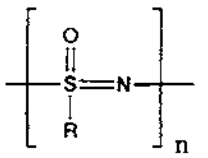
The most well known polymer with a S–N backbone is poly(sulfur nitride) $[SN]_x$ **1** [10]. The main route to this material involves the ring-opening polymerization (ROP) of the cyclic dimer S_2N_2. Poly(sulfur nitride) is remarkable as it represents the only known intrinsic polymeric electrical conductor, and at low temperatures (below 0.3 K) becomes superconducting. However, technological applications of $[SN]_x$ have been prevented owing to its unstable and explosive nature. Another group of sulfur–nitrogen polymers which were first reported, briefly, in the 1960s are the poly(oxothiazenes), $[NS(O)R]_n$ **2** [14]. The recent, exciting discovery of a condensation route to alkyl and aryl derivatives reported by Roy in 1992 has led to a revitalized interest in these materials [15,16]. It is also of importance that in addition to polymers, a large, well developed and fascinating area of small molecule chemistry is also known for sulfur–nitrogen based systems [12].

Phosphorus–nitrogen based polymers have been known since the report by Stokes in 1897 of the ROP of the cyclic phosphazene $[NPCl_2]_3$ at 250–300°C to yield crosslinked poly(dichlorophosphazene), $[NPCl_2]_n$, a hydrolytically sensitive elastomer referred to as "inorganic rubber". However, the key to the further develop-



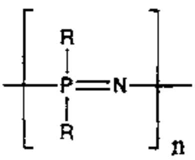
$[S{=}N]_x$

1



$[S(O)(R){=}N]_n$

2



$[PR_2{=}N]_n$

3

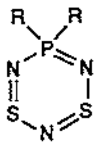
ment of the phosphazene polymer system was the discovery by Allcock and Kugel in the mid 1960s that soluble poly(dichlorophosphazene) could be prepared by an adaptation of Stokes' method and that the chlorine atoms of this polymer could subsequently be replaced in substitution reactions with oxygen and nitrogen-based nucleophiles to yield hydrolytically stable polyphosphazene derivatives $[NPR_2]_n$ 3. Indeed, this macromolecular substitution step gives polyphosphazenes one of their unique features: their remarkable tunability which allows access to a wide range of properties. Polyphosphazenes are used industrially as high-performance elastomers and flame-retardant coatings and are under development for a variety of other applications including biomedical uses [2,3,11,17]. Since the early 1980s a number of important condensation routes to polyphosphazenes have also been reported. In particular, poly(alkyl/arylphosphazenes), which are generally inaccessible via the macromolecular substitution route owing to competitive chain cleavage reactions, have been prepared by Neilson and Wisian-Neilson via the facile elimination of the trimethylsilylether $CF_3CH_2OSiMe_3$ from phosphoranimines of general structure $RR'(CF_3CH_2O){=}NSiMe_3$ at approx. 180°C [18]. Recently, this type of condensation approach has been extended by Matyjaszewski and co-workers to yield alkoxy substituted polymers via a fluoride catalyzed process that operates at relatively low temperatures (approx. 100°C) [19,20]. In addition, a condensation procedure to poly(dichlorophosphazene) involving the thermal elimination of $Cl_3P{=}O$ from appropriate precursors, currently being developed by Atochem, has been reported by de Jaeger and co-workers [21].

It is noteworthy that, similarly to sulfur–nitrogen systems, ring and chain compounds containing skeletal phosphorus and nitrogen atoms have been known since the synthesis of the cyclic trimer $[NPCl_2]_3$ in 1834 and these species have been extensively studied [22]. These compounds, as well as being of interest in their own right, often function as polymerizable monomers and can also provide useful models for the structure and reactivity of the high polymers [23].

3. RINGS AND CHAINS CONTAINING SKELETAL SULFUR, NITROGEN AND PHOSPHORUS ATOMS

The synthesis and study of small molecule ring and chain compounds constructed from sulfur, nitrogen and phosphorus atoms represents an active and exciting area of research. The chemistry of these compounds is now quite well developed and has been reviewed in detail elsewhere [12,13,24,25]. From the perspective of the present article it is important to summarize briefly the main types of compound known, as the existence of stable molecular species provides important clues with respect to the possible preparation of stable polymer structures based on these elements.

Hybrid SN/PN ring systems of varying size are known with sulfur in a range of different coordination numbers and oxidation states. By contrast, in virtually all of the compounds known phosphorus is four-coordinate and is in the +5 oxidation state. Well characterized examples with two-coordinate sulfur in the +3 oxidation state include deep purple colored species of type **4** and their eight-membered ring analogues $(NS)_2(NPR_2)_2$ [12,24]. Compounds containing three-coordinate sulfur(IV) atoms are exemplified by cyclic thiophosphazenes **5** and the related eight- and twelve-membered rings $(NSR)_2(NPR_2)_2$ and $(NSR)_2(NPR_2)_4$, respectively [12,24,26]. The chemistry of six-membered S–N–P rings **6** containing four-coordinate sulfur in the +6 oxidation state has been well developed by van de Grampel and co-workers [27,28]. In addition, Roesky and co-workers have synthesized and characterized linear species such as **7** that also contain stable S(VI)–N–P fragments [29]



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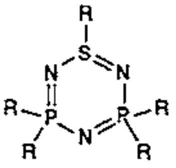

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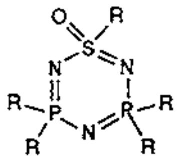

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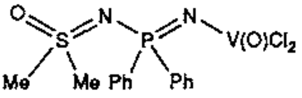

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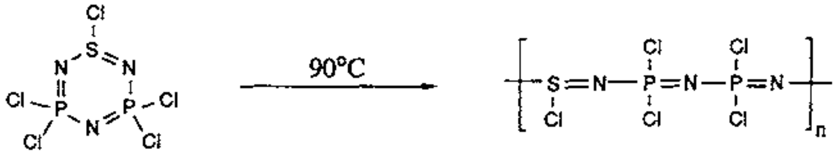
4. POLY(THIOPHOSPHAZENES)

Cyclic thiophosphazenes **5** contain three-coordinate sulfur(IV) atoms in addition to phosphorus and nitrogen and have been known since 1972 when the first example, the highly moisture sensitive, colorless perchlorinated species $(NSCl)(NPCl_2)_2$ **8** (b.p. 72°C, 0.002 mmHg), was reported by Roesky and co-workers [30]. The idea that this species might polymerize in a manner analogous to $[NPCl_2]_3$ was inspired by the comment that an increase in viscosity occurs when the species is heated prior to vacuum distillation [30], and the prior reports of the ROP of the carbon and tungsten analogues $(NCCl)(NPCl_2)_2$ and $(NWCl_3)(NPPh_2)_2$ [31–33]. In 1990 Allcock, Nuyken and co-workers reported that when **8** was heated at 90°C for 4 h ROP took place to yield the poly(thiophosphazene) $[(NSCl)(NPCl_2)_2]_n$ **9**

[34]. The resulting polymer **9** can be isolated from the polymerization mixture as a highly moisture sensitive yellow elastomer.



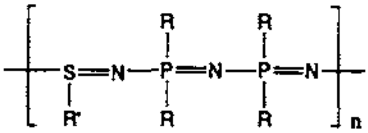
8 **9**

Reaction of **9** with aryloxide nucleophiles such as phenoxide or *p*-phenylphenoxide gives derivatives of structure **10** in which most or all of the halogen substituents are replaced [34,35]. These species are substantially less moisture sensitive than **9** but cannot be isolated via an aqueous workup. However, if very bulky substituents such as *o*-phenylphenoxide are introduced in the halogen replacement step, partially substituted polymers of structure **11** can be prepared which can be subject to an aqueous workup if contact with water is minimized [34] (Table 1). A more successful approach for the isolation of poly[(aryloxy)thiophosphazenes] is to use non-aqueous workup conditions [35].

Attempts to diversify the poly(thiophosphazene) polymer system via reaction of the chlorinated poly(thiophosphazene) **9** with nucleophiles other than aryloxides,

TABLE 1

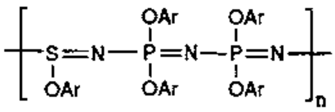
Selected characterization data for poly(thiophosphazenes)



Structure	R′	R	GPC[a]		^{31}P NMR[b] (ppm)	T_g (°C)
			$\bar{M}_w$	$\bar{M}_n$		
9	Cl	Cl	—	—	−4.4	−40
11	OC_6H_4Ph-*o*	35% Cl 65% OC_6H_4Ph-*o*	3.1×10^5	1.0×10^4	−12.3 (br) −16.9 (br)	79
11	OC_6H_4Ph-*m*	12% Cl 88% OC_6H_4Ph-*m*	1.2×10^5	8.5×10^4	−12.1 (br)	32
11	OC_6H_4Ph-*p*	6% Cl 94% OC_6H_4Ph-*p*	1.2×10^5	2.2×10^4	−11.0	69
13	$OC_6H_4Bu^t$-*p*	10% Cl 90% OC_6H_4Ph-*p*	7×10^4 4×10^3		−11.2	54

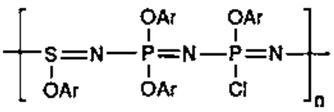
[a] In THF using polystyrene standards; [b] in dioxane.

such as amines or alkoxides, have been unsuccessful. Reactions of this type lead to degradation of the polymer backbone and no stable polymers have been isolated to date [35].



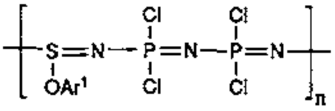
$$\left[-\underset{\mathrm{OAr}}{\mathrm{S}}=\mathrm{N}-\overset{\mathrm{OAr}}{\underset{\mathrm{OAr}}{\mathrm{P}}}=\mathrm{N}-\overset{\mathrm{OAr}}{\underset{\mathrm{OAr}}{\mathrm{P}}}=\mathrm{N}-\right]_n$$

10



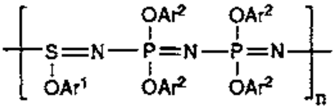
$$\left[-\underset{\mathrm{OAr}}{\mathrm{S}}=\mathrm{N}-\overset{\mathrm{OAr}}{\underset{\mathrm{OAr}}{\mathrm{P}}}=\mathrm{N}-\overset{\mathrm{OAr}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N}-\right]_n$$

11



$$\left[-\underset{\mathrm{OAr^1}}{\mathrm{S}}=\mathrm{N}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N}-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N}-\right]_n$$

12



$$\left[-\underset{\mathrm{OAr^1}}{\mathrm{S}}=\mathrm{N}-\overset{\mathrm{OAr^2}}{\underset{\mathrm{OAr^2}}{\mathrm{P}}}=\mathrm{N}-\overset{\mathrm{OAr^2}}{\underset{\mathrm{OAr^2}}{\mathrm{P}}}=\mathrm{N}-\right]_n$$

13

A particularly interesting feature of the substitution reactions of the poly(thiophosphazene) **9** with aryloxides is the preferential substitution of the chlorine substituents at sulfur compared to those at phosphorus. Thus, reaction of the poly (thiophosphazene) **9** with one equivalent of sodium *p*-(*t*-butyl)phenoxide yielded the regioselectively substituted polymer **12**, and subsequent treatment with excess sodium *p*-phenylphenoxide afforded a polymer of approximate structure **13** ($OAr^1 = OC_6H_4t$-Bu-*p*, $OAr^2 = OC_6H_4Ph$-*p*) (approx. 6% of the chlorine atoms at phosphorus remained unreacted in the second step). The higher reactivity of the S–Cl bonds towards nucleophilic substitution with aryloxides compared to the P–Cl bonds is also found in the chemistry of the small molecule species **8**. For example, reaction of **8** with one equivalent of sodium *o*-phenylphenoxide yields the (S–aryloxy)cyclothiophosphazene $[\{NS(OC_6H_4Ph\text{-}o)\}(NPCl_2)_2]$ as the sole product [34,35].

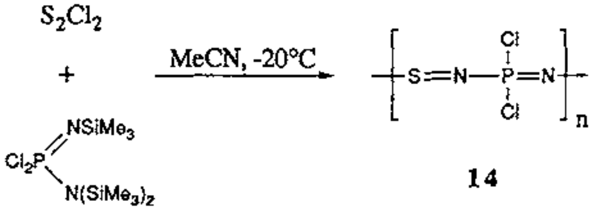
The poly[(halogeno/aryloxy)thiophosphazene] **11** ($OAr = OC_6H_4Ph$-*o*) is sufficiently hydrolytically stable to allow the molecular weight to be estimated by gel permeation chromatography (GPC). Using polystyrene standards for column calibration an approximate weight average molecular weight (M_w) of 310000 and a number average molecular weight (M_n) of 100000 have been determined. Glass transition temperatures for several poly(thiophosphazenes) have been measured by differential scanning calorimetry (DSC) (Table 1). For example, the halogenated polymer **9** has a T_g of −40°C, which compares to a value of −66°C for $[NPCl_2]_n$ and indicates that the conformational flexibility of the poly(thiophosphazene) is lower [35].

Another very interesting result to emerge from the initial work on poly(thiophosphazenes) is the observation that the cyclic species **8** polymerizes slowly even at room temperature. For example, samples of this colorless liquid become yellow and viscous and finally form an elastomeric residue after storage for several weeks at 25°C. The elastomeric material has been found to be insoluble in organic solvents and is presumed to be a crosslinked form of the poly(thiophosphazene) **9**. If a sample of **8** is rocked continuously at room temperature for 4 days soluble **9** is formed, but derivatization with sodium *m*-phenylphenoxide has shown it to be of quite low molecular weight ($M_w = 45000$, $M_n = 9800$) [35].

In summary, poly(thiophosphazenes) represent the first well characterized macromolecules with a S–N–P backbone. However, their relatively fragile polymer main chain, illustrated by their apparent intrinsic sensitivity towards hydrolysis, and their quite limited macromolecular substitution chemistry appear at present to be appreciable hurdles towards the extensive development of this polymer system.

5. POLY(THIAZYLPHOSPHAZENES)

During 1991 the synthesis of the first member of another new class of sulfur–nitrogen–phosphorus polymers, poly(thiazylphosphazenes), was reported by Chivers and co-workers [36]. These materials formally contain two-coordinate sulfur atoms in the +3 oxidation state and can be considered to be macromolecular analogues of cyclic compounds such as **4** and related species. The poly(thiazylphosphazene) **14**, which was synthesized via the reaction of S_2Cl_2 with an aminophosphoranimine, was found to be insoluble in most solvents, but findings from elemental analysis, IR spectroscopy and solution ^{31}P NMR measurements in DMF were found to be consistent with the proposed structure.



14

Poly(thiazylphosphazenes) such as **14** and related derivatives represent true hybrids of poly(sulfur nitride) **1** and polyphosphazenes **3**. It is to be expected that these materials possess very interesting and unusual properties, and further developments in this area are likely to be very significant.

6. POLY(THIONYLPHOSPHAZENES)

6.1. *Rationale*

In an attempt to prepare materials with increased stability and diversity the synthesis of sulfur–nitrogen–phosphorus polymers containing skeletal four-coordinate sulfur atoms in the +6 oxidation state has been investigated [37]. The rationale behind this choice was two-fold. First, four-coordinate sulfur(VI) moieties are present in very stable organic polymers such as poly(ethersulfones) which are widely used as engineering thermoplastics. Secondly, small molecule species containing rings of sulfur(VI), nitrogen and phosphorus atoms, cyclic thionylphosphazenes **6**, have been well studied, and work by van de Grampel and co-workers has shown that the ring skeleton present in these species is generally stable and robust. For example, halogen replacement reactions of species of structure **6** with chlorine side groups using primary and secondary amines have been shown to occur generally without cleavage of the S–N–P skeleton, and the resulting derivatives appear to be stable to hydrolysis [27,28].

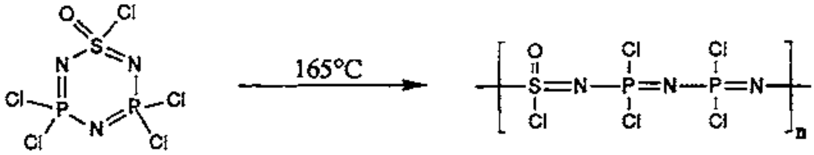
As described below, the ROP of cyclic thionylphosphazenes provides access to poly(thionylphosphazenes), the most stable class of S–N–P polymers prepared to date. Most of the remainder of this review will concentrate on the results that have been forthcoming in this area in the two years since the first report of these polymers in 1991 [37–49].

6.2. Synthesis and ring-opening polymerization of halogenated cyclic thionylphosphazenes

The cyclic thionylphosphazene $(NSOCl)(NPCl_2)_2$ **15** was first prepared in 1972 by two different, low yield routes. Van de Grampel and co-workers reported the synthesis of small quantities of this species via the vacuum thermolysis of $Cl_3P{=}N{-}PCl_2{=}N{-}SO_2Cl$ [50]. In the same year, Glemser and co-workers reported a (3+3) cyclocondensation procedure to prepare **15** which involved the reaction of sulfamide $SO_2(NH_2)_2$ with the salt $[Cl_3P{=}N{=}PCl_3][PCl_6]$ (yield 12%) [51]. A much improved route to **15** which has since been described by Suzuki and co-workers starts with sulfamide and PCl_5 and involves a (5+1) cyclocondensation reaction of the bis(phosphazo)sulfone $(Cl_3P{=}N)_2SO_2$ with $HN(SiMe_3)_2$ as the key ring-forming step [52]. Overall yields of **15** using this procedure are 40–75% and this method is therefore the most useful current route. The perchlorinated cyclic thionylphosphazene **15** is a white, sublimable, crystalline material (m.p. 61°C) which is only slightly sensitive to moisture in the solid state and can be easily handled in air.

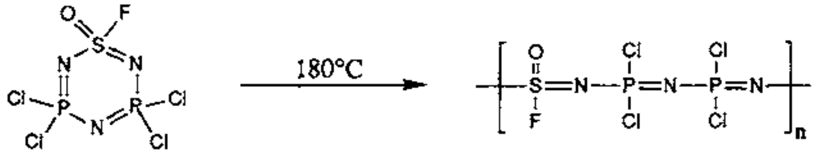
In 1991 our group reported that when **15** is heated in the melt at 165°C, thermal ROP takes place to yield the poly(thionylphosphazene) **16** which possesses chlorine substituents at sulfur and at phosphorus. This is an elastomeric polymer which is sensitive to moisture as a result of the hydrolytically sensitive main group element–chlorine bonds present [38]. Recent work has shown that small quantities of macrocyclic products are also formed under these conditions, such as the cis and trans isomers of the 12-membered ring $[(NSOCl)(NPCl_2)_2]_2$ and the higher cyclics $[(NSOCl)(NPCl_2)_2]_x$ $(x=3–5)$ [49].

Reaction of **15** with a ten-fold excess of AgF_2 leads to regioselective fluorination



15 **16**

at the sulfur center to yield $NSOF(NPCl_2)_2$ **17** which has similar physical properties to the perchlorinated analogue [53]. An improved procedure for the preparation of the latter involves the reaction of **15** with a 2:1 mixture of HgF_2 and $AlCl_3$ in 1,2-dichloroethane [47]. The fluorinated cyclic thionylphosphazene **17** also undergoes thermal ROP in the melt at 180°C, a temperature slightly higher than that necessary for the perchlorinated monomer **15**, to yield the fluorinated poly(thionylphosphazene) **18** as a hydrolytically sensitive elastomer [40].

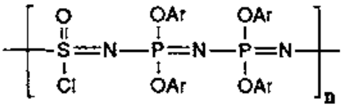


17 **18**

In order to gain insight into the conformational flexibility of the main chain present in poly(thionylphosphazenes) the glass transition behavior of the perhalogenated polymers **16** and **18** has been investigated by DSC [43]. Glass transitions were detected at −46°C for **16** and at −56°C for **18**. It is informative to compare the T_g values for **16** and **18** with those for related polymers. These values are higher than those for the classical polyphosphazenes $[NPCl_2]_n$ (−63°C) and $[NPF_2]_n$ (−96°C) [54], which indicates that the presence of a N=S(O)Cl unit leads to a decrease in conformational flexibility. Additional evidence in favor of this conclusion has been provided by Roy, who has recently reported [15] that the poly(oxothiazene) $[NS(O)Me]_n$ possesses a relatively high T_g value of 55–65°C compared to that of the methylated polyphosphazene analogue $[NPMe_2]_n$ ($T_g = -46°C$) [18]. The most likely explanation for this effect is that the presence of the highly polar S=O groups increases intramolecular interactions, which decreases the free volume present. Another possible explanation is that the skeletal N=S bonds possess a significantly higher conformational energy barrier than N=P bonds. However this is unlikely, as the pπ–dπ nature of the π-bonding between nitrogen and sulfur would be expected to ensure good orbital overlap at all points of the conformational energy profile. This situation is similar to that for a N=P bond and a similar low conformational energy barrier would therefore be anticipated. The T_g of the fluorinated polymer **18** (−56°C) is lower than that of polymer **16** (−46°C) which has chlorine atoms at sulfur. This can be attributed to the smaller size and lower polarizability of a fluorine side group substituent compared to chlorine. Similar trends are observed with classical polyphosphazenes and organic polymers. For example, the T_g of $[NPF_2]_n$ (−96°C) is significantly lower than that of $[NPCl_2]_n$ (−66°C), and the T_g of poly(vinylidenefluoride) $[CH_2CF_2]_n$ (−39°C) is lower than that of poly(vinylidene-chloride) $[CH_2CCl_2]_n$ (−19°C) [55].

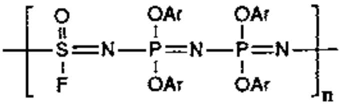
6.3. Synthesis and properties of poly[(aryloxy)thionylphosphazenes] with halogen substituents at sulfur

In order to prepare hydrolytically stable poly(thionylphosphazenes) the perchlorinated polymer **16** and the fluorinated polymer **18** have been reacted with aryloxide nucleophiles possessing different substituents attached to the aromatic nucleus [43]. These reactions proceeded to completion within 6 h at room temperature and, surprisingly, subsequent characterization of the poly(thionylphosphazene) products, **19** and **20** respectively, indicated that aryloxy substituents were present only at phosphorus and that the sulfur–chlorine bonds had remained intact under the reaction conditions used. Evidence for the presence of chlorine atoms at sulfur was provided by ^{13}C and ^{31}P NMR spectroscopy, which showed the presence of a single environment for both the aryloxy groups and the skeletal phosphorus atoms, and this was confirmed by elemental analysis. The ^{13}C NMR spectrum of the phenoxy substituted polymer **19** (OAr = OPh) is shown in Fig. 1 as a representative example. Only one ^{13}C NMR resonance is present for each of the ipso, ortho, meta and para carbon atoms of the phenoxy group. If aryloxy substituents were also present at sulfur, two resonances for each inequivalent carbon atom of the aromatic side group would be expected.



$$\left[-\overset{\mathrm{O}}{\underset{\mathrm{Cl}}{\overset{\|}{\mathrm{S}}}}{=}\mathrm{N}-\overset{\mathrm{OAr}}{\underset{\mathrm{OAr}}{\mathrm{P}}}{=}\mathrm{N}-\overset{\mathrm{OAr}}{\underset{\mathrm{OAr}}{\mathrm{P}}}{=}\mathrm{N}- \right]_n$$

19



$$\left[-\overset{\mathrm{O}}{\underset{\mathrm{F}}{\overset{\|}{\mathrm{S}}}}{=}\mathrm{N}-\overset{\mathrm{OAr}}{\underset{\mathrm{OAr}}{\mathrm{P}}}{=}\mathrm{N}-\overset{\mathrm{OAr}}{\underset{\mathrm{OAr}}{\mathrm{P}}}{=}\mathrm{N}- \right]_n$$

20

The regioselective substitution of the chlorine atoms at phosphorus is very unusual and provides a route to polymers with very well defined microstructures. Remarkably, the regioselective nucleophilic substitution detected for **16** and **18** involving the replacement of the chlorine atoms bonded to phosphorus rather than those at sulfur is exactly opposite to that detected for the analogous sulfur(IV) species, the poly(thiophosphazene) **9**, where nucleophilic substitution takes place preferentially at the sulfur center [34,35]. This can be attributed to the relatively low reactivity of S^{VI}–Cl bonds to nucleophilic halogen replacement compared to P–Cl bonds. By contrast, S^{IV}–Cl bonds are more reactive than the latter. In addition,

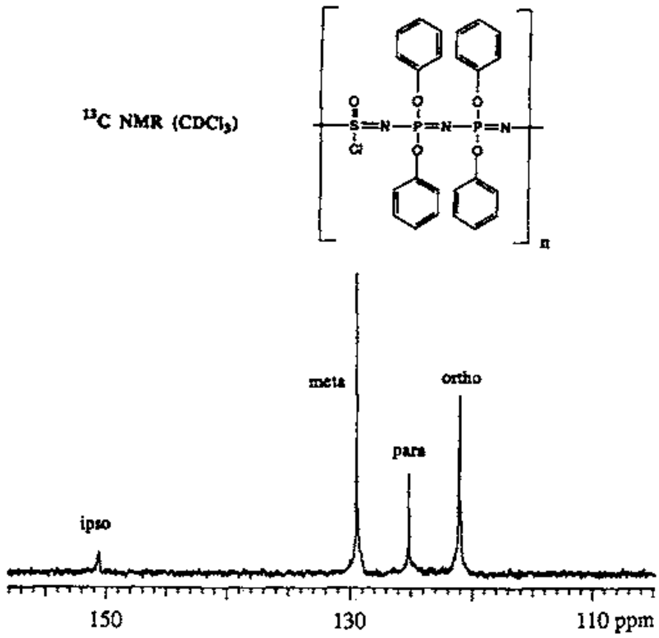


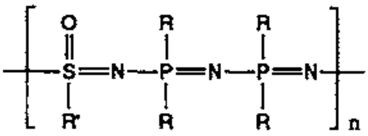
Fig. 1. The ^{13}C NMR spectrum of the poly[(aryloxy)thionylphosphazene] **19** (OAr = OPh).

the regioselective substitution behavior of **16** and **18** with aryloxy nucleophiles contrasts with the behavior of the classical polyphosphazene $[NPCl_2]_n$ under similar conditions. Thus, in general, when the latter is reacted with sodium aryloxides all of the halogen side group substituents are replaced to give the poly(aryloxyphosphazenes) $[NP(OAr)_2]_n$. The regioselective substitution pattern detected for the poly(thionylphosphazenes) **16** and **18** has also been found to occur when the cyclic thionylphosphazenes **15** and **17** are treated with sodium aryloxides. For example, treatment of **17** with excess sodium phenoxide, Na[OPh], at room temperature exclusively yielded the S–fluoro derivative $NSOF[NP(OPh)_2]_2$.

The reaction of **16** and **18** with aryloxide nucleophiles provides access to poly(thionylphosphazenes) of structure **19** and **20** which are elastomers or glasses depending on the steric bulk of the aryloxy side group (Table 2). An example of a fluorinated poly(thionylphosphazene) elastomer, polymer **20** (OAr = OPh), is shown in Fig. 2. Poly(thionylphosphazenes) show considerably improved hydrolytic stability over their sulfur(IV) analogues, the poly(thiophosphazenes), and can be easily purified by precipitation into water. Poly[(aryloxy)thionylphosphazenes] of structure **19** and **20** appear indefinitely stable to atmospheric moisture, with no noticeable change after being stored for over 2 years in air. In addition, no hydrolysis has been detected in solution by ^{31}P NMR or GPC for polymers such as **20** (R = OPh) over a period of months, even at elevated temperatures [40]. However, in solution in the presence of a base (e.g. NaOH) quite rapid decomposition occurs which is presumably initiated

TABLE 2

Selected characterization data for poly(thionylphosphazenes) and halogen or aryloxy side groups



$$\left[-\overset{O}{\underset{R'}{\overset{\|}{\underset{|}{S}}}}=N-\overset{R}{\underset{R}{\overset{|}{\underset{|}{P}}}}=N-\overset{R}{\underset{R}{\overset{|}{\underset{|}{P}}}}=N- \right]_n$$

Structure	R′	R	GPC^a		^{31}P NMR^b (ppm)	T_g (°C)
			$\bar{M}_w$	$\bar{M}_n$		
16	Cl	Cl	–	—	– 10.0^c	–46
18	F	Cl	—	—	–8.6^c	– 56
19	Cl	OPh	5.8×10^4	4.0×10^4	–21.5	10
19	Cl	OC_6H_4Ph-*p*	1.4×10^5	5.1×10^4	–20.9	55
19	Cl	$OC_6H_4CMe_2Ph$-*p*	1.1×10^5	6.3×10^4	–21.0	43
19	Cl	$OC_6H_4Bu^tp$	4.3×10^4	3.7×10^4	–21.0	42
19	Cl	$OC_6H_4CF_3$-*m*	1.8×10^5	1.5×10^5	–21.0	–25
19	Cl	$OC_6H_4CF_3$-*p*	7.4×10^4	5.5×10^4	–21.5	18
20	F	OPh	3.8×10^4	2.5×10^4	–20.3	–15
20	F	OC_6H_4Ph-*p*	9.0×10^4	5.8×10^4	–19.5	48

[a] in THF using polystyrene standards; [b] in THF; in CH_2Cl_2.

Fig. 2. A fluorinated poly(thionylphosphazene) elastomer: Polymer **20** (OAr = OPh). Reproduced from ref. 37 with permission.

by nucleophilic attack at the sulfur(VI) center. In addition, attempts to replace the chlorine atoms at sulfur in polymers of structure **19** via reaction with excess sodium aryloxide at elevated temperatures gives rise to chain cleavage. These results suggest that if poly(thionylphosphazenes) with non-halogen substituents at sulfur as well as phosphorus could be prepared, they might exhibit greater general stability to basic reagents.

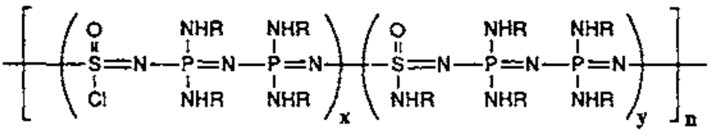
The molecular weights of the poly[(halogeno/aryloxy)thionylphosphazenes] **19** and **20** estimated by GPC using polystyrene standards are typically in the range $M_w = 38\,000$–$180\,000$ and $M_n = 25\,000$–$150\,000$ (Table 2). A low angle laser light scattering study of the poly(thionylphosphazene) with *p*-phenylphenoxy groups at phosphorus (**19**, $OAr = OC_6H_4Ph$-*p*) indicated an absolute value of M_w of 64 000, which for this particular polymer was about half that estimated by GPC. In addition, dynamic light scattering studies indicated that the hydrodynamic radius for the same poly(thionylphosphazene) was approx. 59 Å in THF at 22°C [43].

The thermal transition behavior of the aryloxy polymers of structure **19** and **20** has been studied by DSC, and T_g values for selected examples are listed in Table 2. As expected, the replacement of the chlorine atoms at phosphorus in **16** and **18** by bulkier aryloxy groups leads to a very significant increase in T_g. As was the case with **18** relative to **16**, the fluorinated polymers of structure **20** were found to possess lower T_g values than those of the analogous polymers with chlorine at sulfur. None of the polymers showed evidence of melting transitions, which suggests that they are amorphous [43]. This contrasts with the situation for the analogous single-substituent classical poly(aryloxyphosphazenes) $[NP(OAr)_2]_n$, which are generally microcrystalline [56]. Presumably the presence of a sulfur(VI) atom bearing an oxygen and a chlorine substituent introduces sufficient asymmetry to the polymer structure to prevent side group stacking and crystallization. A detailed discussion of trends in the T_g values for a variety of halogenated poly(thionylphosphazenes) and poly[(aryloxy)thionylphosphazenes] with halogen substituents at sulfur has been published [43]. These studies suggest that two competing effects determine the T_g values of the poly(thionylphosphazenes) relative to their classical polyphosphazene analogues. First, the presence of the highly polar S=O group tends to decrease skeletal flexibility relative to classical polyphosphazenes. Secondly, the smaller number of aryloxy substituents in mixed substituent poly[(aryloxy)thionylphosphazenes] with halogen substituents at sulfur (four per six atom repeat unit) compared to classical poly(aryloxyphosphazenes) (six per six atom repeat unit) tends to increase skeletal flexibility. With small substituents such as halogens or even small aryloxy groups the first effect is the most significant, and the poly(thionylphosphazene) has the higher T_g. By contrast, with bulky and rigid aryloxy side groups the second factor becomes dominant as the S=O groups are sterically shielded from one another, and the poly(thionylphosphazene) has the lower T_g. The importance of the second factor in cases where bulky and rigid side groups are present is illustrated by a comparison of the T_g value of polymer **19** with *p*-phenylphenoxy side groups ($T_g =$ 55°C) with the value for poly[(di-*p*-phenylphenoxy)phosphazene] ($T_g = 93$°C) [56].

6.4. Synthesis of poly[(amino)thionylphosphazenes]

The reactions of **16** and **18** with nucleophiles other than aryloxides have, to date, been much less studied. However, early results involving reactions with amines and alkoxides indicate that a diverse range of new poly(thionylphosphazene) derivatives should be accessible. Moreover, the substitution patterns detected are in some cases significantly different from that found with aryloxides. For these reasons this area is currently under active investigation, but the results to date will be summarized here.

The reactions of primary and secondary amines with the cyclic thionylphosphazene **15** have been well studied by van de Grampel and co-workers [27,28]. Halogen replacement has been shown to occur at both the phosphorus and the sulfur(VI) center. This suggested that analogous reactions with the poly(thionylphosphazenes) **16** and **18** might yield polymers in which the halogen atoms at both phosphorus and sulfur are replaced. Reaction of the poly(thionylphosphazene) **16** with an excess of a primary amine such as aniline or *n*-butylamine yields hydrolytically stable poly[(amino)thionylphosphazenes] **21**, in which, in addition to the chlorine atoms at phosphorus, a substantial proportion of the halogen substituents at sulfur are also replaced (Table 3) [37,41,48]. For example, reaction of **16** with excess aniline over 24 h yields a poly[(anilino)thionylphosphazene] **21** (R = Ph, $x = 0.2$, $y = 0.8$) in which 80% of the chlorine atoms at sulfur have been replaced according to elemental analysis. The presence of anilino substituents at both phosphorus and sulfur is indicated by the presence of two sets of ^{13}C NMR resonances for these side groups (see Fig. 3). In contrast, the ^{13}C NMR spectrum of the aryloxy-substituted poly(thionylphosphazene) **19** (OAr = OPh) which has phenoxy groups only at phosphorus shows only one set of aryloxy side group resonances (Fig. 1). A similar reaction of **16** with butylamine yields a poly[(amino)thionylphosphazene] **21** (R = *n*-Bu, $x = 0.5$, $y = 0.5$) in which 50% of the chlorine atoms at sulfur are replaced in addition to all of the chlorines at phosphorus.



$$\left[\left(\overset{\mathrm{O}}{\underset{\mathrm{Cl}}{\mathrm{S}}}=\mathrm{N}-\overset{\mathrm{NHR}}{\underset{\mathrm{NHR}}{\mathrm{P}}}=\mathrm{N}-\overset{\mathrm{NHR}}{\underset{\mathrm{NHR}}{\mathrm{P}}}=\mathrm{N}\right)_x\left(\overset{\mathrm{O}}{\underset{\mathrm{NHR}}{\mathrm{S}}}=\mathrm{N}-\overset{\mathrm{NHR}}{\underset{\mathrm{NHR}}{\mathrm{P}}}=\mathrm{N}-\overset{\mathrm{NHR}}{\underset{\mathrm{NHR}}{\mathrm{P}}}=\mathrm{N}\right)_y\right]_n$$

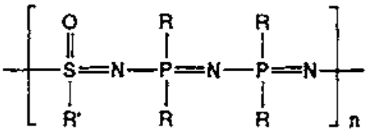
21

6.5. Synthesis of poly(thionylphosphazenes) with alkoxy substituents

Attempts to prepare fully alkoxy-substituted polymers via the reaction of the poly(thionylphosphazene) **16** with an excess of a sodium alkoxide Na[OR] have not yet been successful as chain cleavage appears to occur according to ^{31}P NMR and GPC measurements. Nevertheless, reaction of **16** with a deficiency of sodium alkoxides such as the butoxide, allyloxide, or the less basic trifluoroethoxide leads to poly(thionylphosphazenes) **22** in which a substantial fraction (up to approx. 40%) of the halogen substituents at phosphorus are replaced [44,49]. Treatment of the resulting polymers with an excess of a sodium aryloxide such as sodium *p*-phenylphenoxide yields high molecular weight mixed substituent halogeno/alkoxy/aryloxy poly(thionylphosphazenes) **23** (see Table 3). The ^{31}P and ^{13}C NMR spectra and elemental analysis data for such polymers and studies of the corresponding reactions with cyclic thionylphosphazenes strongly indicate that the replacement of chlorine

TABLE 3

Selected characterization data for poly[(amino)thionylphosphazenes] and poly(thionylphosphazenes) with alkoxy substituents

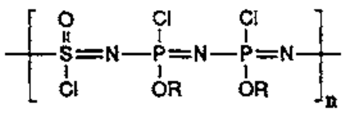


$$\left[\underset{\mathrm{R'}}{\overset{\mathrm{O}}{\mathrm{S}}}=\mathrm{N}-\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{P}}}=\mathrm{N}-\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{P}}}=\mathrm{N}\right]_n$$

Polymer	R′	R	GPC[a]		^{31}P NMR[b] (ppm)	T_g (°C)
			$\bar{M}_w$	$\bar{M}_n$		
21	10% Cl 90% NHMe	NHMe	-	—	5.0 (br)	—
21	50% Cl 50% NHBu^n	NHBu^n	1.4×10^5	6.7×10^4	2.1, 2.4	−17
21	50% Cl 50% NHCH$_2$ CH=CH$_2$	NHCH$_2$CH=CH$_2$	7.1×10^4	2.9×10^4	0.1, 0.2	−40
21	20% Cl 80% NHC$_6$H$_5$	NHC$_6$H$_5$	1.3×10^5	7.4×10^4	−18.6	101
23	Cl	40% OCH$_2$CF$_3$ 60% OC$_6$H$_4$Ph-*p*	1.2×10^5	7.7×10^4	−14 (br), −17 (br), −21	25
23	Cl	25% OBu^n 75% OC$_6$H$_4$CF$_3$-*m*	1.3×10^5	9.5×10^4	−19.7 (br), −21.6	−14
23	Cl	25% OCH$_2$CH=CH$_2$ 75% OC$_6$H$_4$CF$_3$-*m*	7.9×10^4	4.6×10^4	−19.0 (br), −19.5 (br), −21.5	−18

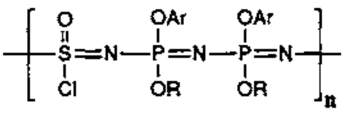
[a] In THF using polystyrene standards; [b] in THF.

atoms by alkoxy and aryloxy groups occurs randomly but exclusively at the phosphorus atoms and not at the sulfur(VI) centers. These reactions are, at present, unoptimized and it is possible that substantially higher loadings of alkoxy side groups will be achieved in the future.



$$\left[-\overset{\overset{O}{\|}}{\underset{\underset{Cl}{|}}{S}}{=}N{-}\overset{\overset{Cl}{|}}{\underset{\underset{OR}{|}}{P}}{=}N{-}\overset{\overset{Cl}{|}}{\underset{\underset{OR}{|}}{P}}{=}N-\right]_n$$

22



$$\left[-\overset{\overset{O}{\|}}{\underset{\underset{Cl}{|}}{S}}{=}N{-}\overset{\overset{OAr}{|}}{\underset{\underset{OR}{|}}{P}}{=}N{-}\overset{\overset{OAr}{|}}{\underset{\underset{OR}{|}}{P}}{=}N-\right]_n$$

23

As expected, the incorporation of smaller and more flexible alkoxy groups leads to a significant decrease in the glass transition temperatures detected compared to poly(thionylphosphazenes) with aryloxy groups at phosphorus. For example, polymer **23** (OR = OCH_2CF_3, OAr = OC_6H_4Ph-*p*, ratio 1:3), which possesses both trifluoroethoxy and *p*-phenylphenoxy substituents at phosphorus, has a T_g of 25°C, which is substantially lower than that of polymer **19** with only *p*-phenylphenoxy side groups attached to phosphorus (T_g = 55°C).

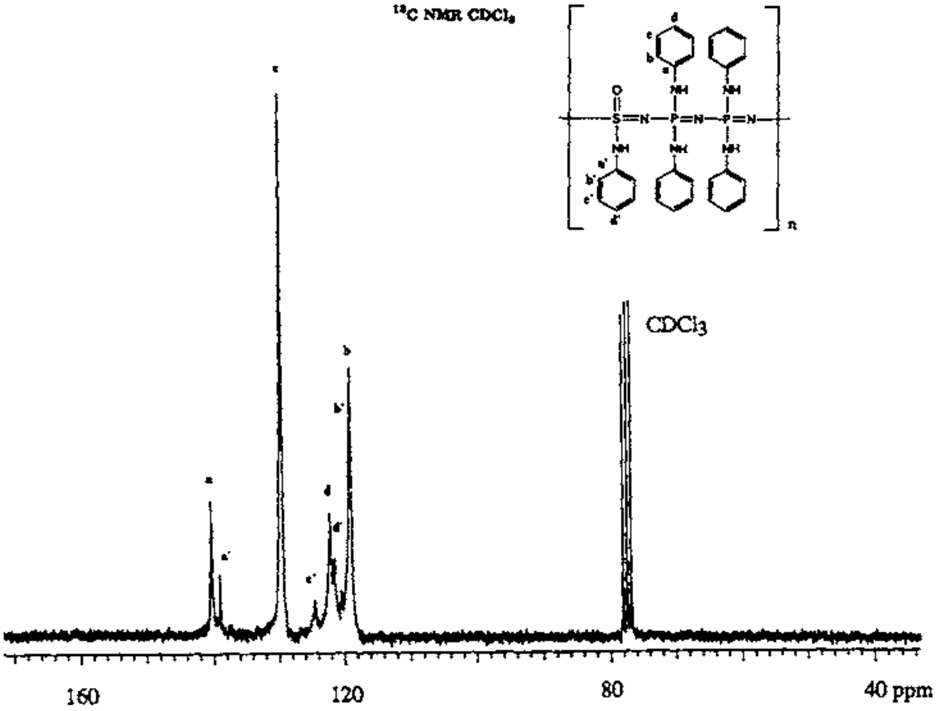


Fig. 3. The ^{13}C NMR spectrum of the poly[(anilino)thionylphosphazene] 21 (NHR = NHPh).

6.6. The mechanism for the ring-opening polymerization of halogenated cyclic thionylphosphazenes

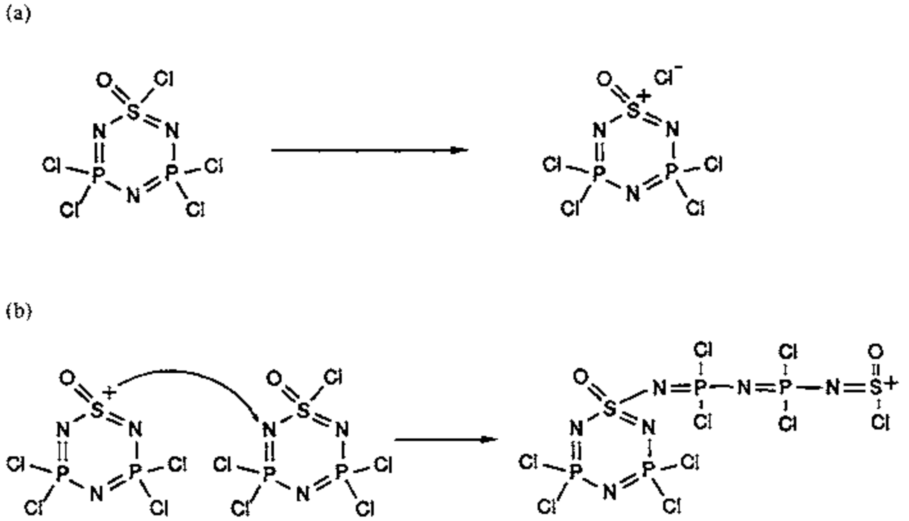
The most likely pathway for the ROP of **15** or **17** is a cationic, chain growth process [37,42]. A cationic mechanism is common for the polymerization of cyclic organic molecules and is believed to operate for classical cyclic phosphazenes [2]. The operation of such a mechanism for the ROP of cyclic thionylphosphazenes is supported by the detected catalytic effects of Lewis acids such as Ag^+ and $AlCl_3$ which have been found to lower the temperature required for the polymerization of **15** to approx. 135°C [47].

For a cationic mechanism two possible initiation steps might be envisaged [37,42]. These involve either ionization of a S–Cl bond or, alternatively, ionization of a P–Cl bond. Studies by van de Grampel suggest that the small molecule nucleophilic substitution reactions of **15** with amines proceed via an S_N1 mechanism at sulfur, and an S_N2 process at phosphorus [27]. This would tend to indicate that the first alternative, which is identical to the first step of an S_N1 process, is more likely. Further support for ionization at sulfur as the initiating step comes from the observation that cyclic thionylphosphazenes with phenyl or halogenoalkyl substituents at sulfur, $(NSOR)(NPCl_2)_2$ ($R = Ph$ or CH_2CHCl_2), do not undergo ROP at elevated temperatures [47]. This supports ionization at sulfur as the initiating step, as a sulfur–carbon bond is expected to be highly resistant to heterolytic cleavage and so the presence of alkyl or aryl groups at sulfur would be expected to prevent polymerization.

If we speculate that ionization at sulfur is the first step, chain propagation might occur via attack of the thionylphosphazene cation on another molecule of **15** to give a cationic cyclolinear species, which could then continue chain propagation (Scheme 1) [37,42]. Chain termination could occur by cation–anion recombination, and chain transfer by the cationic active site abstracting a chloride anion from an adjacent polymer chain.

6.7. Summary

Work carried out over the past two years has shown that the incorporation of skeletal four-coordinate sulfur(VI) atoms yields the most stable and potentially diverse class of sulfur–nitrogen–phosphorus polymers, poly(thionylphosphazenes), reported to date. Although the poly(thionylphosphazene) system is still at an early stage of development and much additional work is required with respect to studies of the synthesis and properties of these polymers, a number of unusual features and significant differences from poly(oxythiazenes) **2** and classical polyphosphazenes **3** have already emerged. For example, significant differences from each of the latter classes of polymer in terms of thermal transition temperatures and/or polymer morphology are evident. In addition, the substitution patterns detected differ from



Scheme 1. A possible mechanism for the ROP of the cyclic thionylphosphazene **15** involving ionization at sulfur as the initiation step: (a) initiation; (b) propagation.

those found with classical polyphosphazenes, which allows access to novel polymer structures such as that of the fluorinated elastomer **20** (OAr = OPh) (Fig. 2). In contrast, classical polyphosphazenes with halogen side groups are generally very sensitive to hydrolysis. The presence of skeletal sulfur(VI) atoms also leads to interesting polymer conformation effects. Thus, recent theoretical work on mimics using a 6–31G* basis set has led to the prediction of a cis–trans helical structure for perhalogenated poly(thionylphosphazenes) such as **16** [45,46] which contrasts with the cis–trans planar structure adopted by classical polyphosphazenes such as $[NPCl_2]_n$ [3,54].

7. CONCLUSIONS AND FUTURE WORK

The study of sulfur–nitrogen–phosphorus polymers represents a very new area of research at the interface of main group element chemistry and polymer and materials science. The first well characterized class of these macromolecules, the poly(thiophosphazenes), possess skeletal three-coordinate sulfur(IV) atoms and were first reported in 1990. These particular materials show a number of interesting features; however, the examples reported to date suffer from the disadvantage of a relatively fragile polymer backbone and associated moisture sensitivity. Nevertheless, small molecule cyclic thiophosphazenes **5** with aryl side groups such as $(NSPh)(NPPh_2)_2$ are reported to be stable to moisture and thermally stable up to 200°C [58]. This suggests that if synthetic routes to polymers with aryl or related side groups can be devised then the resulting poly(thiophosphazenes) should show much improved stability.

Poly(thionylphosphazenes), with four-coordinate skeletal sulfur(VI) atoms, were first reported in 1991 and represent the most stable and potentially diverse class of sulfur–nitrogen–phosphorus polymers developed so far. If improved synthetic routes to some of these polymers can be achieved various possible applications can be foreseen. Future work will also concentrate on understanding the different and unusual substitution patterns observed with these polymers and, in particular, on detailed investigations of the properties of the polymers prepared, especially those with the most novel structures (such as **20**).

The synthesis and study of other classes of S–N–P polymers should continue to be an exciting area in the future. In particular, it is to be expected that the poly(thiazylphosphazenes) with two-coordinate skeletal sulfur(III) atoms will possess extremely interesting properties. A variety of other cyclic species with sulfur–nitrogen–phosphorus skeletons are known besides cyclic thio- and thionylphosphazenes. For example, cyclic compounds such as *cis*-$(NSOCl)_2(NPCl_2)$ are well known, though studies of their polymerization behavior have not yet been reported [27,57,59,60]. Thus, the synthesis and study of new sulfur–nitrogen–phosphorus polymer systems with different ratios of sulfur to phosphorus should also be of interest in the next few years, in addition to the further development of the polymer systems reported so far.

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