Synthesis of Polyphosphazenes with Isothiocyanato, Thiourethane, and Thiourea Side Groups

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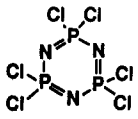
ABSTRACT: The isothiocyanatophosphazene, $[NP(NCS)_2]_3$, undergoes ring-opening polymerization when heated at temperatures above 100 °C to form a low molecular weight polymer, $[NP(NCS)_2]_n$. The copolymerization of $[NP(NCS)_2]_3$ and $[NPCl_2]_3$ was examined, and mechanistic implications for cyclophosphazene polymerization are discussed. High molecular weight $[NP(NCS)_2]_n$ was prepared by the metathetical exchange reaction of $(NPCl_2)_n$ with potassium thiocyanate. Treatment of $[NP(NCS)_2]_n$ with alcohols and amines to form thiourethane and thiourea derivatives was examined. Steric and electronic effects prevented full reaction of the isothiocyanato side groups with alcohols. However, thiourea derivatives, $[NP(NHCSNHR)_2]_n$, were prepared by the reactions of $[NP(NCS)_2]_n$ with amines. Mixed-substituent thiourethane and thiourea phosphazene polymers with trifluoroethoxy or 2-(2-methoxyethoxy)ethoxy cosubstituent groups were also synthesized. The characterization and properties of the thiourethane and thiourea phosphazene polymers are described.

The cyclic trimeric phosphazene $(NPCl_2)_3$ (1) and the cyclic tetrameric analogue 2 undergo ring-opening polymerization when heated at 250 °C to form poly(dichlorophosphazene) (3).[1-4] The chlorine atoms of 1-3 can be replaced by a wide variety of organic groups by reaction with sodium alkoxides or aryl oxides, and with primary or secondary amines. The reactions and structures of cyclic phosphazenes such as 1 or 2 are useful models to develop conditions for the reactions of the high polymers.[5]



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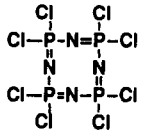

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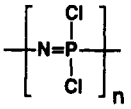

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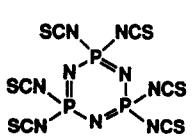
Other cyclotriphosphazenes with halogeno side groups such as $(NPF_2)_3$ and $(NPBr_2)_3$ also polymerize when heated at high temperatures. However, phosphazenes that lack halogeno side groups such as $[NP(OR)_2]_3$ (R = CH_2CF_3, C_6H_5) ring–ring equilibrate to form higher cyclic species rather than polymerize, except when transannular metallocenyl substituents are present.[6]

In 1958, Audrieth et al. reported the first synthesis of phosphazenes that bear isothiocyanato side groups.[7,8] Cyclic compounds 4 and 5 were prepared by the metathetical exchange reactions of 1 and 2 with potassium thiocyanate. When 4 or 5 were heated at 145 °C they were converted to a rubbery material that was believed to be the polymeric analogue 6. Isothiocyanates react with alcohols and amines to form thiourethanes and thioureas (Scheme I).[9-11] The reaction of 4 and 5 with alcohols and amines to yield thiourethanes and thioureas was apparently achieved in the earlier work, but few characterization data were given. Brief reports of isothiocyanatophosphazenes have appeared since that original report,[12-22] but the chemistry of these species has not been studied in detail, particularly at the macromolecular level.



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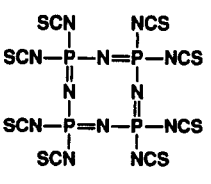

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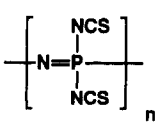

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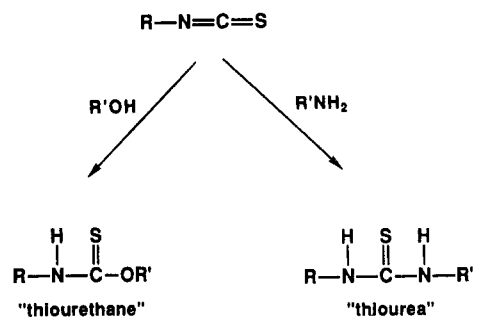
Scheme I



Several reasons exist for an interest in the macromolecular chemistry of isothiocyanatophosphazenes. For example, the conversion of 4 or 5 to an elastomer occurs at a surprisingly low temperature, and hence, these compounds could be useful as low-temperature initiators or comonomers for the polymerization of 1. In addition, phosphazene polymers with isothiocyanato side groups may be useful for the covalent linkage of hydroxy or amino compounds (including many biologically important species) to surfaces, hydrogels, or water-soluble polymers. Thiourethane and thiourea linkages are characterized by restricted rotation about the C–N bonds as a consequence of electronic resonance effects. Hence, the incorporation of these side groups into a polyphosphazene structure offers opportunities for the synthesis of polymers with rigid side groups. To the best of our knowledge, no reports exist of linear phosphazene polymers that bear thiourethane or thiourea side groups.

In a separate paper, the chemistry and structure of small-molecule isothiocyanatophosphazenes such as 4 and 5 were reported as a prelude to the present work, and the electronic and steric effects that control the reactivity of the isothiocyanato side group were examined.[23] In the present paper, we have transposed the small-molecule chemistry to the macromolecular level and have attempted to answer the following questions: (1) Do 4 and 5 indeed polymerize to 6 at moderately low temperatures? (2) Do 4 and 1 copolymerize at temperatures below 250 °C, and what mechanistic information might be obtained from such a copolymerization? (3) Can stable thiourethane or

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thiourea polymers be prepared by the reaction of 6 with alcohols or amines? (4) Can stable mixed-substituent alkoxy/thiourethane or alkoxy/thiourea phosphazene polymers be synthesized?

Results and Discussion

Polymerization of $[NP(NCS)_2]_3$. The polymerization of 4 was found to proceed in a manner similar to the polymerization of other cyclotriphosphazenes such as 1, except that polymerization occurred at a relatively low temperature. The cyclic trimer 4 was heated at 145 °C in glass tubes that had been evacuated and sealed. After 2 h the contents of the tubes had become yellow and viscous, which suggested that a polymerization may have occurred. At 100 °C, the contents became viscous after 48 h. No increase in viscosity could be detected at temperatures below 100 °C. The cyclic tetramer, 5, showed an increase in melt viscosity after 12 h at 145 °C. The controlled addition of traces of water (<0.1%) did not affect the rate of polymerization significantly.

After the polymerizate had become viscous, the tubes were allowed to cool to 25 °C and were opened for spectroscopic analysis of the products. The yellow products were soluble in common solvents such as THF or chloroform, but only if the polymerization was terminated before the melt became completely immobile. The ^{31}P NMR spectra of the crude polymerizate from 4 consisted of resonances for unreacted 4 (singlet at δ = −26 ppm), higher cyclic species such as the tetramer 5 (singlet at δ = −47 ppm), and polymer **6a** (broadened resonances at δ = −54 ppm). The ^{31}P NMR chemical shifts for higher cyclic phosphazene species and polymers are normally shifted upfield from the cyclic trimer.

The ^{13}C NMR spectra of the polymerizate consisted of resonances for the isothiocyanato carbon atoms of 4, 5, and **6a** (singlets at δ = 147, 146, and 145 ppm, respectively). No evidence for *thiocyanato* (P–SCN) side groups could be found from the ^{13}C NMR spectra. Similarly, the IR spectra of the crude products showed a major absorption for the isothiocyanato group (2000 cm^{-1}), but no absorptions for thiocyanato linkages (2100–2200 cm^{-1}) were found. Thus, all the spectroscopic data strongly suggested that **6a** was a linear polymer, and that polymerization of 4 did not occur by cycloaddition reactions of isothiocyanato side groups to form a cyclomatrix polymer. Further evidence that **6a** is not a cyclomatrix polymer is the fact that a form of 6 (designated **6b**) can be prepared by the alternative reaction of 3 with potassium thiocyanate (see later).

The polymer became cross-linked if the polymerization of 4 or 5 was allowed to continue until the polymerizate became immobile. It then only swelled in solvents such as THF or chloroform but did not dissolve. Similar cross-linking behavior is found for chlorophosphazene polymers. Integration of the ^{31}P NMR spectra showed that, typically, 60% of 4 was consumed to form higher cyclic oligomers and polymer after 2 h of polymerization at 145 °C. After removal of the cyclic oligomers by several precipitations into dry heptane, **6a** was isolated as a yellow, hydrolytically sensitive gum. However, **6a** was isolated as an elastomer if it was allowed to cross-link at prolonged polymerization times. Polymer 6 could not be stored for extended periods of time in an inert atmosphere without cross-linking, which again reflects the high reactivity of the P–NCS linkage.

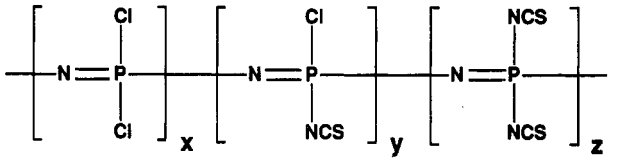
The glass transition temperature (T_g) of **6a**, prepared by the polymerization of 4 at 145 °C, was −57 °C, based on the results of differential scanning calorimetric (DSC) analysis. This is similar to the glass transition temperature of 3 (−63 °C). However, intrinsic viscosity measurement (0.2 dL/g in THF at 25 °C) indicated that the molecular weight of **6a** was relatively low compared to 3 and other phosphazene polymers (2–4 dL/g). This was consistent with the gumlike character of the polymer.

Table I
Copolymerization Data for $(NPCl_2)_3$ (1) and $[NP(NCS)_2]_3$ (4)

temp, °C	time, h	ratio 1:4	% consumed 1	% consumed 4
100	24	50:50	0	44
145	8	50:50	0	83
145	48	90:10	no polymer	
170	1.5	50:50	0	92
170	9	90:10	1	47
170	48	90:10	9	100
170	71	90:10	12	110
170	71	95:5	no polymer	
200	0.75	50:50	0	78
200	17	90:10	40	100
200	27	90:10	48	100
200	13	95:5	9	100
200	23	95:5	18	100
200	50	95:5	36	100
250	1	90:10	22	100
250	1.25	90:10	30	100

Copolymerization of 1 with 4. Strong interest exists in the search for initiators that lower the temperature required for polymerization of 1. Hence, the copolymerization of 1 and 4 was studied at various temperatures and with different ratios of 1 to 4 (Table I). The products of the copolymerization reactions were analyzed by ^{31}P NMR and electron impact mass spectral (EIMS) analysis. The NMR analysis allowed the percent reaction of each cyclic trimer to be measured, and EIMS analysis allowed the low molecular weight products to be identified.

It was found that 1 can be induced to polymerize in the presence of 4 to form copolymer 7 at temperatures below



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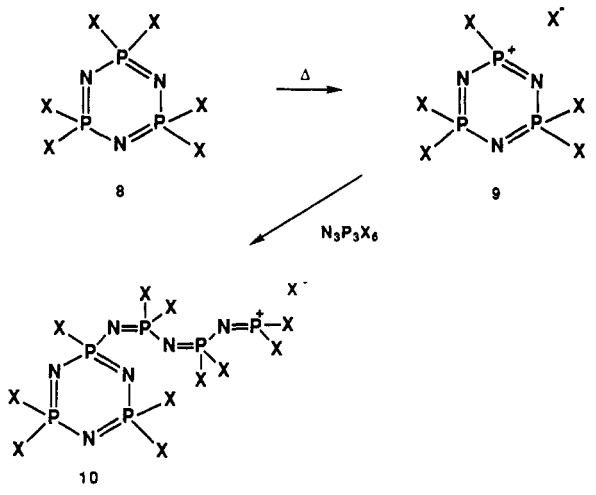
250 °C. When 1 and 4 were heated together at 100 or 145 °C, 1 acted only as a "molten solvent" for the polymerization of 4. This conclusion is based on both ^{31}P NMR and EIMS analysis of the polymerization products. However, copolymerization of the two trimers was detected by both ^{31}P NMR and EIMS analyses for reactions carried out at 170 °C, although the percent incorporation of 1 into the copolymer was relatively low. A significant incorporation of 1 into the copolymer did not occur until the polymerization temperature was raised to 200 or 250 °C. At 200 °C, a 48% conversion of 1 to higher cyclic species and polymer was achieved after 27 h when a 90:10 ratio of 1 to 4 was used. Control experiments in which 1 was heated in the absence of 4 confirmed that 4 served as an initiator.

EIMS analyses of the polymerization products provided good evidence that the two trimers had copolymerized and had not polymerized independently of each other. Higher cyclic species with both chloro and isothiocyanato side groups, such as $N_6P_6Cl_6(NCS)_5^+$ (m/e = 772, Cl-6 isotope pattern) and $N_6P_6(NCS)_6Cl_5^+$ (m/e = 795, Cl-5 isotope pattern), were detected consistently by EIMS analysis. In addition, scrambling of chloro and isothiocyanato side groups was detected by ^{31}P NMR analysis, particularly during the later stages of copolymerization

Scheme II



when most or all of 4 had been consumed. The PCl_2 and $P(NCS)_2$ units of 7 were detected as resonances at $\delta = -18$ and −54 ppm. However, a third resonance was also evident at $\delta = -37$ ppm which was assigned to P(NCS)Cl units. Confirmation of this assignment for the resonance at $\delta = -37$ ppm was the observation that 7 could also be prepared by the metathetical exchange reaction of 3 with a deficiency of potassium thiocyanate, as discussed below.

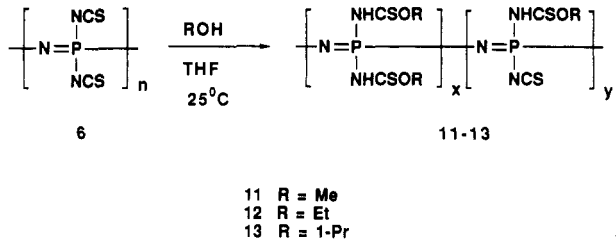
Implications for the Mechanism of Polymerization. The facile polymerization of 4 and the copolymerization of 1 with 4 provided some insight into the mechanism of cyclotriphosphazene polymerization. A plausible mechanism for the initiation and propagation steps of the polymerization of a cyclotriphosphazene with halogeno side group X, $(NPX_2)_3$ (8), is shown in Scheme II.[24] In this mechanism, initiation follows the ionization of a side unit from 8 to form the phosphazenyl cyclic species 9, and the first propagation step results from electrophilic attack by 9 on the backbone of a molecule of 8 to form the cyclolinear species 10. However, it is important to note that cyclic end groups for phosphazene high polymers have not yet been identified.

Although the X-ray crystal structures of 4 and 5[21,22] suggest that donation of the lone-pair electron density of the isothiocyanato nitrogen atom occurs into the phosphazene ring, the relatively low temperature required for polymerization of 4 and 5 is consistent with the known propensity for isothiocyanato groups to ionize from organic units when heated.[9] It may also reflect the ability of isothiocyanato side groups to stabilize the positive charge of an initiating species such as 9 or propagating species 10. Stabilization of the positive charge of species 9 and 10 would also help to explain the relatively low molecular weight of **6a**, since the reactivity of a propagating unit is inversely proportional to the stability of the propagating site.[25]

The copolymerization behavior of 1 and 4 provides further insight into the mechanism of polymerization. Although initiation and propagation species from 4 were apparently present at 100 and 145 °C in the copolymerization experiments, these species were not reactive enough to induce ring opening of 1.

It is also significant that the isothiocyanato side groups do not react with each other during the polymerization. In an anionic polymerization mechanism, the propagation site would react with the side groups. It should also be noted that attempts to detect intermediate species 9 and 10 were carried out. The polymerization of 4 was conducted in the heated probe of a multinuclear NMR spectrometer, and the ^{31}P NMR and ^{13}C NMR spectra

Scheme III



were measured at intermediate stages of polymerization. However, no intermediate species could be detected, despite the low molecular weight of polymer **6a**.

Alternative Synthesis of $[NP(NCS)_2]_n$. Because the molecular weight of **6a** prepared by ring-opening polymerization of 4 was relatively low, an alternative pathway for the synthesis of 6 was explored. It was found that polymer 6 can also be prepared by the metathetical exchange reaction of 3 with potassium thiocyanate in THF solution. The ^{31}P NMR spectrum of the product of this reaction (**6b**) consisted of a singlet at $\delta = -54$ ppm, the same resonance detected for the product of the ring-opening polymerization. GPC analysis of polymers prepared from the reaction of **6b** with alcohols and amines indicated that the molecular weight of **6b** is relatively high (see later). Reaction of 3 with a *deficiency* of potassium thiocyanate resulted in the formation of the mixed-substituent polymer 7.

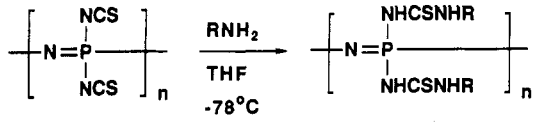
Synthesis of Thiourethane and Thiourea Polymers. The cyclic trimeric and tetrameric chemistry reported elsewhere[23] was vital for the establishment of optimum conditions for polymer reactions. Consistent with previous studies,[5] tetramer 5 is a better model for polymer 6 than is the trimer 4. In the model compound study, tetramer 5 was less reactive than trimer 4.

When THF solutions of **6b** were treated with an excess of methanol, ethanol, or 1-propanol at 25 °C, a reaction occurred immediately. This reaction could be followed by ^{31}P NMR spectroscopic analysis. As in the cyclic trimer and tetramer chemistry, a nongeminal addition pathway to form thiourethane derivatives 11–13 was detected (Scheme III). The ^{31}P NMR analysis showed that approximately 60% of the isothiocyanato side groups could be converted to thiourethane groups by reaction with the alcohol at 25 °C.

However, the reactivity of the isothiocyanato groups in 11–13 was reduced as the reaction proceeded, and full conversion to thiourethane groups could not be achieved, even with forcing conditions. This low reactivity of the isothiocyanato units in 11–13 was attributed to steric hindrance by the bulky thiourethane side groups. The reactivity of isothiocyanato groups is also lowered by the presence of electron-releasing cosubstituent groups (see later). The thiourethane side group may act as an electron-releasing unit by donation of the lone-electron pair on the nitrogen atom into the phosphazene backbone. The inability of **6b** to undergo complete reaction was consistent with the model compound study,[23] where it was found that tetramer 5 was less reactive with alcohols than trimer 4.

In the model compound study, primary amines reacted easily with all the isothiocyanato side groups of 5. At the macromolecular level, reaction of **6b** in THF with aniline, 1-butylamine, or 1-octylamine at −78 °C resulted in the facile formation of thiourea polymers 14–16 (Scheme IV). Based on ^{31}P NMR spectroscopic analyses of the reaction mixtures, no preference for geminal or nongeminal pathways was detected during thiourea formation. Characterization data for 14–16 are given in a later section.

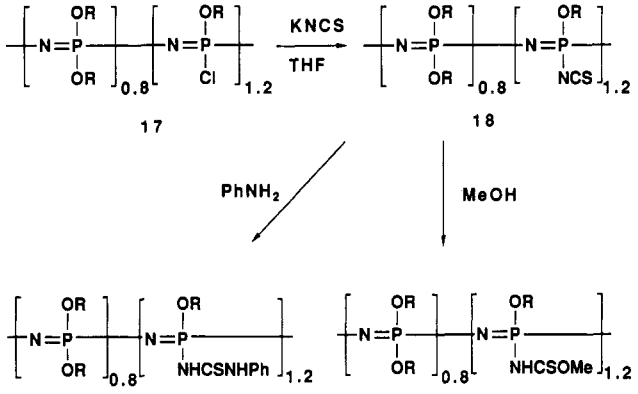
Scheme IV



6 14-16

14 R = Ph
15 R = 1-Bu
16 R = 1-Octyl

Scheme V



17 18 20 19

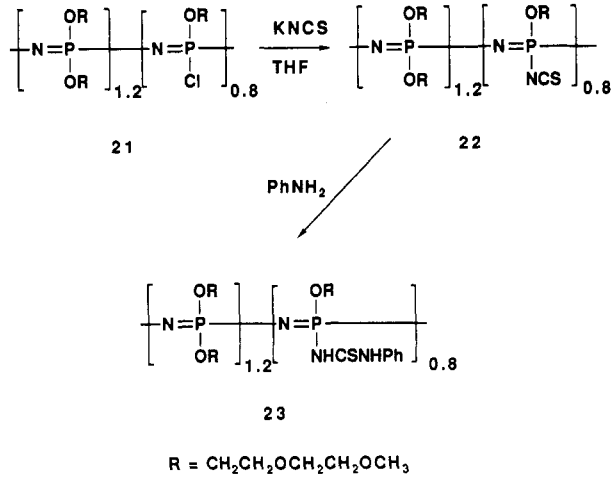
R = CH_2CF_3

Synthesis of Mixed-Substituent Thiourethane and Thiourea Polymers. Fluoroalkoxy polyphosphazenes are used in technology as high-performance elastomers. Thus, mixed-substituent polymers with trifluoroethoxy groups and thiourethane or thiourea units are of interest (Scheme V). The trifluoroethoxy group is an electron-withdrawing unit, which should increase the reactivity of nearby isothiocyanato side groups. Polymer **3** was allowed to react with a deficiency of sodium trifluoroethoxide in THF to yield **17**, which contained 30% residual P–Cl bonds. The reaction stoichiometry was designed to ensure that no residual PCl_2 units were present. Polymer **17** was then converted to **18** by reaction with potassium thiocyanate. Reaction of **18** with methanol in THF at 66 °C or with aniline in THF at 25 °C resulted in the formation of thiourethane (**19**) and thiourea (**20**) derivatives.

Polyphosphazenes with 2-(2-methoxyethoxy)ethoxy side groups have shown excellent promise as solid-state electrolytes and as biomedical materials. Thus, this side group was also examined as a cosubstituent unit (Scheme VI). Polymer **3** was allowed to react with a deficiency of the sodium salt of 2-(2-methoxyethoxy)ethanol in THF to yield **21**, in which 20% of the P–Cl bonds remained unreacted. Again, the reaction stoichiometry was designed so that no PCl_2 units would be present. The reaction of **21** with potassium thiocyanate then resulted in the formation of **22**. Although the interaction of **22** with aniline in THF at 25 °C gave the thiourea derivative **23**, no reaction was detected between **22** and methanol in THF at 66 °C. The reduced electrophilicity of the isothiocyanato groups of **22** can probably be attributed to the electron-releasing character and steric bulk of 2-(2-methoxyethoxy)ethoxy side groups.

Attempts were also made to use the phenoxy group as a cosubstituent. However, chloro side groups geminal to phenoxy side groups could not be converted to isothiocyanato side groups by treatment with potassium thiocyanate, presumably due to the steric bulk of the phenoxy units. This too was consistent with the model compound

Scheme VI



21 22 23

R = $CH_2CH_2OCH_2CH_2OCH_3$

chemistry.[23]

Characterization of Thiourethane and Thiourea Phosphazene Polymers. The thiourethane and thiourea polymers, **14–16**, **19**, **20**, and **23** were characterized by a combination of multinuclear NMR, IR, elemental analysis, and gel permeation chromatography (GPC) (Table II). The ^{31}P, ^{13}C, and ^{1}H NMR spectra of the polymers resembled those of their cyclic trimeric and tetrameric analogues (Figures 1–3), except that the resonances for the polymers were broader. Broadening of the resonances was particularly significant in the ^{31}P NMR spectra of **14–16**, which possess *geminal* thiourea side groups. The thiocarbonyl carbon atoms were detected in the ^{13}C NMR spectra in the region of $\delta = 180$ ppm for the thioureas and at $\delta = 190$ ppm for the thiourethanes. Elemental analysis data were consistent with the structures. They indicated that residual chlorine atoms were not present. IR analysis showed bands at 3100–3400 cm^{-1} for N–H, 3000–2800 cm^{-1} for C–H, and 1200–1300 cm^{-1} for P–N stretching modes. GPC analysis (measured relative to polystyrene standards) indicated that the M_w molecular weights were above 10^5.[26]

The glass transition (T_g) and melting temperatures (T_m) were determined by DSC analysis. The T_g's of the single-substituent polymers $[NP(OCH_2CF_3)_2]_n$ and $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ are −66 and −84 °C, respectively. DSC analysis showed that the thiourethane and thiourea side groups raised the T_g's for the mixed-substituent polymers **19**, **20**, and **23** to −44, 25, and −37 °C, respectively. These increased T_g's can probably be explained by the bulk, rigidity, and hydrogen-bonding capability of the thiourethane and thiourea side groups. No melting transitions were detected for the mixed-substituent polymers. Films of **19** were tough, flexible, and partially elastomeric at room temperature, while films of **20** were brittle. Films of **23** were flexible and adhesive at 25 °C.

The T_g's of the thiourea homopolymers **14–16** could not be detected unambiguously by DSC analysis. Films of **14–16** were extremely brittle at room temperature, which suggests that the T_g's of **14–16** are above 25 °C. Melting transitions for **14–16** were detected at 130 °C, by DSC analysis. This was confirmed by optical analysis of the polymers with the use of a polarizing microscope equipped with a hot stage.

Finally, the thermal stability of the trifluoroethoxy derivative **19** was investigated briefly. Thermogravimetric analysis showed a 10% weight loss at 180 °C. It is known that the thiourethane linkage has only a limited thermal stability.[9]

Experimental Section

Materials. Hexachlorocyclotriphosphazene (**1**) was supplied by Ethyl Corp. and was recrystallized from hexane and vacuum

Table II
Characterization Data

polymer	^{31}P NMR, ppm	^{13}C NMR, ppm	^{1}H NMR, ppm	GPC ($\times 10^5$) M_n	GPC ($\times 10^5$) M_w	elem anal.	calcd	expt
14	−26 (br)	120, 125, 130, 150, 180	6.6–8.4	0.5	4	C	48.40	47.84
						H	4.06	4.51
						N	20.16	21.05
						Cl	0.00	0.33
15	−23 (br)	14, 21, 31, 45, 181	0.9, 1.4, 1.6, 3.5, 8.3	0.2	9	C	39.06	37.52
						H	7.23	6.98
						N	22.78	22.41
						Cl	0.00	0.28
16	−25 (br)	14, 23, 27, 28, 29, 30, 32, 46, 181	0.9, 1.3–1.6, 3.5, 8.3	0.4	6	C	51.52	52.00
						H	9.13	9.33
						N	16.69	16.02
						Cl	0.00	0.11
19	−10, −19	64 (q), 125 (q), 59, 192	4.1, 4.6, 9.0	2	8	C	20.21	20.32
						H	2.21	2.34
						N	9.43	9.24
						Cl	0.00	0.20
20	−10, −16	64 (q), 125 (q), 125, 127, 130, 139, 181	6.6–8.0 (m), 4.6	0.3	2	C	30.64	29.93
						H	2.57	2.77
						N	11.23	12.05
						Cl	0.00	0.05
23	−3, −13	59, 67, 70, 71, 72, 124, 126, 129, 140, 181	3.4–4.2 (m), 6.7–8.0	0.5	5	C	43.81	44.71
						H	6.95	6.98
						N	8.52	9.04
						Cl	0.00	0.10

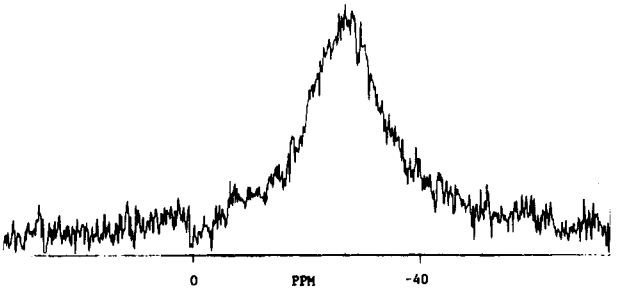


Figure 1. ^{31}P NMR spectrum of 14 in chloroform.

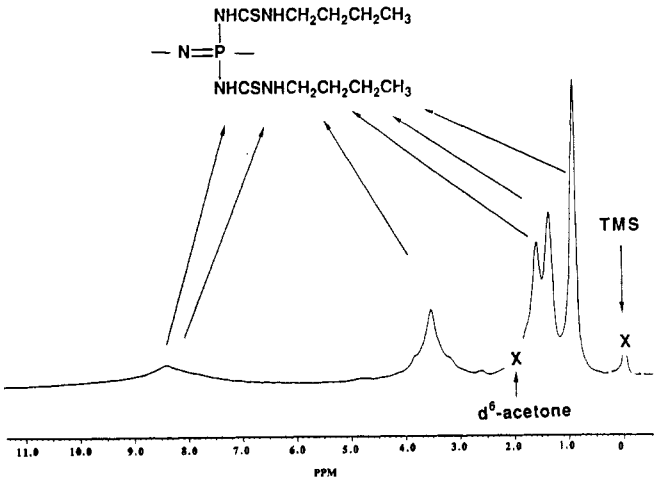


Figure 2. ^{1}H NMR spectrum of 15 in acetone-d_6 with tetramethylsilane (TMS) added.

sublimed. Poly(dichlorophosphazene) (3) was prepared by the polymerization of 1 in an evacuated, sealed glass tube at 250 °C. Polymerization was terminated by cooling when the tube contents were nearly immobile. Compounds 4 and 5 were prepared by reaction of 1 or 2 with potassium thiocyanate in THF, as described elsewhere.[28] Purification of 2 was carried out by recrystallization from heptane. Methanol, ethanol, and 1-propanol (Aldrich) were purified by distillation over barium oxide and stored over molecular sieves. Aniline, 1-butylamine, and 1-octylamine (Aldrich) were purified by distillation from calcium hydride and stored over molecular sieves. 18-Crown-6 ether was recrystallized from acetonitrile.

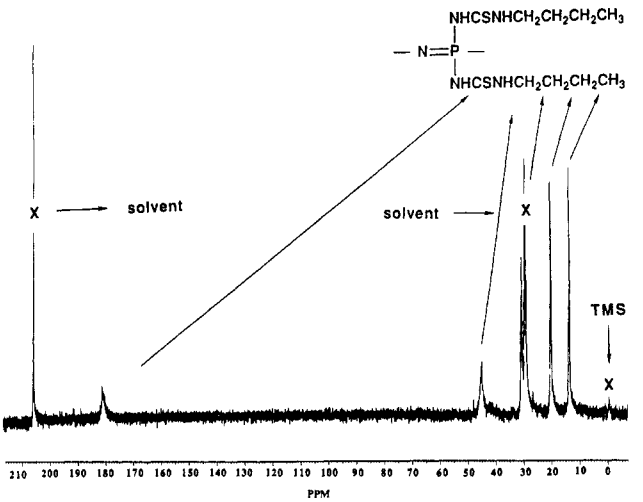


Figure 3. ^{13}C NMR spectrum of 15 in acetone-d_6 with tetramethylsilane (TMS) added.

Instrumentation and Methods. All reactions were carried out with use of conventional inert atmosphere techniques. ^{31}P and ^{13}C NMR spectra were obtained with the use of a JEOL FX90Q spectrometer. High-field ^{1}H and ^{13}C NMR spectra were obtained with the use of a Bruker WM-360 spectrometer. Infrared spectra were obtained with a Perkin-Elmer 1710 FT-IR. Samples were analyzed as KBr pellets or as thin films cast on NaCl disks. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Approximate molecular weights were determined with a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF through Polymer Laboratory PL gel columns (10^6, 10^6, and 10^3 Å), and narrow molecular weight distribution polystyrene standards were used.[26] DSC analysis was performed with the use of a Perkin-Elmer DSC-7 differential scanning calorimeter. A heating rate of 10 °C/min was employed. The samples were analyzed under a nitrogen atmosphere in crimped aluminum pans. Solution viscosity was measured with a Cannon-Ubbelohde capillary viscometer held in a temperature-controlled water bath. Thermogravimetric analysis was carried out with a Perkin-Elmer TGA-7 system. The heating rate was 10 °C/min. Mass spectral analysis was carried out with a Kratos MS9/50 spectrometer.

Polymerization Experiments. Constricted Pyrex glass polymerization tubes (1 × 10 cm) were equipped with ground glass

joints. The tubes were soaked in a concentrated KOH/ethanol bath for at least 24 h and were washed thoroughly with dilute acid, tap water, and distilled–deionized water (5× each). The tubes were inverted, allowed to air-dry, and were then dried in an oven at 200 °C for at least 24 h. Compounds to be polymerized were loaded into the tubes in a glovebox. The tubes were then evacuated (10 μm) and sealed with a flame torch at the constriction end. The tubes were placed in a thermoregulated oven equipped with a mechanical rocker.

Reaction of 6 with Alcohols. The following is a typical procedure. Polymer **3** (2.0 g, 0.034 mol of PCl) was dissolved in THF (100 mL). Potassium thiocyanate (5.0 g, 0.051 mol) and 18-crown-6 ether (0.10 g, 0.38 mmol) were added, and the reaction mixture was refluxed for 12 h. The ^{31}P NMR spectroscopic analysis of the reaction mixture showed a clean singlet at $\delta = -54$ ppm, which indicated that **6** had formed. 1-Propanol (25 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 12 h. The ^{31}P NMR spectroscopic analysis indicated that the reaction was complete and that **13** was formed. The $P(NHCSOR)_2$ units were detected from the ^{31}P NMR spectrum at $\delta = -27$ ppm, and the P(NHCSOR)(NCS) units at $\delta = -42$ ppm. However, full reaction could not be achieved with reflux for several days, based on ^{31}P NMR spectral analyses. Attempts to achieve complete reaction were also carried out by treatment of **13** with refluxing 1-propanol in the absence of THF, but these attempts were also unsuccessful. Polymers **11–13** were not characterized further.

Synthesis of $[NP(NHCSNHR)_2]_n$ (14–16). The synthesis of **15** was typical. Polymer **3** (2.55 g, 0.0440 mol of PCl) was dissolved in THF (100 mL). Potassium thiocyanate (8.5 g, 0.088 mol) and 18-crown-6 ether (0.10 g, 0.38 mmol) were added, and the reaction solvent was refluxed for 12 h. ^{31}P NMR spectroscopic analysis showed that the formation of **6** occurred. The reaction mixture was cooled to −78 °C. A stoichiometric amount of 1-butylamine (3.21 g, 0.0440 mol) was added dropwise. The stoichiometry was designed so that only 1 equiv of amine was used per equivalent of isothiocyanato side group.[23] Characterizable products could not be isolated if an excess of amine was used. The reaction mixture was then allowed to warm to room temperature over a period of several hours. The ^{31}P NMR spectral analysis showed that **15** had formed. The polymer was isolated by precipitations from THF into water (5×) and into hexane (1×). The polymer was dried under high vacuum for 1 week. Polymers **14–16** were soluble in common organic solvents such as THF and chloroform. Reaction of **6** with ammonia under these conditions yielded an insoluble product. The yields of **14–16** were 25–40%.

Synthesis of $[NP(OCH_2CF_3)_{1.4}(NHCSOMe)_{0.6}]_n$ (19). Polymer **3** (4.0 g, 0.069 mol of PCl) was dissolved in THF (300 mL). A solution of sodium trifluoroethoxide was generated from sodium hydride (1.92 g of a 60% dispersion, 0.048 mol) and trifluoroethanol (4.83 g, 0.048 mol) in THF (100 mL). The salt solution was then added dropwise to the polymer solution. The reaction mixture was stirred at 25 °C for 16 h and at 66 °C for 1 h to form **17**. The ^{31}P NMR analysis of the reaction mixture showed a broadened singlet ($\delta = -11$ ppm) for overlapping $P(OCH_2CF_3)_2$ and $P(OCH_2CF_3)Cl$ units. Potassium thiocyanate (10.5 g, 0.11 mol) and 18-crown-6 ether (0.5 g, 0.002 mol) were added to the reaction mixture, which was heated at 66 °C for 8 h to form **18**. The ^{31}P NMR analysis of the reaction mixture showed resonances at $\delta = -9$ ppm for $P(OCH_2CF_3)_2$ units and $\delta = -31$ ppm for $P(OCH_2CF_3)(NCS)$ units. Integration of the resonances in the ^{31}P NMR spectrum confirmed that 30% of the side groups were isothiocyanato units. Methanol (50 mL) was added to the reaction mixture. Full derivatization of the isothiocyanato groups could not be achieved at room temperature, but was achieved after 16 h at reflux. The ^{31}P NMR analysis showed resonances at $\delta = -10$ ppm for $P(OCH_2CF_3)_2$ units and $\delta = -19$ ppm for $P(OCH_2CF_3)(NHCSOMe)$ units. Solvent was removed under vacuum, and the polymer was isolated by precipitation into water (3×). No hydrolysis was found with precipitation into water. The polymer was further purified by dialysis in methanol for 4 days. Methanol was removed under vacuum to yield **19**. The yield was 4.6 g (40%).

Synthesis of $[NP(OCH_2CF_3)_{1.4}(NHCSNHPh)_{0.6}]_n$ (20). Polymer **20** was prepared in THF solution, as described for the synthesis of **19**. Aniline (10 mL) was added to the THF solution of **18**, and the solution was stirred for 2 h at 25 °C. Solvent was removed under vacuum, and the polymer was isolated by precipitation into water (5×) and hexane (1×) and dried under vacuum. The yield was 3.1 g (31%).

Synthesis of $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_{1.6}(NHCSNHPh)_{0.4}]_n$ (23). Polymer **3** (4.94 g, 0.0852 mol) was dissolved in THF (250 mL). A solution of the sodium salt of 2-(2-methoxyethoxy)ethanol was prepared from sodium hydride (2.70 g of a 60% dispersion in mineral oil, 0.0675 mol) and 2-(2-methoxyethoxy)ethanol (8.11 g, 0.0676 mol) and was added to the polymer solution dropwise. The reaction mixture was stirred for 3 h at 25 °C to yield **21**. The ^{31}P NMR analysis indicated resonances at $\delta = -9$ ppm for $P(OCH_2CH_2OCH_2CH_2OCH_3)_2$ units and at $\delta = -13$ ppm for $P(OCH_2CH_2OCH_2CH_2OCH_3)Cl$ units. Potassium thiocyanate (5.6 g, 0.058 mol) and 18-crown-6 ether (0.7 g, 0.003 mol) were added, and the mixture was heated at 66 °C for 24 h to form **22**. The ^{31}P NMR analysis showed resonances at $\delta = -7$ ppm for $P(OCH_2CH_2OCH_2CH_2OCH_3)_2$ units and at $\delta = -31$ ppm for $P(OCH_2CH_2OCH_2CH_2OCH_3)(NCS)$ units. Integration of the resonances in the ^{31}P NMR spectrum confirmed that 20% of the side groups were isothiocyanato groups. Aniline (10 mL) was added to the solution of **22** at 25 °C to form **23**. THF was removed under vacuum, and **23** was isolated by precipitations from THF into water (4×) and hexane (1×). The yield was 3.3 g (26%).

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Registry No. **4**, 1858-42-0; **6** (homopolymer), 26747-42-2; **6** (SRU), 56529-02-3; **7** (copolymer), 132980-63-3; hexachlorocyclotriphosphazene, 940-71-6.