Macromolecules **1992,** *25,* 2802–2810

Synthesis of Poly[bis(phosphazo)phosphazenes] Bearing Aryloxy and Alkoxy Side Groups

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Received July 30, 1991; Revised Manuscript Received December 27, 1991

ABSTRACT: The synthesis of a new class of phosphazene polymers through the thermal ring-opening polymerization of 1,1-bis(trichlorophosphazo)tetrachlorocyclotriphosphazene, *gem*-$(NPCl_3)_2N_3P_3Cl_4$ (1), is reported. The resultant polymer possesses controlled short-chain branching sites along the phosphazene backbone. The chlorine atoms in this polymeric intermediate were replaced by organic side groups to yield novel organic–inorganic polymers that are stable to ambient conditions. The macromolecules were characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, elemental analysis, differential scanning calorimetry, and gel permeation chromatography. Glass transition temperatures of these new materials in general are higher than those of classical poly(organophoshazenes) that bear similar side groups, and the tendency for crystallization is lower. Computer simulations of 1 were carried out to provide structural information about the cyclic trimer. The results suggested that the molecule contains a strained phosphazene ring. Kinetic studies showed that the activation energy for the initiation of the polymerization of 1 is about 46 kcal/mol, which is lower than some of the values suggested for the polymerization of hexachlorocyclotriphosphazene, $[NPCl_2]_3$. This feature, combined with the unusual structural characteristics of 1, appears to contribute to the relatively mild polymerization conditions required for this molecule. A mechanism is proposed for the polymerization of 1.

Introduction

Most polyphosphazenes are prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, to high molecular weight poly(dichlorophosphazene), $(NPCl_2)_n$, followed by replacement of the chlorine atoms in the polymer by organic groups.[1-4] These organophosphazene polymers are essentially linear and often have a symmetric side-group structure that generates microcrystallinity. Phosphazocyclophosphazenes are molecules that contain a cyclic phosphazene ring with one or two phosphazenyl units ($N{=}PX_3$) bonded to a ring phosphorus atom. The small-molecule chemistry of this class of compounds has been studied,[5-8] and the molecular structures of several derivatives have been reported.[9-14] However, to date, interest in this class of molecules has been limited to the small-molecule level. In view of the similarity between the structures of cyclic chlorophosphazophosphazenes and the classical hexachlorocyclotriphosphazene, the possibility existed that the former may undergo ring-opening polymerization to yield polymers that would contain controlled phosphazene branches. This would provide a method for introducing molecular asymmetry and materials free volume at the polymerization stage.

In a brief communication,[15] we reported that 1,1-bis(trichlorophosphazo)tetrachlorocyclotriphosphazene (1) undergoes a low-temperature, ring-opening polymerization to form a high molecular weight poly(chlorophosphazophosphazene) (8). Polymer 8 possesses well-characterized short-chain branching sites and can be derivatized with organic reagents to give stable polymers. The existence of branching sites is potentially useful because it allows a tailoring of the properties of the polymers by the selective introduction of side groups.

As part of our continuing effort to explore the chemical and physical properties of this new system, we have now extended this work to the synthesis of a series of phosphazophosphazene polymers that bear organic side units. The research was guided by the following questions: (1) In what ways do the physical properties of organophosphazophosphazene polymers differ from those of classical polyphosphazenes with similar side groups? In particular, how do the glass transition temperatures (T_g) differ? (2) What degree of halogen replacement by organic side groups can be achieved with phosphazo polymers? If all of the halogen atoms cannot be replaced, how stable are the remaining P–Cl bonds to hydrolysis by atmospheric moisture? (3) What factors allow compound 1 to undergo facile ring-opening polymerization at a relatively low temperature?

In this paper, we report the synthesis of phosphazophosphazene polymers that bear phenoxy, 4-chlorophenoxy, 4-methylphenoxy, 4-methoxyphenoxy, trifluoroethoxy, and (methoxyethoxy)ethoxy side groups. Theoretical studies of the structure of 1 and kinetic studies of the polymerization were also carried out. Finally, a mechanism for polymerization is proposed.

Results and Discussion

Synthesis of Cyclic Trimeric Model Compounds. The small-molecule model compounds were synthesized according to the reaction sequence in Scheme I. Thus, 1,1-bis(trichlorophosphazo)tetrachlorocyclotriphosphazene (1)[16] was allowed to react with $NaOC_6H_5$, $NaOC_6H_4Cl$, $NaOC_6H_4Me$, $NaOC_6H_4OMe$, $NaOCH_2CF_3$, and $NaOCH_2CH_2OCH_2CH_2OCH_3$ to give species 2–7 (Chart I). In all cases, when the model compound substitutions were carried out at room temperature, halogen replacement occurred only at the exocyclic phosphazo ($N{=}PCl_3$) groups. One of these partially substituted species, *gem*-$[NP(OPh)_3]_2N_3P_3Cl_4$ was isolated and characterized.[15] This is in agreement with the earlier observation that terminal PCl_3 units are more reactive than PCl_2 units.[17] Complete replacement of all PCl units was achieved only following heating of the reaction mixtures. The cyclic compounds were studied by ^{31}P NMR, ^{1}H NMR, and ^{13}C NMR spectroscopy and elemental analysis. The characterization data are summarized in Table I. The ^{31}P NMR spectra of all the model compounds contained an A_2B_2C spin pattern, with the ring phosphorus atom $P(OR)_2$ appearing at a chemical shift of about +6 ppm, the exocyclic phosphorus atom at about −30 ppm, and the branch site phosphorus at about −9 ppm. The chemical shifts for

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Scheme I

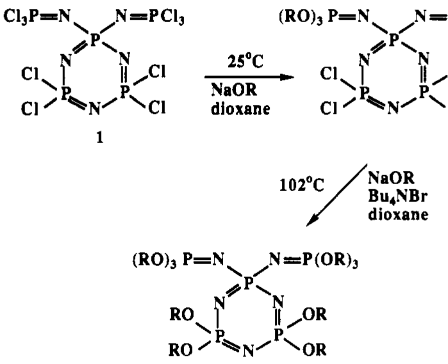
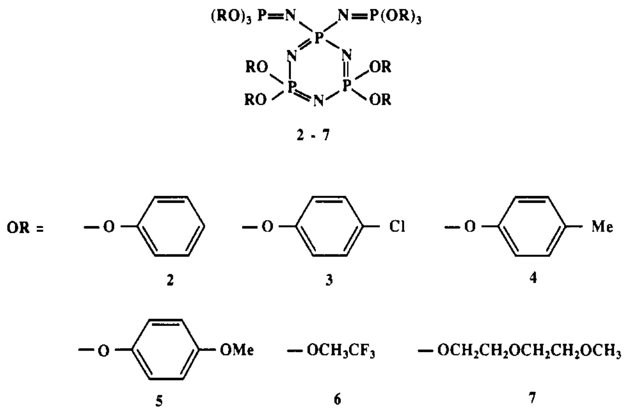


Chart I



the ring phosphorus and the exocyclic phosphorus atoms are similar to the values found for classical cyclic phosphazenes[2] and short-chain linear phosphazenes,[17-19] respectively. The ^{31}P NMR of **2** is typical and is shown in Figure 1.

Synthesis of Phosphazophosphazene High Polymers. The synthesis of poly(chlorophosphazophosphazene) (**8**) is outlined in Scheme II. Polymer **8** was prepared by the thermal polymerization of **1** at 150 °C under reduced pressure for about 2 h.[15] Unreacted trimer **1** was extracted from polymer **8** by treatment with warm heptane. Because polymer **8** is extremely sensitive to hydrolysis, all manipulations were carried out under an atmosphere of argon.

By analogy with the behavior of poly(dichlorophosphazene), $[NPCl_2]_n$, polymer **8** functions as a reactive macromolecular intermediate. It was allowed to react with a range of aryloxides and alkoxides according to Scheme II to yield stable new organic–inorganic polymers (Charts II and III). These polymers were prepared to allow a comparison to be made between their properties and those of their classical polyphosphazene counterparts, **19–25** (Chart IV). Three classes of polymers were prepared. Class 1 polymers (**9–12**) contained organic side groups at the phosphazo units only, with the remaining repeating units bearing chlorine side units. Class 2 polymers (**16–18**) contained organophosphazo side units plus other repeating units in which 75% of the chlorine atom units on the main chain were replaced by organic substituents. Class 3 polymers (**13–15**) contained organic side units only.

The polymers were examined by ^{31}P NMR, ^{1}H NMR, and ^{13}C NMR methods and elemental analysis (Table I). The molecular weights were determined by gel permeation chromatography. Glass transition temperatures were measured by differential scanning calorimetry (DSC).

The formation of class 1 polymers was followed by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of **8** consisted of an A_2B_2C spin system[15] with chemical shifts at $\delta_A = -20$ ppm (PCl_2), $\delta_B = -26$ ppm (PCl_3), and $\delta_C = -36$ ppm (branch site). Polymer **8** reacts very quickly with nucleophiles at room temperature to yield partially halogen-replaced polymers, in which substitution has occurred at the phosphazo units only. This reactivity parallels that of the cyclic small-molecule species. The ^{31}P NMR spectra of this class of polymers are similar to each other. As an example, the spectrum of polymer **9** will be described. The ^{31}P NMR spectrum of **9** (Figure 2) is unusual in that it showed only two groups of resonances near −30 and −35 ppm, in a ratio of 3:2. It appears that the peak at −30 ppm is actually a combination of two overlapping resonances. By comparison of the NMR resonances of this polymer with the chemical shifts of the small-molecule model compounds, the chemical shift assignments for polymers in class 1 are as follows: $\delta_A = \delta_C = -30$ ppm (PCl_2 and branch site phosphorus; peak integration = 3), $\delta_B = -36$ ppm ($P(OR)_3$; peak integration = 2). All class 1 polymers were isolated as white, flexible, film-forming materials. Even though they possessed unreacted PCl units, the polymers appeared to be quite stable to moisture. Evidence for this stability was shown by the absence of changes in the ^{31}P NMR spectra after the polymers had been precipitated into water several times during the purification steps. The polymers also retained their solubility in organic media after exposure to moisture.

Class 2 polymers are more difficult to prepare. In the case of polymer **13**, the addition of a catalytic amount of *n*-Bu_4NBr as an accelerator was needed to assist halogen replacement. Even so, the reactions required several days at reflux in dioxane (102 °C) to achieve complete substitution. By contrast, preparation of the classical poly(diphenoxyphosphazene) required only 72 h at reflux in dioxane.[21] The difficulty encountered in the preparation of fully substituted (aryloxy)phosphazophosphazene polymers is probably a consequence of the steric hindrance imposed by the side groups that are bonded to the phosphazo units. These exceedingly bulky phosphazo units may shield the nearby skeletal PCl units from attack by a nucleophile. This shielding may also explain why the partially-substituted polymers (class 1) are relatively stable toward hydrolysis, even though they possess unreacted PCl units. Despite the use of forcing reaction conditions, polymers **16–18** still contained one PCl unit per repeating unit. Nevertheless, as in the case of class 1 polymers, these macromolecules were stable to moisture.

By contrast, the reaction of **8** with trifluoroethoxide and (methoxyethoxy)ethoxide ions proceeded under less vigorous conditions with the replacement of all the chlorine atoms, to yield polymers **14** and **15**. In both cases, complete substitution was accomplished in 24 h at reflux in dioxane. Apparently, the inherent flexibility of the alkoxy groups allows them to interact more easily with the PCl units. The trifluoroethoxy-substituted polymer **14** was isolated as a white fibrous material, while the (methoxyethoxy)ethoxy polymer was obtained as a soft, brown elastomer that was soluble in water and methanol. The ^{31}P NMR spectrum of class 2 polymers consisted of A_2BC_2 spin systems, except for **14**, where the spectrum consisted of an unresolved broad singlet. A typical NMR spectrum is shown in Figure 3.

Amorphous versus Crystalline Character. Classical polyphosphazenes such as $[NP(OCH_2CF_3)_2]_n$ or $[NP(OPh)_2]_n$ are microcrystalline materials, with the crystalline domains being generated by the regular packing of the symmetrically substituted repeating units into an ordered array. By contrast, only one of the polymers

Table I
Characterization Data

	^{31}P NMR,[a] ppm						elem anal.		mol wt	
compd	P_A	P_B	P_C	^{1}H NMR, ppm	^{13}C NMR, ppm		found	calcd	M_n	M_w
1[a]	20.4	−11.2	−20.3							
2	11.2	−25.2	−4.0	6.5–7.7 (m)	120 (d), 124 (d), 129 (d), 151 (d)	C	62.35	62.34		
						H	4.31	4.33		
						N	5.92	6.06		
						Cl	0.07	0.00		
3	7.3	−30.8	−9.7	6.9–7.2 (m)	117 (d), 120 (d), 130 (d), 154 (d)	C	47.53	48.03		
						H	2.74	2.69		
						N	3.98	4.07		
						Cl	23.92	23.63		
4	6.8	−29.3	−8.9	3.4 (b), 6.8 (7.2)	22, 116 (d), 130 (d), 154 (d)	C	64.92	64.86		
						H	5.41	5.44		
						N	5.32	5.40		
						Cl	0.15	0.00		
5	7.0	−28.4	−7.6	6.8–7.0 (b)	57 (d), 114 (d), 148 (d), 156 (d)	C	57.61	57.73		
						H	4.74	4.85		
						N	4.95	4.81		
						Cl	0.08	0.00		
6	18.1	−5.4	−8.0	4.5–4.8 (m)	64 (q), 124 (q)	C	19.94	19.77		
						H	1.66	1.66		
						N	5.89	5.76		
7	18.2	2.3	−7.4	3.4–3.7 (m)	72, 70.3–70.2, 66.9–65.5, 58					
8[b]	−20	−26	−36[b]							
9	−29	−30	−35	6.8–7.4 (m)	121, 125, 130, 151	C	47.06	46.70	6 × 10^4	9 × 10^5
						H	3.79	3.24		
						N	6.99	7.57		
						Cl	14.81	15.35		
10	−30	−34	−31	6.2–7.6 (m)	119, 121, 132, 152	C	38.12	38.20	5 × 10^4	7 × 10^5
						H	2.24	2.14		
						N	5.62	6.19		
						Cl	30.37	31.32		
11	−34	−40	−36	6.4–7.5 (m)	26, 118, 131, 155	C	49.00	49.97	5 × 10^4	2 × 10^5
						H	4.30	4.19		
						N	7.15	6.94		
						Cl	14.26	14.05		
12	−29	−37	−31	6.6–7.1 (m)	55, 112, 117, 146, 155	C	48.05	45.63	7 × 10^4	2 × 10^5
						H	4.22	3.83		
						N	6.27	6.34		
						Cl	11.60	12.83		
13	−7	−19	−36	6.5–7.1 (m)	121, 125, 130, 151	C	59.97	62.34	1 × 10^5	7 × 10^5
						H	4.14	4.33		
						N	7.08	6.06		
						Cl	0.75	0.00		
14	+1 to −9, broad			4.5–4.8 (m)	64 (q), 124 (q)	C	19.73	19.77	4 × 10^4	1 × 10^5
						H	1.59	1.66		
						N	6.12	5.76		
						Cl	0.094	0.00		
15	−1	−8	−23.5	3.4–3.7 (m), 3.3	72, 70.3–70.2, 66.9–65.5, 58	C	39.09	42.40	6 × 10^3	6 × 10^4
						H	7.43	7.83		
						N	5.95	4.95		
						Cl	<0.13	0.00		
16	−26	−35	−30	6.3–7.2 (m)	122 (d), 129 (d), 130 (d), 149 (d)	C	45.07	46.05	2 × 10^4	4 × 10^5
						H	2.72	2.58		
						N	4.67	4.97		
						Cl	24.61	25.17		
17	−27	−35	−31	2.0 (d), 6.1–7.7 (m)	22, 120 (d), 128 (d), 132 (d), 150 (d)	C	59.91	61.79	7 × 10^4	2 × 10^5
						H	5.03	5.19		
						N	5.98	5.72		
						Cl	3.74	2.90		
18	−25	−34	−31	3.3 (d), 5.6–7.6 (m)	52 (d), 113 (d), 122 (d), 145 (d), 156 (d)	C	55.47	55.29	2 × 10^5	6 × 10^5
						H	4.98	4.64		
						N	5.11	5.12		
						Cl	2.30	2.59		

[a] P_A = P(OR)$_2$, P_B = P(OR)$_3$, P_C = P(branch site). [b] P_A = PCl$_2$, P_B = PCl$_3$.

prepared in this present investigation was crystalline. This was species 14, in which all side groups were OCH_2CF_3 units. Even here the crystallinity could be detected only by optical birefringence between 23 and 68 °C, and no melt or crystallization transitions were detected by DSC analysis. Thus, it appears that the presence of the bulky phosphazo side units introduces sufficient free volume and perhaps linear disorder along the chain that crystallization is inhibited. This is particularly understandable for polymers that contain both chloro and organic side units.

Thermal Analysis Data. It was of interest to compare the glass transition temperatures (T_g) of the poly(phosphazophosphazenes) with those of classical polyphosphazenes to determine the effect of branching on the solid-state properties. The T_g's for the polymers studied in this work are listed in Table II. Their values were then compared with those of classical poly(organophospha-

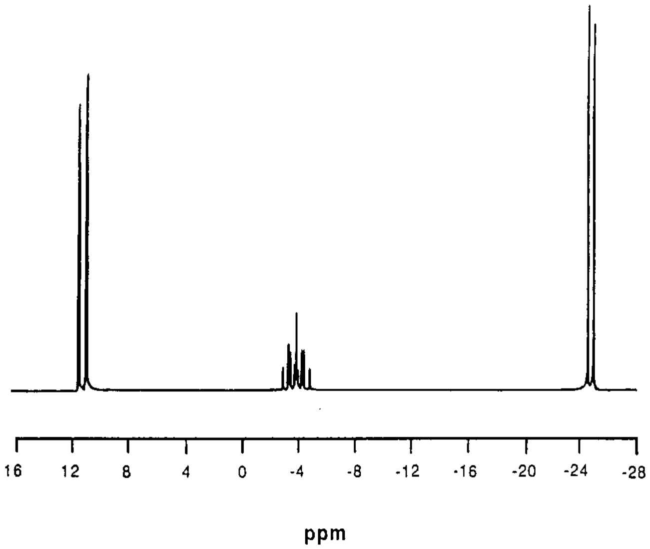


Figure 1. ^{31}P NMR spectrum of cyclic trimer 2.

zenes) that bear similar side groups. The T_g's of class 1 polymers in general are similar to those of the fully-substituted classical systems. Even though the aryloxy groups on the phosphazo units impart considerable bulkiness to the structure, the $-NPCl_2-$ units in the polymer backbone appear to contribute enough flexibility to the polymer as a whole to maintain low T_g values. By contrast, class 2 and 3 polymers showed a significant increase in T_g's when the side groups were aryloxy units. The glass transition temperature is influenced by a variety of molecular, structural, and materials factors. In theory, the introduction of short branches into the polymer structure would be expected to generate amorphous character by inhibiting chain packing, and this could lower the T_g. Moreover, the branches should increase the free volume of the material and also decrease T_g's. However, the T_g's measured for the phosphazo polymers do not agree with this expectation. The glass transition temperatures of class 2 and 3 poly(phosphazophosphazenes) are significantly higher than those of their classical polyphosphazene counterparts. For example, the T_g's of polymers 8 and 13 are −37 and +26 °C, respectively. By contrast, the T_g's of classical polyphosphazenes, $[NPCl_2]_n$ (19) and $[NP(OPh)_2]_n$ (20), are −66 and −8 °C, respectively. One explanation may be that the phosphazo groups are so bulky that they hinder the torsional mobility of the polymer backbone. This would be a particularly important influence for class 2 or 3 polymers since the linkage of organic groups to the main chain would increase the stiffness of the polymer. As a result, the T_g's would increase dramatically compared to those of class 1 polymers. However, the T_g's do not change significantly when the side groups are alkoxy units. Flexible alkoxy groups may easily adapt to new conformations as the main chain undergoes torsional motion. Therefore, the effect of alkoxy side groups on the mobility of the backbone may not be significant.

Computer Modeling of the Structure of 1. The unusual ability of 1 to undergo ring-opening polymerization under mild conditions raised some fundamental questions about the properties of this molecule. For example, what unusual structural characteristics that are inherent in this compound allow it to polymerize with such ease? An X-ray crystal structure of 1 was an obvious source of such information. However, several attempts were made by us to obtain the crystal structure of 1, but crystals of 1 decomposed before sufficient diffraction data could be obtained. As an alternative we have attempted to obtain preliminary structural information for this compound by means of computer simulation. The modeling software employed was the SYBYL Molecular Modeling Software,[20] with appropriate force-field parameters for chlorophosphazenes[21] imported into the program. Simulation was first attempted on a known molecule, specifically hexachlorocyclotriphosphazene, which has been investigated extensively.[22] This provided a control against which the simulated structure could be compared. The results from the simulation for hexachlorocyclotriphosphazene are summarized in Table III. As can be seen, the structural parameters derived from the simulation compared extremely well with those obtained by X-ray crystallography. This suggests that the modeling software, with the imported force-field parameters, is capable of generating the structures of this class of molecule with a high degree of accuracy. With this in mind, a simulation of 1 was carried out. The results are shown in Table IV. The simulated structure contained a planar cyclic phosphazene ring with two short-chain linear phosphazene units bonded to one of the ring phosphorus atoms. The simulation gave an average ring P–N bond distance of 1.57 Å. This value is similar to that of hexachlorocyclotriphosphazene. However, the similarity ends here. The angle at P_1 collapsed to 102° (normal N–P–N angle is 118°), while the angles at N_1 and N_3 widened to 134° (normal P–N–P angle is 121°). The angles at P_2, P_3, and N_2 are closer to normal values. The exocyclic P–N–P angles of 146° are similar to the values found in a short-chain phosphazenes.[17–19] On the basis of the results from the simulation of hexachlorocyclotriphosphazene, it seems likely that the simulated structure of 1 has some validity. A comparison of the different energy values of the energy-minimized model compounds is listed in Table V. The results suggest that 1 has a significantly higher energy than $[NPCl_2]_3$. The greatest contribution to the total energy of 1 appears to arise from the angle bending of the molecule. Thus, the results suggest that this molecule contains appreciable ring strain, and this may be responsible for the facile ring-opening polymerization. A space filling model of 1 was generated and is shown in Figure 4. It illustrates the spatial relationship between the chlorine atoms of the ring and those exocyclic to the ring. The steric interactions associated with the phosphazo units are shown clearly. This steric effect influences the reactivity of the molecule and explains why it is more difficult to replace the chlorine atoms linked directly to the phosphazene ring. It also lends support to the argument that shielding by the organic groups on the phosphazo units causes a lowering of the reactivity of the chlorine atoms attached to the ring. We believe that this shielding effect is also present at the high polymeric level and that this explains the forcing reaction conditions needed to produce fully-substituted phosphazo polymers.

Kinetic Studies of the Polymerization of 1. The "uncatalyzed" ring-opening polymerization of hexachlorocyclotriphosphazene has been studied kinetically by a number of investigators.[23–30] However, the products of this polymerization often include higher cyclic oligomers, un-cross-linked polymers, and cross-linked products, and the kinetic results were often complicated. By contrast, the rate of the polymerization of 1 can be studied with relative ease. The close similarity between the structure of 1 and hexachlorocyclotriphosphazene suggests that the polymerization kinetics and mechanism of polymerization for both compounds should be quite similar. We have carried out preliminary experiments to investigate the rate

Scheme II

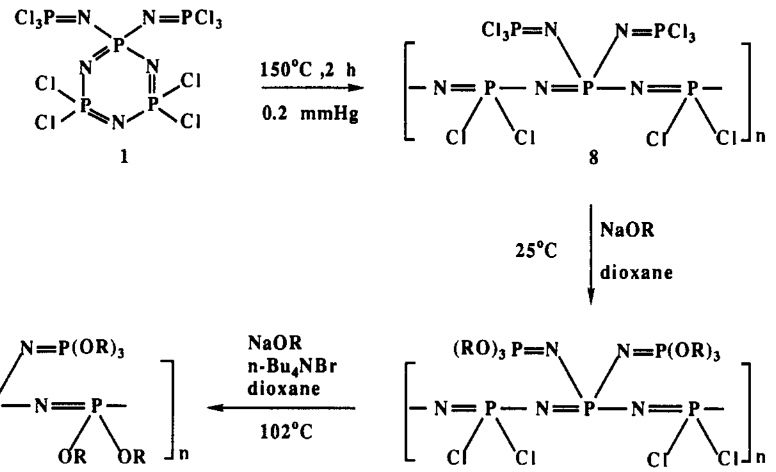


Chart II
Organochloro Derivative Polymers

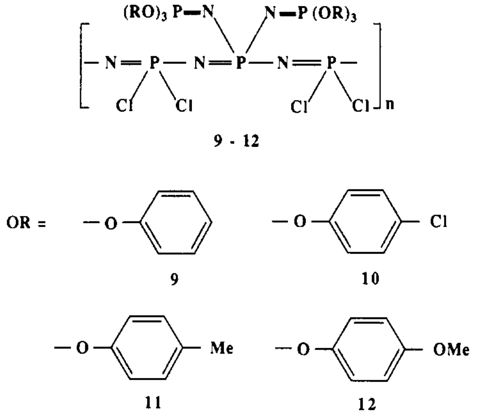


Chart III
Single-Substituent and Mixed-Substituent Organochloro Derivative Polymers
$[N_3P_3(OR')_xCl_{4-x}(N{=}P(OR)_3)_2]_n$

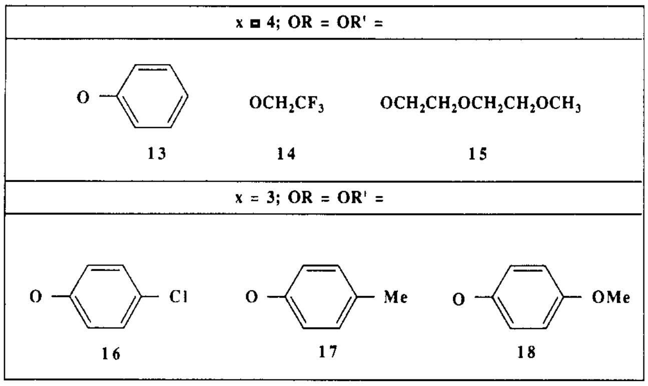
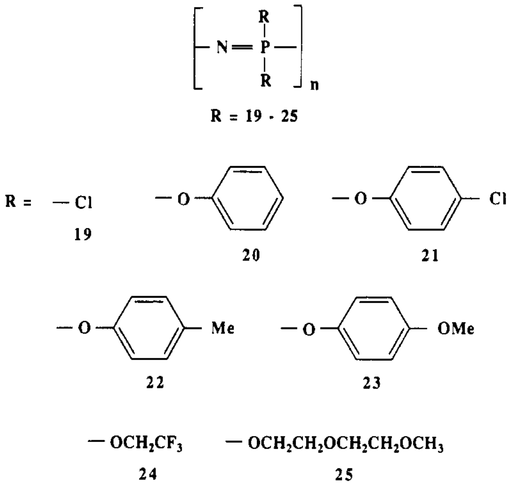


Chart IV



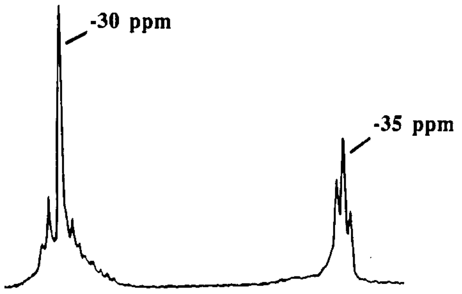


Figure 2. ^{31}P NMR spectrum of polymer 9.

of the polymerization of 1. The conversion of 1 to high polymer 2 was followed by ^{31}P NMR spectroscopy. The ^{31}P NMR spectra at 157 °C for a series of polymerizations at different time intervals is shown in Figure 5. The percent conversion of 1 to polymer was calculated by integrating the resonances corresponding to 1 and to polymer 8. An important feature of the NMR spectra is the absence of peaks that might correspond to reaction intermediates. This suggests that the initiation step follows first-order kinetics. Furthermore, the sharpness of the polymer resonances also suggested a high regularity of the polymer structure, perhaps resulting from a single head to tail polymer microstructure, **26** (Chart V). A mixture of head to head and head to tail, **27**, polymer microstructure would be expected to give rise to a more complex ^{31}P NMR spectrum or broadening of peaks. A plot of log [Trimer] vs time (Figure 6) showed a linear relationship between log [Trimer] and time, and this suggests first-order kinetics with respect to the initiation step. The first-order rate constants are $k_{150\,°C} = 9.93 \times 10^{-5}\ s^{-1}$ and $k_{157\,°C} = 24.4 \times 10^{-5}\ s^{-1}$, respectively. The activation energy, E_a, calculated from the Arrhenius equation is $E_a = 46.4$ kcal/mol. The activation energies for the polymerization of hexachlorocyclotriphosphazene were reported to be 42,[27] 51.34,[28] and 57 kcal/mol.[29] Except for the value reported in ref 27, the E_a for the polymerization of 1 is considerably lower than that of hexachlorocyclotriphosphazene. This result is consistent with the experimental observation that lower temperatures are required for the polymerization of 1.

Mechanism of the Polymerization of 1. A tentative polymerization mechanism is outlined in Scheme III. The mechanism begins with a rate-determining ionization of the P–Cl bond of a phosphazo unit in 1. The ionization

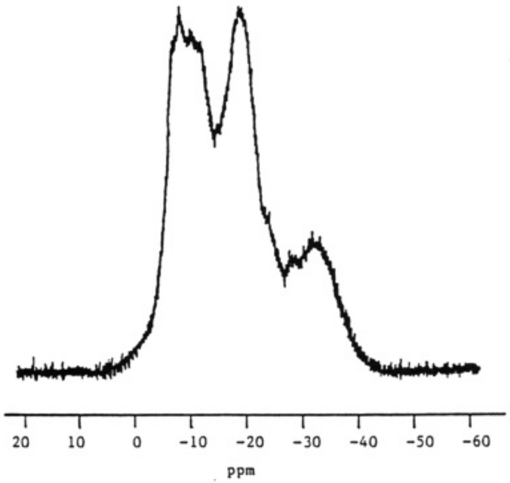
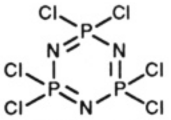


Figure 3. ^{31}P NMR spectrum of polymer **13**.

Table II
Glass Transition Temperature Data

	T_g, °C		T_g, °C
$\{N_3P_3Cl_4[NP(Cl_3)_2]\}_n$		$(NPCl_2)_n$	
8	−37	**19**	−66
$\{N_3P_3Cl_4[(NP(OR)_3)_2]\}_n$		$\{N_3P_3(OR)_4[(NP(OR)_3)_2]_n$	
9	−6	**13**	26
10	0	**14**	−70
11	−1	**15**	−74
12	5		
$\{N_3P_3Cl(OR)_3[(NP(OR)_3)_2]\}_n$		$[NP(OR)_2]_n$	
16	31	**20**	−8
17	22	**21**	4
18	30	**22**	0
		23	12
		24	−66
		25	−85

Table III
Structural Data for $[NPCl_2]_3$



	experimental	simulated
P–N, Å	1.58	1.57
N–P–N, deg	118.4	118.5
P–N–P, deg	121.4	121.5
Cl–P–Cl, deg	101.4	102.2

of a side group PCl_3 unit is probably more facile than that of a ring PCl_2 unit. This is supported by the observation that **1** appears to initiate the polymerization of THF. THF is known to undergo cationic catalyzed polymerization, and this suggests that an ionic species is present in the solution. Such behavior is not found for hexachlorocyclotriphosphazene. Another item of evidence for the higher reactivity of the PCl_3 unit came from the reaction of **1** with nucleophiles such as NaOPh where, as discussed earlier, halogen replacement occurs preferentially at the phosphazo sites. The ease of ionization of the PCl_3 group is consistent with a lower activation energy for the polymerization of **1**.

The ionic intermediate, **1a**, could then react with another molecule of **1** via preferential attack on the ring nitrogen atom furthest from the phosphazo units. A reaction with this nitrogen atom is preferred for two reasons. (1) This nitrogen has the most basic character. (2) The phosphazo units sterically shield the nitrogen atoms closest to the branches. Thus, the ring may always cleave at the same site, leading to a high regularity of the polymer structure. The polymerization is terminated when the reaction flask is cooled. During the cooling, Cl^- probably recombines with PCl_2^+ to yield the neutral species.

The polymerization mechanism suggested here is very similar to that proposed for the polymerization of hexachlorocyclotriphosphazene.[2] The most notable difference is the site of initiation. For compound **1**, initiation occurs at a branch PCl_3 unit. For hexachlorocyclotriphosphazene, initiation can occur only at a ring PCl_2 unit. Because the PCl_3 group is more reactive and ionizes more easily, this results in a lower activation energy, which in turn leads to a lower temperature requirement for polymerization. From the structural simulation studies described above, it is likely that an inherent ring strain is associated with molecule **1** and that it is probably more strained than hexachlorocyclotriphosphazene. This ring strain will

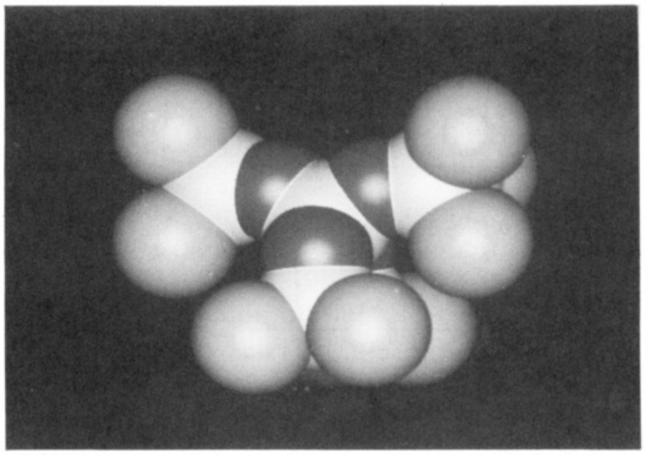
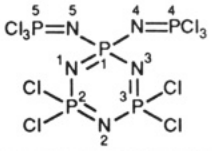


Figure 4. Space filling model of cyclic trimer **1**.

Table IV
Simulated Structure for Compound 1



Bond Distance, Å	
P–N	1.57
Bond Angle, deg	
$N–P_1–N$	102.3
$N–P_2–N$	115.2
$N–P_3–N$	
$P–N_2–P$	119.7
$P–N_1–P$	133.8
$P–N_3–P$	
$P–N_4–P$	146.1
$P–N_5–P$	

Table V
Calculated Energy Values for $[NPCl_2]_3$ and Trimer 1

	$[NPCl_2]_3$	$(NPCl_3)_2$ *gem*-$N_3P_3Cl_4$
bond stretching energy	0.013	1.321
angle bending energy	85.817	591.322
torsional bending energy	0.120	4.213
out-of-plane bending energy	0.000	0.000
1–4 van der Waals energy	−2.276	−4.456
van der Waals energy	−0.894	−4.981
1–4 electrostatic energy	−4.042	33.570
electrostatic energy	−0.470	51.013
total energy, kcal/mol	77.818	672.002

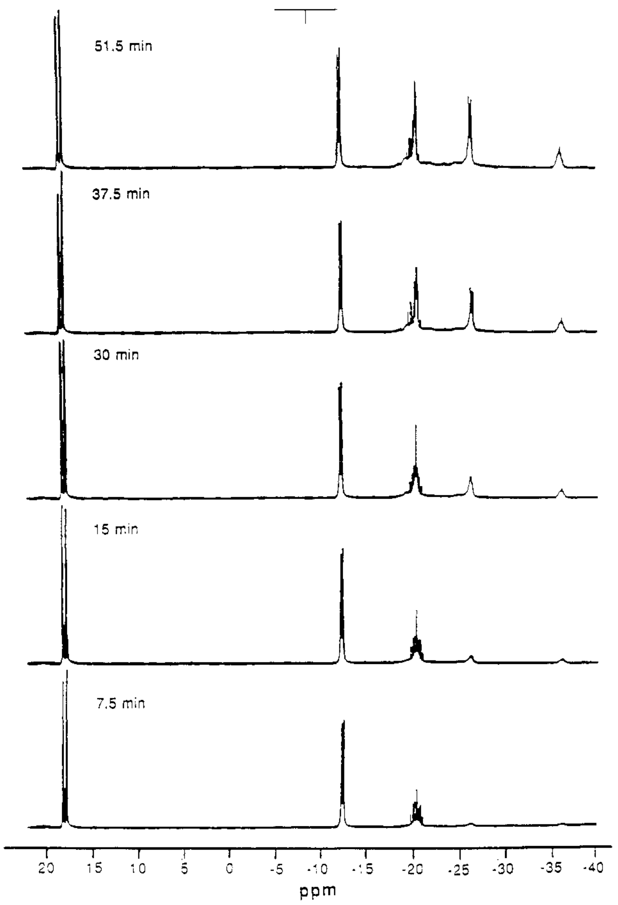
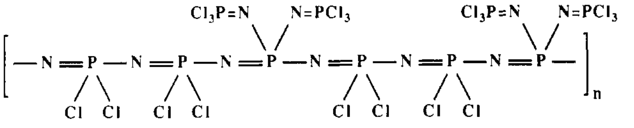


Figure 5. ^{31}P NMR spectra at various time intervals during the polymerization of 1.

Chart V



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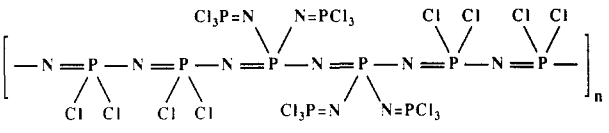

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facilitate the ring-opening process during the propagating step. This in turn leads to faster polymerizations.

Conclusions. In this study, we have shown that 1,1-bis(trichlorophosphazo)tetrachlorocyclotriphosphazene (1) undergoes thermal ring-opening polymerization to form a new class of phosphazene polymers that contain controlled side-chain branches. The conditions for polymerization are relatively mild compared with the polymerization of hexachlorocyclotriphosphazene. The reactions of this new high polymeric intermediate with organic nucleophiles yield stable organic–inorganic polymers, and these are expected to further increase the range of properties that can be tailored into phosphazene type polymers.[31-33]

Experimental Section

Materials. Hexachlorocyclotriphosphazene was supplied by Ethyl Corp. and was purified by two fractional sublimations at 0.05 Torr. Phenol, 4-chlorophenol, 4-bromophenol, 4-methylphenol, 4-methoxyphenol, 4-phenylphenol, trifluoroethanol, and (methoxyethoxy)ethanol were obtained from Aldrich. The phenols were purified by sublimation. Sodium hydride (60% dispersion in mineral oil; Aldrich), phosphorus pentachloride (Aldrich), and ammonia (anhydrous; Matheson) were used as received. Tetrahydrofuran (THF) and 1,4-dioxane (Curtin-Matheson) were distilled into the reaction flask under an atmosphere of dry argon from a sodium–benzophenone ketyl drying agent. Heptane and dichloromethane were dried by stirring with calcium hydride and were also distilled into the reaction flask. All reactions were performed under an atmosphere of dry argon by using standard Schlenk techniques.

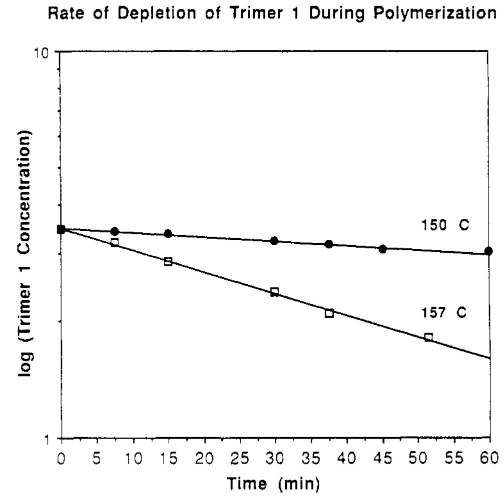
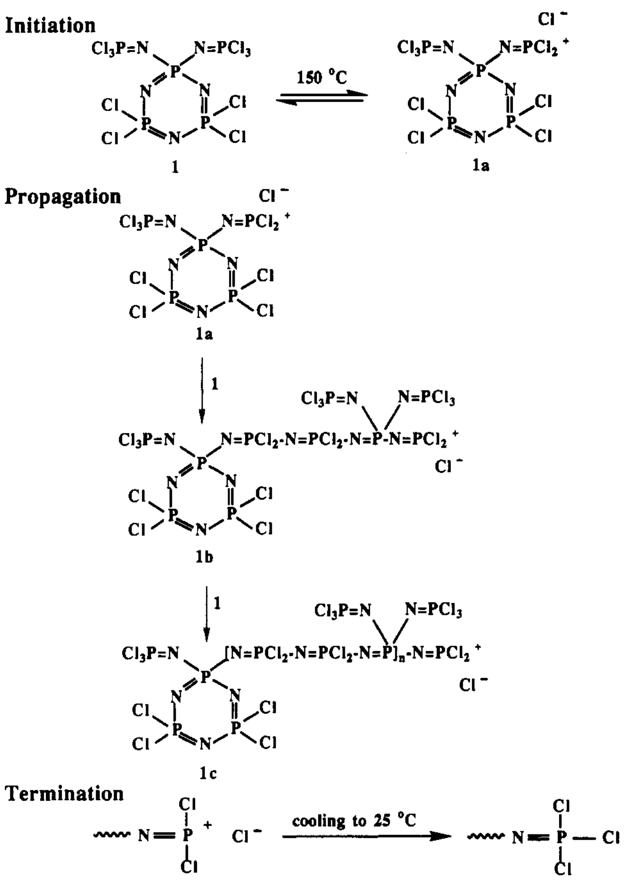


Figure 6. Rate of depletion of trimer 1 during polymerization.

Scheme III



Equipment. ^{31}P NMR spectra were recorded on a JEOL FX 90Q NMR spectrometer operating at 36.2 MHz and with a Bruker WP-360 NMR spectrometer at 146 MHz. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as external reference, with positive shift values downfield from the reference. ^{1}H and

^{13}C NMR spectra were recorded with a Brucker WP-360 spectrometer operating at 360 and 90.27 MHz, respectively. Most of the elemental analyses were obtained by Midwest Microlab, Indianapolis, IN. For compounds 6 and 14, the elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Samples were dried under vacuum before analysis. Gel permeation chromatography data were obtained with the use of a Hewlett-Packard 1090 liquid chromatograph with a refractive index detector. Polymer Laboratories PL gel columns were calibrated with narrow molecular weight polystyrene standards. A 0.1% solution of $(n\text{-}C_4H_9)_4NBr$ in THF was employed as the eluent. Glass transition temperatures (T_g) were recorded with the use of a Perkin-Elmer DSC-7 unit controlled by a PE 7500 computer. The samples were analyzed in crimped aluminum pans with a heating rate of 10 °C/min and a helium flow rate of 10 mL/min. Molecular modeling was carried out by using SYBYL Molecular Modeling Software on an Evans and Sutherland molecular graphics unit.

Synthesis of Trimer 1 and Polymer 8. The synthesis of 1 followed a procedure reported in the literature.[16] It should be noted that trimer 1 is very hydrolytically sensitive and should be stored in a drybox. Polymer 8 was prepared by the thermal ring-opening polymerization of 1. In a typical polymerization, 1 (4.0 g, 6.9×10^{-3} mol) was charged into a Schlenk flask, which was then connected to a vacuum line. The contents of the flask were evacuated under dynamic vacuum for 10 min. Still under dynamic vacuum, the flask was lowered into an oil bath set at 150 °C. Over a period of about 2 h, 1 changed from a free flowing melt to a viscous gel (polymer). After cooling, the polymer was dissolved in dichloromethane. The polymer solution was transferred into a dried Schlenk flask via a double-tipped syringe needle. Care was taken to avoid transferring insoluble materials from the polymerization flask. The polymer solution was concentrated, and dry heptane was added into the polymer-containing flask to extract unreacted trimer 1 and precipitate the polymer as a white, soft, adhesive material. After stirring for 20 min with gentle warming, the heptane was removed. This extraction procedure was repeated two more times. The polymer was used immediately in subsequent reactions. The yield of 2 was typically about 60%. It should be noted that polymerization times longer than 2 h at 150 °C generally led to cross-linking of polymer 8 and to the formation of species that were insoluble.

Synthesis of Polymers 9–12. Since the synthesis of these polymers followed the same procedure, only the preparation of 9 will be described in detail to serve as an example. Sodium phenoxide was prepared by the reaction of NaH (3.1×10^{-2} mol) with phenol (3.1×10^{-2} mol) in THF (150 mL). The sodium salt solution was added dropwise to a solution of 8 (2 g, 3.4×10^{-3} mol) in dioxane. The reaction mixture was stirred at room temperature for 1 h, and the solvent was then removed in a rotary evaporator until a viscous solution remained. This viscous solution was poured slowly with stirring into a large beaker containing methanol. An elastomeric and slightly adhesive polymer was precipitated. The polymer was removed and dried overnight under vacuum and was then redissolved in THF. The controlled precipitation process was repeated several times into methanol (2×), water (2×), and hexane (2×). The purified polymer was white and flexible. Films could be solution cast from the polymer.

By a similar procedure, $NaOC_6H_4Cl$, $NaOC_6H_4Me$, and $NaOC_6H_4OMe$, were used in place of $NaOC_6H_5$ to give polymers 10–12, respectively.

Synthesis of Polymers 13–18. The synthesis of 13 will be described in detail. Polymer 8 (2.5 g, 4.3×10^{-3} mol) was dissolved in 1,4-dioxane (75 mL). The polymer solution was added to a solution of sodium phenoxide (2.2×10^{-1} mol, with 1.1×10^{-2} mol of $n\text{-}Bu_4NBr$ added) in dioxane. The reaction mixture was then refluxed for 10 days. The volume of the mixture was reduced to a concentrated solution and was then poured into a beaker filled with methanol to precipitate the polymer. The precipitation process was repeated several times into methanol (2×), water (2×), and hexane (2×). The polymer was isolated as a finely divided material that could be solution cast to form brittle films. Similarly, sodium trifluoroethoxide and sodium (methoxyethoxy)ethoxide were used in place of sodium phenoxide to give polymers 14 and 16. Polymer 14 was purified in the same manner as polymer 13. Polymer 16 is a water-soluble material. It was purified by dialysis (dialysis tubing molecular weight cutoff: 6000–8000) against deionized water for 3 days to remove sodium chloride, and against methanol to remove low molecular weight reactant species.

Table VI
Data for Polymerization Kinetic Experiments with Trimer 1

time, min	150 °C: trimer concn × 10^3, mol	157 °C: trimer concn × 10^{-3}, mol
0.0	3.450	3.450
7.5	3.413	3.200
15.0	3.370	2.860
30.0	3.220	2.380
37.5	3.158	2.090
51.5		1.810
45.0	3.070	
60.0	3.028	

Synthesis of Cyclic Species 2–7. The syntheses of 2–7 are similar. Therefore, only that of 2 is described in detail. Trimer 1 (2 g, 3.4×10^{-3} mol) was dissolved in dioxane (50 mL). This solution was added to a solution of sodium phenoxide (1.0×10^{-1} mol) in dioxane, and the reaction mixture was refluxed for 5 days. The mixture was then filtered through Fuller's earth, and solvent was removed from the filtrate to give an oily product. This was redissolved in diethyl ether. The product solution was extracted with 10% NaOH solution in a separatory funnel to remove excess phenol. The ethereal layer was collected and was dried with anhydrous $MgSO_4$. The solvent was removed, and the crude product was chromatographed on a silica gel column with CH_2Cl_2 as eluent. Compound 7 is a water-soluble liquid. Attempts to purify it by chromatography were unsuccessful, and it was obtained as an impure liquid. The formation of 7 was confirmed by mass spectrometry. Compound 2 was isolated as a white solid and was recrystallized from a dichloromethane/hexane mixture to give colorless crystals. Compounds 3–6 were obtained as oils.

Kinetic Studies of the Polymerization of Trimer 1. The polymerization of 1 was carried out as described earlier. Trimer 1 (2 g) was used in each polymerization reaction, and several experiments were conducted, corresponding to a range of polymerization times. At the end of each time interval, the ^{31}P NMR spectrum of the product was obtained. The percentage of conversion from trimer to polymer was determined by integration of the peaks corresponding to the trimer (−11.2 ppm) and polymer (−26 ppm). The polymerization experiments were performed at 150 and 157 °C. The results were listed in Table VI.

Acknowledgment. This work was supported by a grant from the U.S. Army Research Office.

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Registry No. 1, 15469-51-9; **2**, 139427-16-0; **3**, 139427-17-1; **4**, 139427-18-2; **5**, 139427-19-3; **6**, 139427-20-6; **7**, 139493-17-7; $NaOC_6H_5$, 139-02-6; $NaOC_6H_4Cl$, 1193-00-6; $NaOC_6H_4Br$, 7003-65-8; $NaOC_6H_4Me$, 1121-70-6; $NaOC_6H_4OMe$, 1122-95-8; $NaOCH_2CF_3$, 420-87-1; $NaO(CH_2)_2O(CH_2)_2OCH_3$, 19278-10-5.