Poly[(vinyloxy)cyclophosphazenes]

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ABSTRACT: The vinyloxycyclophosphazene derivatives, $N_3P_3Cl_5OCH{=}CH_2$ (**1**) and $N_4P_4Cl_7OCH{=}CH_2$ (**6**), undergo radical polymerization to produce the highly functionalized homopolymers $[CH(ON_3P_3Cl_5)CH_2]_n$ (**7**) and $[CH(ON_4P_4Cl_7)CH_2]_n$ (**8**). These materials undergo a remarkable two-step thermal decomposition process. The first step is an exothermic cross-linking reaction involving the elimination of HCl at modest temperatures. The activation energy for the first step is lower for **7** than for **8**. The second step is an endothermic elimination of the oxo-bridged cyclophosphazene dimer, $(N_3P_3Cl_5)_2O$. Copolymers have been obtained from mixtures of **1** and **6**. The calculated reactivity ratios show a preference for incorporation of **1** over **6** into the copolymers. Attempted copolymerization of **1** with styrene leads to mixtures of the respective homopolymers. Attempts to polymerize $N_3P_3X_5OCH{=}CH_2$ [(X = F(**2**), OCH_3 (**3**), OCH_2CF_3 (**4**), $N(CH_3)_2$ (**5**)] lead to various outcomes including insoluble materials, oligomers, or recovery of unreacted monomer. The sensitivity of the polymerization to the nature of the phosphazene substituents has been related to monomer electronic structure and reactivity of the exocyclic groups.

Introduction

Inorganic ring systems can be transformed into polymeric materials via three independent methologies.[1] Ring-opening polymerization leads to inorganic backbone polymers such as poly(siloxanes) and poly(phosphazenes).[2−4] The reactions of difunctional reagents with reactive inorganic ring systems can lead to cyclolinear and cyclomatrix materials.[3,5] If the substituent on the inorganic ring is an olefin, addition polymerization at the exocyclic position leads to carbon chain polymers with the inorganic ring system as the substituent.[1,6] The most extensively studied inorganic ring systems which have served as substituents on an organic backbone have been the cyclophosphazenes.[1,6] Earlier studies involved monomers in which the olefinic moiety is directly bonded to the phosphorus center in the cyclophosphazene. Detailed reactivity ratio determinations show that, under the conditions of radical-initiated polymerization, the phosphazene ring acts as a strong σ-electron-withdrawing group; thus, the propagating radical is highly polarized and does not exhibit any significant resonance stabilization with the cyclophosphazene ring.[7] This model is consistent with the electronic structure of these monomers as demonstrated by recent photoelectron spectroscopy investigations.[8] In response to these observations, emphasis has been shifted to cyclophosphazene monomers in which an insulating group is interposed between the olefinic center and the cyclophosphazene. Using this strategy, our group[1−6,9−12] as well as those of Inoue[1,13] and van de Grampel[1,14] have produced a wide range of polymers and copolymers with cyclotriphosphazenes as substituents. These insulating moieties are complex functional groups such as aryl,[9,14] aryloxy,[12,13] or polyalkyloxy[10,11] units. In each case, the complexity of the organic moiety obscures any direct relationships between the insulating unit and the reactivity of the olefin or the physiochemical behavior of the resulting polymers. To precisely examine all of these effects and to focus on systems in which inorganic ring system plays a significant or dominate role in determination of properties and behavior of the polymers in question, we have focused on systems wherein the insulating function is a single oxygen atom. Monomers exhibiting this structure are conveniently available from the reactions of enolate anions with cyclophosphazenes [15−18] and the reactions of these derivatives with various nucleophiles.[19] In this paper, we explore the polymerization of vinyloxycyclophosphazenes and the properties of the resulting polymers. Preliminary reports of certain aspects of these studies have appeared.[20]

Experimental Section

Materials and Methods. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (Nippon Soda), was converted to $N_3P_3Cl_5OCH{=}CH_2$ (**1**)[15,18] or $N_3P_3F_5OCH{=}CH_2$ (**2**).[19] In turn, (**1**) was converted to $N_3P_3X_5OCH{=}CH_2$ (X = OCH_3 (**3**), OCH_2CF_3 (**4**), $N(CH_3)_2$ (**5**)) by previously reported procedures.[19] Octachlorocyclotetraphosphazene, $N_4P_4Cl_8$ (Nippon Soda), was converted to $N_4P_4Cl_7OCH{=}CH_2$ (**6**) by a previously reported procedure.[17] Azobis(isobutyronitrile), AIBN (Aldrich), was recrystallized from ethanol/water and purified by vacuum sublimation at ambient temperature. All other reagents and solvents were obtained from Aldrich and purified by standard methods.

NMR spectra were recorded on a Bruker WM250 spectrometer with an Aspect 3000 computer. Operating frequencies were 250.1 MHz (^1H), 62.9 MHz (^{13}C), and 101.12 MHz (^{31}P). Tetramethylsilane (^1H and ^{13}C) was used as an internal reference, and 85% H_3PO_4 (^{31}P) was used as an external reference. Chemical shifts upfield from the reference were given a negative sign. Broad-band ^1H decoupling was used for ^{13}C and ^{31}P spectra. Infrared spectra were obtained as thin films on NaCl disks or as KBr disks using a Perkin-Elmer 1430 spectrophotometer. Polymer films were cast from dichloromethane solutions. Mass spectra were recorded on a Finnigan 4610 spectrometer operating at 80 eV. Gel permeation chromatography was performed on a Waters 6000A high-performance liquid chromatograph equipped with Waters 10^4 and 10^5 Å microstyragel columns and were measured relative to polystyrene standards. Membrane osmometric data were obtained on a Wescan model 230 recording membrane osmometer with toluene as the solvent. Thermal analyses were performed on a Perkin-Elmer thermal analysis data station interfaced with a TGS-2 thermogravimetric system, a DSC-4 differential scanning calorimeter, and a DTA differential thermal analysis system. Reactivity ratios were calculated

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Table 1. Composition of Pentachloro(vinyloxy)cyclotriphosphazene−Heptachloro(vinyloxy)cyclotetraphosphazene Copolymers

feed ratio (**1**/**6**)	IR intensity[a] ratio	product ratio (**1**/**6**)
3.047	1.375	3.148
1.913	1.080	2.262
1.202	0.839	1.520
0.797	0.669	0.996
0.738	0.584	0.975
0.567	0.530	0.754

[a] Ratio of integrated intensity of the ν_{PN} band of respective cyclophosphazenes.

using the Mortimer−Tidewell nonlinear least-squares approach.[7,21] Elemental analyses were performed by the Robertson Laboratory.

Synthesis of Poly[pentachloro(vinyloxy)cyclotriphosphazene], $[CH(ON_3P_3Cl_5)]CH_2]_n$ (7). The preparation of **7** was accomplished by a modification of an established procedure.[18] A polymerization tube was filled with 1.26 g (0.0035 mol) of freshly distilled **1** and 15 mg of AIBN. The mixture was degassed by performing three freeze−pump−thaw cycles and then sealed under vacuum. The tube was placed in a 65 °C water bath for 3 h,[22] at which time the polymerization mixture was extremely viscous and a clear golden color. The tube was opened, and 25 mL of CH_2Cl_2 was added. The resulting solution was added to a beaker containing 250 mL of CH_3OH with vigorous stirring. After being allowed to settle to the bottom of the beaker, the polymer was filtered, washed with methanol, and dried under vacuum. A milky white solid (0.590 g, 46.8% yield) was obtained. The polymer was identified by NMR and IR spectroscopic comparison to previously reported materials.[18] Molecular weight (GPC): $M_w = 513\,000$, $M_n = 398\,000$.

If the polymerization reaction is carried out at 100 °C using benzoyl peroxide in place of AIBN as the initiator, the resulting product is a black insoluble mass exhibiting small holes on the surface indicating outgassing.

Synthesis of Poly[heptachloro(vinyloxy)cyclotetraphosphazene], $[CH(ON_4P_4Cl_7)CH_2]_n$ (8). (Monovinyloxy)-heptachlorocyclotetraphosphazene (**6**) was distilled from crushed P_2O_5 into a polymerization tube with a 24/40 outer joint followed by addition of 1−2% of AIBN. A vacuum adapter was fitted to the top of the vessel and connected to a Schlenk line. After freeze−pump−thaw cycles, the tube was backfilled with nitrogen and placed in a bath at 60 ± 2 °C. Polymerization followed by isolation of the milk-white solid was conducted as above. Molecular weight (GPC): $M_w = 210\,000$, M_n 8000; molecular weight (membrane osmometry) = 136 000.

Polymerization of $N_3P_3F_5OCH{=}CH_2$ (2). The polymerization of **2** was carried out as described above. The resulting material was soluble in CH_2Cl_2 but could not be precipitated. After removal of solvents used for precipitation, the product was insoluble in all solvents tested.

Polymerization of $N_3P_3(OCH_3)_5OCH{=}CH_2$ (3). The polymerization of **3** was carried out as described above. Solutions of the resulting product slowly precipitated insoluble polymer over a period of a few weeks. Anal. Calcd for $[CH(ON_3P_3(OCH_3)_5)CH_2]_n$: C, 25.22; H, 5.41. Found: C, 25.08; H, 5.24.

Polymerization of $N_3P_3(OCH_2CF_3)_5OCH{=}CH_2$ (4). The polymerization of **4** was carried out as described above. The resulting product was soluble in methanol even after 3 years of storage. GPC: low molecular weight oligomers.

Polymerization of $N_3P_3\,[N(CH_3)_2]_5\,OCH{=}CH_2$ (5). The attempted polymerization of **5** was carried out as described above. No polymerization was observed.

Copolymerization of $N_3P_3Cl_5OCH{=}CH_2$ (1) and $N_4P_4Cl_7$-$OCH{=}CH_2$ (6). Mixtures of **1** and **6** in various mole ratios were copolymerized as described above. Molecular weight (GPC) for a typical (49.4% tetramer in copolymer): $M_w = 1\,054\,000$; $M_n = 14\,700$. The composition vs feed ratio data are summarized in Table 1.

Attempted Copolymerization of $N_3P_3Cl_5OCH{=}CH_2$ (1) and Styrene. Mixtures of **1** and styrene in various mole ratios were subjected to the copolymerization conditions described above. Bulk samples were isolated, and the bulk composition was established by elemental analysis. However, GPC analysis showed two separate distributions. The existence of the separate homopolymer of **1** was demonstrated by collection of separate GPC fractions followed by infrared analysis.

Copolymerization of $N_3P_3Cl_5OCH{=}CH_2$ (1) and Methyl Methacrylate. Mixtures of **1** and methyl methacrylate were subjected to the copolymerization conditions described above. Only very small, random incorporation of **1** was observed.

Attempted Copolymerization of $N_3P_3Cl_5OCH{=}CH_2$ (1) and Vinyl Acetate or *N*-Vinyl-2-pyrrolidinone. Mixtures of **1** and vinyl acetate or *N*-vinyl-2-pyrrolidinone were subjected to the copolymerization conditions described above. In each case, the isolated product was a black, rubbery insoluble substance similar to that observed in the homopolymerization of **1** initiated by benzoyl peroxide.

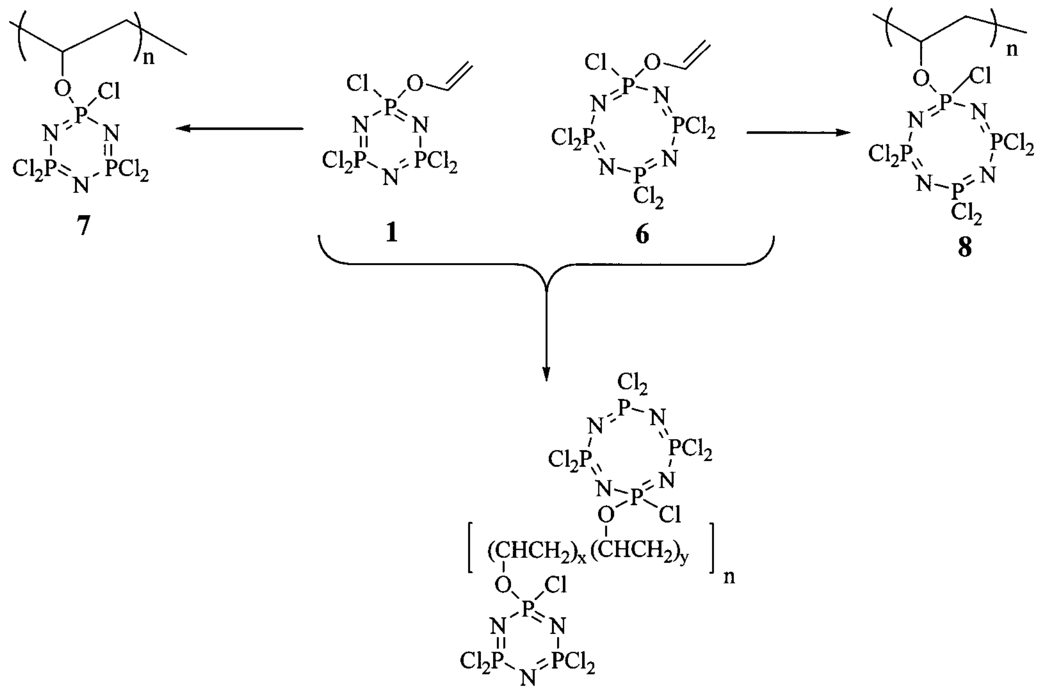
Results and Discussion

Homopolymerization of both the monovinyloxypentachlorocyclotriphosphazene (**1**) and the heptachlorocyclotetraphosphazene (**6**) under conditions of radical initiation leads to polymers having cyclotriphosphazene (**7**) and cyclotetraphosphazene (**8**) rings as substitutents on a carbon−carbon backbone (Scheme 1). The resulting, air-stable, materials are soluble in a broad range of organic solvents and are easily cast into thin films, which are inflammable in simple flame tests.

If, however, benzoyl peroxide at 100 °C rather than AIBN at 65 °C is used for initiation, a black insoluble solid is obtained rather than a soluble polymer. The retention of the cyclophosphazene rings in the soluble homopolymers **7** and **8** is demonstrated by the similarity of the infrared spectra of the monomers and the polymers in the phosphazene region.[23] The ^{31}P NMR spectrum of **7** (Figure 1) shows chemical shifts and coupling constants which are essentially equivalent to those observed for the monomer (**1**).[15] Given the high molecular weight of the polymer, the relatively narrow lines indicate a considerable degree of motional freedom of the cyclophosphazene side group at elevated temperatures. The high molecular weight observed for **7** indicates that there are no significant chain transfer processes involving the pentachlorocyclotriphosphazene unit in the radical polymerization process. The lower molecular weight and increased polydispersity observed for the cyclotetraphosphazene (**8**) suggests potential side reactions involving the phosphazene unit during the polymerization reaction. This observation is consistent with the higher reactivity of tetrameric vs trimeric cyclophosphazene.[24] The homopolymers (**7**, **8**) exhibit the highest ratios of a cyclophosphazene to the carbon−carbon backbone in hybrid organic−inorganic polymers which have inorganic rings as substituents. This ratio is significantly higher than previously described members[1,6] of this class of phosphazene polymers. The fact that there are five reactive phosphorus−chlorine bonds in **7** and seven reactive phosphorus−chlorine bonds in **8** per monomer unit makes the homopolymers in question among the most highly functionalized materials that have been reported in the polymer literature. This study also represents an unusual case of incorporation of a cyclotetraphosphazene as a substituent on the polymer chain.

The attempted polymerization of a variety of other monovinyloxycyclotriphosphazenes leads to conflicting results. On the basis of the similarity of the ^{13}C NMR and ultraviolet photoelectron spectra data of the pentafluoro derivative (**2**) and **1**,[19] similar polymerization

Scheme 1



behavior would be expected.[1,7] However, after removal of solvent, the polymer could not be redissolved. This suggests the possibility of a difference in the reactivity of **7** and the polymer obtained from **2**. The reactivity of the fluorophosphazenes has in some cases been shown to be greater than in the corresponding chlorophosphazenes.[25] Thus, one possible explanation of the lack of solubility would be cross-linking at the cyclophosphazene sites initiated by displacement of a fluoride ion. The poor solubility of polymeric fluorophosphazenes[26] may also be a factor. The slow development of insolubility in the polymer obtained from the penta(methoxy) derivative (**3**) is consistent with the phosphazene–phosphazane rearrangement which is well-established for (methoxy)cyclophosphazene derivatives.[27] We have demonstrated that the phosphazene–phosphazane rearrangement proceeds through a dissociative process,[28] thus generating a reactive intermediate on the polymer chain which could lead to cross-linking. The formation of low molecular weight oligomers in the polymerization of the penta(trifluoroethoxy) derivative (**4**) may reflect a decreased reactivity of persubstituted cyclotriphosphzenes or chain transfer processes involving the fluoroalkoxy exocyclic unit. Finally, the absence of any detectable polymerization in the reactions of the penta(dimethylamino) derivative (**5**) is significant. While the ^{31}C NMR data for **1** indicate an electronic similarity to vinyl acetate, a monomer which undergoes facile polymerization under conditions of radical initiation, the NMR data for **5**[19] show that the olefinic center is relatively electron rich and is typical of monomers such as vinyl ethers which do not undergo radical polymerization.[29] The behavior of monomers **2**–**5** indicates the sensitivity and complexity of the role of the exocyclic group in the determination of the polymerizability, or lack thereof, of vinylphosphazene derivatives.

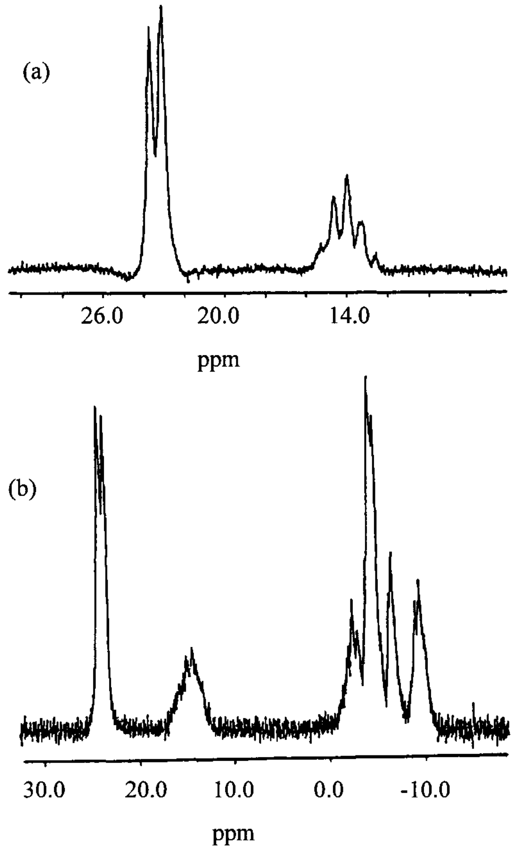


Figure 1. ^{31}P NMR of polymers (a) **7** in chlorobenzene at 380 K (b) copolymer of **1** and **6** in CDCl$_3$ at 305 K.

Copolymerization represents another approach to elucidation of the behavior of the olefinic center in vinyloxycyclophosphazenes. The formation of a series of copolymers (Scheme 1) from **1** and **6** is reasonable in light of the expected electronic similarity between the two monomers. The ^{31}P NMR spectrum of a typical copolymer of **1** and **6** (Figure 1) shows chemical shifts and coupling constants which are essentially equivalent to those observed for the respective monomers. Copolymer composition was established from the integrated intensities of the phosphorus–nitrogen ring-stretching modes in the infrared spectra.[23] The measured intensities in the copolymers were converted to mole ratios from a working curve obtained from mixtures of **1** and **6**. The compositional data, which is summarized in Table 1, can be converted to reactivity ratios[7,21] for **1** (r_1, 0.98) and **6** (r_2, 0.59), respectively. The approximately circular plot of the 95% joint confidence limits of the two monomers shows that the reactivity ratio data are consistent with a terminal model of copolymerization. NMR and photoelectron spectroscopy studies indicate that the electronic structure of the olefin in **1** is similar to that of vinyl acetate.[19] Using the Q, e values for vinyl acetate (0.026, −0.88)[29] to approximate those for **1**, one can calculate the corresponding values for **6** (0.014, −0.17). The virtually identical Q values are consistent with experimental[19] and computational[30] studies which show the absence of significant mesomeric interactions between the cyclophosphazene and the vinyloxy unit in **1**. The significant difference in e values between **1** and **6** has some basis in the difference in the β-carbon chemical shifts in the two monomers but not to the degree suggested by the reactivity data. This may be due to other factors, such as steric effects, contributing to the e values[29] or uncertainty in the compositional data. The copolymerization of **1** with various organic monomers was also attempted. Only small, adventitious degrees of incorporation of **1** into poly(methyl methacrylate) were observed. The electronic similarity of **1** and vinyl acetate[19] would lead one to expect that this would be a good comonomer pair; however, the product obtained was a black infusible solid, the nature of which is discussed below. Similar results were obtained when *N*-vinyl-2-pyrrolidinone was employed as the comonomer. The styrene/**1** system presents an interesting and instructive study. Bulk polymer samples were isolated and shown spectroscopically to contain components of both monomers. However, GPC analysis shows two separate distributions. Manual collections of the separate fractions containing each of the components were collected, and it was shown by infrared spectroscopy that one of the homopolymers corresponds to **7**. This behavior mimics that observed in the attempted copolymerization of styrene and vinyl acetate.[29] In the styrene/vinyl acetate system the reactivity ratios indicate that styrene-based radicals react only with styrene and vinyl acetate radicals react only with styrene until the styrene is consumed. Then the homopolymer of vinyl acetate is obtained. In the styrene/**1** system, the absence of resonance stabilization of the vinyloxyphosphazene radical and the electronic similarity of **1** and vinyl acetate would lead to copolymerization behavior which is analogous to that observed for the vinyl acetate/styrene system.

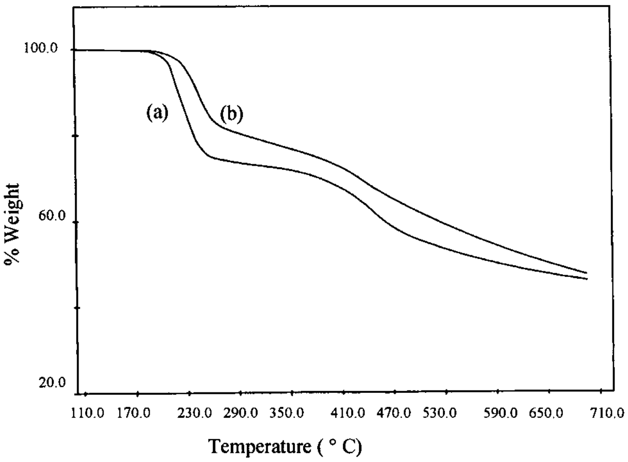


Figure 2. TGA scans for polymers (a) **7** and (b) **8**.

Scheme 2

9

Table 2. Activation Energies and Enthalpies from the Thermal Decomposition of 7 and 8

compound	E_A (kJ/mol)	ΔH (kJ/mol)
7	114.0	−38.0
8	128.2	−36.7

The TGA scans for **7** and **8** (Figure 2) show an initial process just above 110 °C corresponding to the weight loss of two moles of HCl. A second, broader transition occurs around 400 °C. Identical results are obtained in air or nitrogen as the carrier gas. The identity of the volatile products was established by pyrolysis mass spectrometry. The first process is the elimination of HCl which continues until the second event. The gaseous product in the high-temperature process was identified as the novel oxo-bridged dimer, $(N_3P_3Cl_5)_2O$, by the molecular mass, the isomeric distribution peak corresponding to 10 chlorine atoms and observation of both $N_3P_3Cl_5^+$ and $N_3P_3Cl_5O^+$ fragment ions. The oxo-bridged cyclophosphazene dimer has previously been observed in solution.[31] Polymer **9**, obtained from the polymerization of the cyclothiaphosphazene (Scheme 2),[32] exhibits a TGA which is analogous to that of **7** except that the weight loss of the first process corresponds to 1 mol of HCl. The activation energies (Table 2) for the first decomposition step of **7** and **8** were determined using the Flynn and Wall analysis[33] of multiple scan rate TGA experiments (Supporting Information). The DSC plot for **7** is shown in Figure 3. Similar results are obtained for **8**. Thermal events in the DSC studies corresponding to the two steps in the TGA are observed. The first is a relatively sharp exotherm while the second is a broad endotherm. The corresponding enthalpy values may be found in Table 2.

The elimination of HCl in the solid state indicates a cross-linking process involving formation of phosphorus−

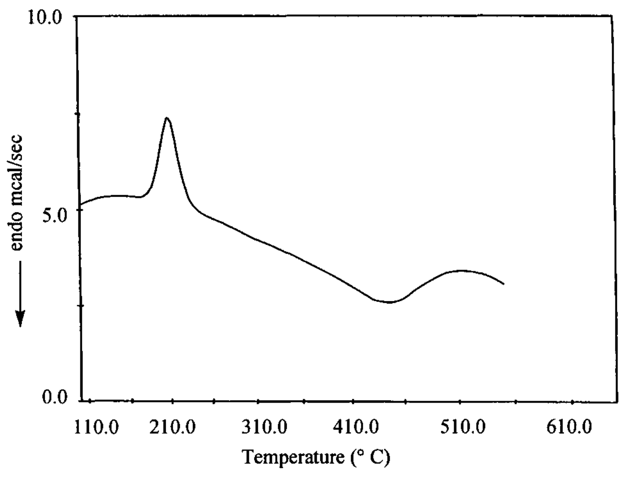
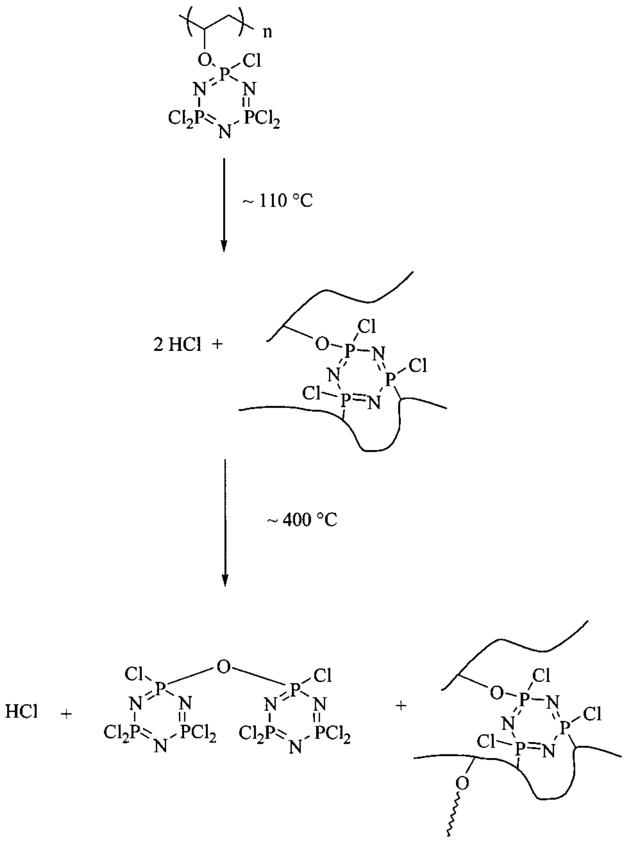


Figure 3. DSC scan for polymer **7**.

Scheme 3



carbon bonds (Scheme 3). A comparison of the structures of the cyclophosphazene substituted polymer (**7**) and the corresponding cyclothiaphosphazene (**9**) leads to the conclusion that one chlorine atom in each of the two/ PCl$_2$ centers in **7** is involved in the cross-linking reaction. The activation energy (Table 2) for the cross-linking reaction involving the cyclotetraphosphazene substituent in **8** is higher than that of the trimeric species (**7**). In the reactions of monomeric trimers and tetramers with nucleophiles in solution, the tetrameric species undergo reactions at faster rates than the trimer.[24] The lower reactivity of **8** relative to **7** suggests that proper alignment to bring the phosphorus−chlorine and carbon−hydrogen bonds in close proximity is a major factor in the process and is more difficult for the larger, more sterically demanding tetramer. The similarity of the residue after the first pyrolysis step to that obtained in the attempted polymerization of **1** using benzoyl peroxide as the initiator suggests that this remarkable exothermic cross-linking reaction can also occur in a fluid phase at moderate temperatures. Elemental analyses of the residue from the benzoyl peroxide polymerization were low in both chlorine and hydrogen relative to **7**. Elimination of the oxo-bridged phosphazene dimer (Scheme 3) is an endothermic event due to the rigidity of the cross-linked material. The first step in the phosphazene−phosphazane rearrangement of alkoxycyclophosphazenes involves heterolytic cleavage of a exocyclic carbon oxygen bond to give the $N_3P_3Cl_5O^-$ species.[28] A similar reaction in the second decomposition step of **7** would provide a oxyanion positioned to displace a $N_3P_3Cl_5^+$ unit and form the observed oxo-bridged dimer. As this process progresses, the residue becomes increasingly carbon-rich.

The T_g values for **7** and **8** are 76 and 72 °C, respectively, which are significantly lower than that observed for poly(styrene) (100 °C). This most likely reflects rotational freedom about the carbon−oxygen and phosphorus−oxygen bonds.

In summary, chlorocyclotri- and tetraphosphazenes with a vinyloxy substituent are converted to high molecular weight homo- and copolymers by radical addition polymerization. The monomers resemble vinyl acetate in their polymerization behavior. The resulting hybrid organic−inorganic polymers are very rich in the inorganic component, and their chemical modification behavior will be described in a subsequent publication. The sensitivity of the reactivity of vinyloxyphosphazene monomers to the remaining phosphazene substituents has been correlated to known electronic properties and chemical behavior of the cyclophosphazenes. Elucidation of the polymer thermolysis of the homopolymers **7** and **8** has uncovered a novel cross-linking reaction at moderate temperatures.

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