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Thermal Polymerization of Hexakis(pyridinoxy)cyclotriphosphazenes: Ring-Opening Polymerization of Ring-Strain-Free Cyclic Trimers Fully Substituted by Organic Groups

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ABSTRACT: Thermal polymerization of cyclotriphosphazenes fully substituted with 2-, 3-, and 4-pyridinoxides have been attempted both in the solid state and in solution. Among these ring-strain-free trimeric isomers, hexakis(3-pyridinoxy)cyclotriphosphazene (**1**) did not undergo polymerization either in the solid state or in solution, but 4-pyridinoxy (**2**) and 2-pyridinoxy analogues (**3**) have been found to undergo polymerization at 150 and 200 °C, respectively, in the absence of any catalyst. In particular, the thermal solution polymerization of **2** in 1,2,4-trichlorobenzene at 200 °C resulted in a linear polymer in 80% yield which was the same as the product obtained by a nucleophilic substitution of poly(dichlorophosphazene) with 4-pyridinoxide. DSC analysis of the trimers has shown that **2** and **3** have exothermic peaks at 179.4 and 224.1 °C, respectively, whereas **1** does not have an exothermic peak, and it has been found that the polymerizability and temperature range for polymerization of the cyclic trimers are closely related to their thermal properties: trimers having an exothermic peak are amenable to the thermal polymerization reaction, and the temperature range for polymerization can be predicted therefrom. Along with such a finding, the results of the thermal conductivity measurements of trimers **1**, **2**, and **3** conclusively support the cationic ring-opening mechanism. The difference in polymerizability of these trimeric isomers may be explicable in terms of an electronic difference of the substituent isomers: 4- and 2-pyridinoxide anions are more resonance stabilized than the 3-pyridinoxide anion, which probably makes a difference in the degree of ionization of the substituents from the trimeric phosphazene ring at the initial step of the ring-opening polymerization.

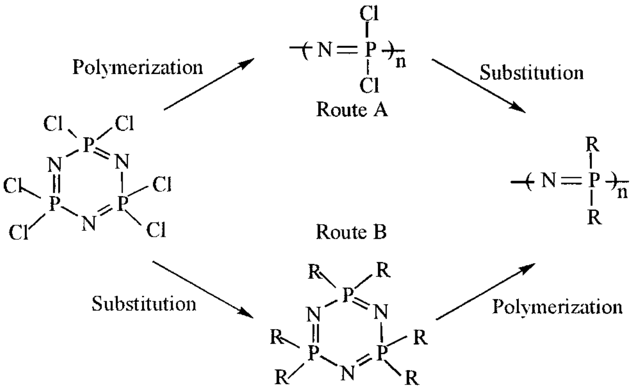
Introduction

In recent years one of the most exciting and rapidly expanding branches of materials science has been the area of inorganic and organometallic polymers. Especially, the poly(organophosphazenes), $(R_2P{=}N)_n$, consisting of a backbone of alternating phosphorus and nitrogen atoms with two substituents at each phosphorus atom, are the most versatile class of inorganic polymers from a synthetic viewpoint.[1] Since a tremendous variety of substituents can be attached to the backbone phosphorus atom, these polymers exhibit a very broad spectrum of chemical and physical properties which make them suitable for many applications.[2]

The most widely used synthetic route to the poly(organophosphazenes) involves the ring-opening polymerization of hexachlorocyclotriphosphazene at about 250 °C to give a linear and soluble high molecular weight poly(dichlorophosphazene).[1−4] Chlorine atoms of poly(dichlorophosphazene) are then replaced by reaction with appropriate nucleophilic groups to yield a variety of stable polymers (via route A in Scheme 1).

On the other hand, an alternative process involves an initial introduction of organic side groups in the cyclic trimer, followed by a ring-opening polymerization of the cyclic organophosphazenes (via route B).[5,6] Such a synthetic method is especially attractive because substitution reactions on the cyclic phosphazenes, and isolation and purification of the resultant products, are generally much easier than the corresponding processes for the high molecular weight polymer. However, all the attempts to polymerize cyclic trimers that are fully substituted with organic groups have failed to yield high molecular weight polymers,[7,8] except for the fully substituted cyclic trimers with a transannular metallocenyl unit or a transannular bridge inducing ring strain,[9−11] and no example is known for ring-opening polymerization of the ring-strain-free cyclic trimers bearing the same six organic groups. Furthermore, it was implied that steric substituents such as phenoxy groups on the cyclic trimer hinder polymerization reaction while ring expansion is favored due to the crowding of the side groups in a linear polyphosphazene compared to the situation in a cyclic oligomer.[10,11] Thus, the polymerization of the organophosphazene trimers is very sensitive to the structure of the organic substituents attached to the skeletal phosphorus atoms.

Scheme 1



Surprisingly, from such points of view, we have found the first examples of thermal polymerization of ring-strain-free hexakis(pyridinoxy)cyclotriphosphazenes, and here we describe the results of their polymerization and characterization of the resultant polymers.

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Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (Aldrich), was purified by sublimation at 55 °C under vacuum (ca. 0.1 mmHg). Tetrahydrofuran (Baker) and toluene (Baker) were dried and distilled over sodium benzophenone, and triethylamine (Junsei) was distilled over BaO under a dry nitrogen atmosphere. All other reagents purchased from Aldrich were used without further purification. Sodium pyridinoxide isomers were prepared by reaction of the corresponding hydroxypyridine isomers (Aldrich) with sodium metal in THF. $[NP(OCH_2CF_3)_2]_3$, $[NP(OPh)_2]_3$,[3] $[NP(OPhNO_2\text{-}p)_2]_3$,[12] and $N_3P_3(OPh)_5Cl$[13] were synthesized according to literature procedures.[3] Poly(dichlorophosphazene) was prepared as previously described.[14] All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk line techniques.

Measurements. IR spectra were recorded on an Analect FX-6160FT-IR spectrometer as KBr pallets. NMR spectra were measured on a Varian Gemini 300NMR spectrometer in DMSO-d_6. The chemical shifts for ^{31}P NMR spectra are relative to the external standard of triphenyl phosphate, with positive shifts downfield from this reference. Molecular weights were determined using a Waters model 590 gel permeation chromatograph equipped with a Waters 410 differential refractometer and two Ultrastyragel linear columns. DMF was used as the eluent. Calibration of the column was accomplished by means of a narrow molecular weight polystyrene standards obtained from Waters. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out on a Perkin-Elmer TGA-2 at heating rate of 20 °C/min under flowing nitrogen. Elemental analysis was performed by the Advanced Analysis Center at KIST. Measurements of electrical conductivity were performed according to Valdes' technique, which was briefly described in the previous papers.[15]

X-ray Structure Determination. All the X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell dimensions were determined from 25 machine-centered reflection in the 2θ range of 15−25°. The variation of intensities was monitored with repeated check of intensities of three reflections every 1 h during the data collection period. Absorption corrections were applied by an empirical psi scan on two or three reflection planes with a chi value near 90°. A direct or Patterson method (SHELXS-86) was employed to locate heavy atoms, and subsequent cycles of Fourier map and least-squares refinements located other atoms (SHELXS-93). Hydrogen atoms were included in the structure factor calculation using a riding model. All the calculations were carried out using VAX and PC computers.

Synthesis of Hexakis(pyridinoxy)cyclotriphosphazenes. To a suspension of sodium 3-pyridinoxide (12.12 g, 103 mmol) in THF (350 mL) was added a solution of $(NPCl_2)_3$ (3.0 g, 8.63 mmol) in THF (100 mL) under a nitrogen atmosphere. The mixed solution was refluxed for 2 days. After NaCl formed was filtered off, the filtrate was concentrated under reduced pressure. The condensed solution was poured into a large excess of water. The resultant oily precipitate was dissolved in THF, and the solution was added to excess ethyl ether to obtain a white solid product $[NP(3\text{-}OC_5H_4N)_2]_3$ (**1**) in 88% yield. The product was recrystallized twice from a solvent pair of THF and ethyl ether. Colorless crystals suitable for X-ray crystallography were obtained by slow diffusion of ethyl ether into the THF solution of the product. Mp 108 °C. Anal. found (calcd for $C_{10}H_8N_3O_2P$): C, 52.1 (51.5); H, 3.5 (3.5); N,17.9 (18.0). IR (KBr, cm^{-1}): ν(P=N), 1182, 1240. ^{1}H NMR (DMSO-d_6, ppm): 7.4 (m), 8.3 (s), 8.4 (d). ^{13}C NMR (DMSO-d_6, ppm): 124.7, 127.8. 141.9, 146.2, 146.9. ^{31}P NMR (DMSO-d_6, ppm): 32.3.

The isomeric analogues $[NP(4\text{-}OC_5H_4N)_2]_3$ (**2**) and $[NP(2\text{-}OC_5H_4N)_2]_3$ (**3**) were prepared using the same procedure as described for the synthesis of **1**.

$[NP(4\text{-}OC_5H_4N)_2]_3$ (**2**): Yield 92%. Mp 168 °C. Anal. found (calcd for $C_{10}H_8N_3O_2P$): C, 51.5 (51.5); H, 3.3 (3.5); N, 17.7 (18.0). IR (KBr, cm^{-1}): ν(P=N), 1180, 1227. ^{1}H NMR (DMSO-d_6, ppm): 7.1 (d), 8.5 (d). ^{13}C NMR (DMSO-d_6, ppm): 115.7, 151.9, 155.8. ^{31}P NMR (DMSO-d_6, ppm): 29.5.

$[NP(2\text{-}OC_5H_4N)_2]_3$ (**3**): Yield 90%. Mp 179 °C. Anal. found (calcd for $C_{10}H_8N_3O_2P$): C, 51.4 (51.5); H, 3.4 (3.5); N, 17.7 (18.0). IR (KBr, cm^{-1}): ν(P=N), 1186, 1223. ^{1}H NMR (DMSO-d_6, ppm): 7.1 (d), 7.2 (t), 7.8 (t), 8.2 (d). ^{13}C NMR (DMSO-d_6, ppm): 113.4, 121.1, 140.1, 147.8, 156.5. ^{31}P NMR (DMSO-d_6, ppm): 28.8.

Melt Polymerization of Hexakis(pyridinoxy)cyclotriphosphazenes. A sample of crystalline cyclotriphosphazene (~0.5 g) was placed in an ampule (4 cm × 2 cm Pyrex tube), which was subjected to vacuum (0.1 mmHg) and then sealed. The ampule was maintained at the desired temperature in a specially designed oven in which a metal axle holding the ampules was rotating at 1 rpm for stirring the reactants. After the thermal reaction was carried out for a desired period of time, the ampule was cooled and broken, and the resultant solid was washed with excess hexane. Among the trimers, only **2** and **3** were subjected to melt polymerization. Anal. found {calcd for $[NP(4\text{-}OC_5H_4N)_2]_n$}: C, 49.4 (51.2); H, 3.78 (3.46); N, 17.0 (18.0). IR (KBr, cm^{-1}): ν(P=N), 1200, 1244. ^{31}P NMR (DMSO-d_6, ppm): 10 to −4 (b). Anal. found {calcd for $[NP(2\text{-}OC_5H_4N)_2]_n$}: C, 50.8 (51.5); H, 3.54 (3.46); N,17.5 (18.0). IR (KBr, cm^{-1}): ν(P=N), 1216, 1276. ^{31}P NMR (DMSO-d_6, ppm): −1 to −8 (b).

Solution Polymerization of Hexakis(pyridinoxy)cyclotriphosphazenes. A sample of cyclotriphosphazene derivatives (~1.0 g) was dissolved in 1,2,4-trichlorobenzene (50 mL), and the solution was heated at 200 °C for 4 days. Among the derivatives **1**, **2,** and **3**, only **2** gave a polymeric product precipitated from the solution during the polymerization reaction. The resultant precipitate was filtered, washed with excess hexane and ethyl ether, and then dried under vacuum. Anal. found {calcd for $[NP(4\text{-}OC_5H_4N)_2]_n\cdot 2H_2O$}: C, 45.3 (44.6); H, 3.47 (4.49); N, 15.8 (15.6). IR (KBr, cm^{-1}): ν(P=N), 1196, 1246. ^{31}P NMR (DMSO-d_6, ppm): −4.5 (s).

Substitution of Poly(dichlorophosphazene) with Pyridinoxides in Solution. To compare with the results of melt and solution polymerizations of **1**, **2**, and **3**, poly[bis(pyridinoxy)phosphazenes] were prepared by substitution of poly(dichlorophosphazene)[13] instead of $(NPCl_2)_3$ with pyridinoxides by following the same procedure as described for **1**.

$[NP(3\text{-}OC_5H_4N)_2]_n$ (**4**): Yield 60%. IR (KBr, cm^{-1}): ν(P=N), 1207, 1248. ^{1}H NMR (DMSO-d_6, ppm): 6.9 (b), 7.9 (b), 8.2 (b). ^{13}C NMR (DMSO-d_6, ppm): 123.3, 126.8, 141.5, 145.9, 146.7. ^{31}P NMR (DMSO-d_6, ppm): 3.5. Molecular weight (from GPC): M_w, 6.1 × 10^4; M_n, 4.5 × 10^4.

$[NP(4\text{-}OC_5H_4N)_2]_n$ (**5**): Yield 45%. IR (KBr, cm^{-1}); ν(P=N), 1195, 1242. ^{31}P NMR (DMSO-d_6, ppm): 0.2.

$[NP(2\text{-}OC_5H_4N)_2]_n$ (**6**): Yield 55%. IR (KBr, cm^{-1}): ν(P=N), 1242, 1261. ^{31}P NMR (DMSO-d_6, ppm): −5.1.

Results and Discussion

Synthesis and Properties of Hexakis(pyridinoxy)cyclotriphosphazenes. Hexakis(pyridinoxy)cyclotriphosphazenes were smoothly prepared by reaction of hexachlorocyclotriphosphazene with sodium pyridinoxides in THF. Reaction of hexachlorocyclotriphosphazene with hydroxypyridines in the presence of triethylamine as HCl acceptor in THF also produced the same desired products. In both cases, the products were obtained in higher yields (>90%) compared with that reported in the literature.[16] The ^{31}P NMR spectra of all the isomeric hexakis(pyridinoxy)cyclotriphosphazenes have shown a singlet resonance for the ring phosphorus atoms, which is very sensitive to the isomeric pyridinoxy substituents as is seen in Table 1. These compounds are colorless crystals with sharp melting points in the range 108−179 °C, which are soluble in polar organic solvents such as THF, dimethyl sulfoxide, and dimethylformamide.

Table 1. ^{31}P Chemical Shifts[a] for Fully Substituted Trimers and Polymers

compounds	δ (ppm)
$[NP(3\text{-}OC_5H_4N)_2]_3$ (**1**)	32.3
$[NP(4\text{-}OC_5H_4N)_2]_3$ (**2**)	29.5
$[NP(2\text{-}OC_5H_4N)_2]_3$ (**3**)	28.8
$[NP(3\text{-}OC_5H_4N)_2]_n$ (**4**)	3.5
$[NP(4\text{-}OC_5H_4N)_2]_n$ (**5**)	0.2
$[NP(2\text{-}OC_5H_4N)_2]_n$ (**6**)	−5.1

[a] In DMSO-d_6.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

P(1)−N(1)	1.568(3)	P(1)−N(3)	1.574(3)
P(1)−O(1)	1.579(2)	P(1)−O(2)	1.584(2)
P(2)−N(1)	1.569(3)	P(2)−N(2)	1.574(3)
P(2)−O(4)	1.577(2)	P(2)−O(3)	1.583(2)
P(3)−O(5)	1.572(2)	P(3)−N(3)	1.577(3)
P(3)−O(6)	1.575(2)	P(3)−N(2)	1.575(3)
N(1)−P(1)−N(3)	117.5(2)	N(1)−P(1)−O(1)	106.0(2)
N(3)−P(1)−O(1)	112.4(2)	N(1)−P(1)−O(2)	110.7(2)
N(3)−P(1)−O(2)	109.4(2)	O(1)−P(1)−O(2)	99.2(2)
N(1)−P(2)−N(2)	117.2(2)	N(1)−P(2)−O(4)	106.9(2)
N(2)−P(2)−O(4)	111.9(2)	N(1)−P(2)−O(3)	111.2(2)
N(2)−P(2)−O(3)	109.3(2)	O(4)−P(2)−O(3)	98.8(2)
O(5)−P(3)−N(3)	110.3(2)	O(5)−P(3)−O(6)	96.1(2)
N(3)−P(3)−O(6)	110.7(2)	O(5)−P(3)−N(2)	110.5(2)
N(3)−P(3)−N(2)	117.2(2)	O(6)−P(3)−N(2)	110.0(2)
P(1)−N(1)−P(2)	122.5(2)	P(2)−N(2)−P(3)	122.4(2)
P(3)−N(3)−P(1)	121.8(2)		

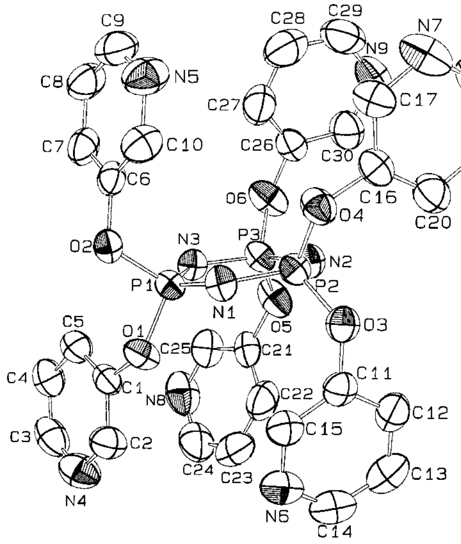


Figure 1. ORTEP drawing of **1**.

The X-ray crystallographic analysis of **1** was carried out, and its molecular structure was compared with those of its isomeric analogues **2** and **3** reported in the literature.[16] The main structural data for compound **1** are summarized in Table 2, and its ORTEP drawing is shown in Figure 1. The structure contains a cyclic trimeric phosphazene ring with six 3-pyridinoxy groups attached through P−O−C linkages. The P−N and P−O bond distances range from 1.568(3) to 1.577(3) Å and from 1.572(2) to 1.584(2) Å, respectively. The P−N−P angles range between 121.8(2)° and 122.5(2)°, and the N−P−N angles vary from 117.2(2)° to 117.5(2)°. These relevant bond lengths and bond angles are in keeping with those encountered in cyclic phosphazenes.[17] The phosphazene ring of **1** is slightly distorted from the regular hexagonal plane similar to those of **2** and **3**. The largest deviation from the least-squares planes defined by the N_3P_3 ring in compound **1** is that of the atom P(1) (−0.073(1)), which is comparable to those of **2** (−0.088(3)) and **3** (−0.083(3)).[16] Therefore, the phosphazene rings of all the trimeric isomers **1**, **2**, and **3** are almost planar and ring-strain-free.

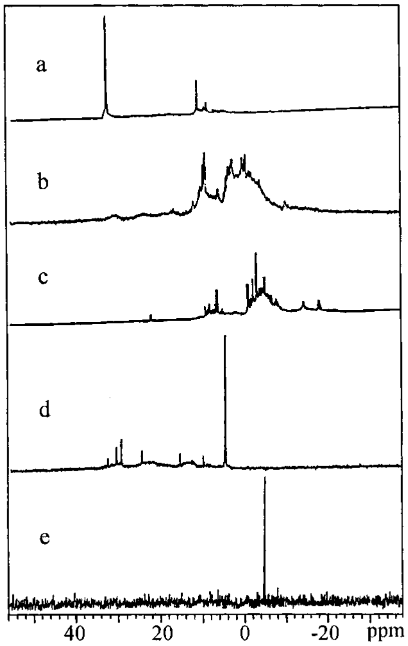


Figure 2. ^{31}P NMR spectra after direct melt polymerization reaction of **1** (for 5 h at 270 °C) (a), **2** (for 30 min at 170 °C) (b), **3** (for 5 h at 250 °C) (c), and $N_3P_3(OPh)_5Cl$ (for 3 h at 320 °C) (d) and of solution polymerization product of **2** (for 4 days at 200 °C) (e).

Melt Polymerizaion of Hexakis(pyridinoxy)cyclotriphosphazenes. The direct melt polymerization for the fully substituted trimers **1**, **2**, and **3** was attempted at temperatures between 150 and 300 °C, and the resultant products were examined by ^{31}P NMR spectroscopy. Compounds **2** and **3** easily underwent polymerization reaction at temperatures above 150 and 200 °C, respectively, in the absence of any catalyst. In particular, compound **2** immediately changed into a polymeric material above its melting point within 30 min, while it took 12 h for complete conversion of **3**. Such results will be discussed along with the results of their DSC analysis in the following section. In contrast, heating **1** at 200 °C for 1 day brought about virtually no change, and when heated at 250 °C only trace amounts of ring expansion species could be detected. No polymeric products could be obtained from **1** even at 300 °C, which is the limit of its thermally stable temperature (decomposition temperature 320 °C) similar to those reported for phenoxy analogues, $[NP(OPh)_2]_3$[18] and $[NP(OPhNO_2\text{-}p)_2]_3$.[12] The same results were obtained even when a catalyst such as $(NPCl_2)_3$, $AlCl_3$, or water was used. The ^{31}P NMR spectra of the melt reaction products of **1**, **2**, and **3** are depicted along with that of the solution polymerization product of **2** in Figure 2. As seen in the figure, the ^{31}P NMR spectra of the melt polymerization products of **2** and **3** (−8 to 5 ppm) exhibit broad and complicated resonances with remarkable upfield shifts relative to the trimers, which is clearly indicative of polymerization of the trimers similarly to other cyclophosphazenes such as $(NPCl_2)_3$.[19−21] Such complicated and broad ^{31}P resonance peaks for the melt-polymerized products indicate that these polymers resultant from the melt polymerization of **2** and **3** have not a linear but complicated structures, which will be discussed later in detail. However, the ^{31}P NMR spectrum of the melt polymerization product of **2** shows that no unreacted trimer remained after the reaction, which indicates complete conversion of the trimer to polymers. The soluble parts of the melt polymerization products of **2** and **3** in dimethylformamide were subjected to GPC measurement, which gave low molecular weights in the range of $M_w \cong 5000$. The P═N stretching frequencies of these products are significantly blue-shifted from those of their corresponding trimers, which also indicates their polymeric nature.

It is generally known that the cyclic trimers bearing both halogen and organic substituents within the same cyclic phosphazene ring could be polymerized,[22−24] but previous works[10,11] have shown that cyclic trimers fully substituted only with organic groups, except for the trimers ring-strained by a transannular bridge, do not polymerize at elevated temperature, and this reduced tendency for polymerization may be explained by the increase in steric crowding of the side groups in a prospective linear polyphosphazene compared to the situation in a cyclic oligomer. Surprisingly, however, it has been found in this study that the cyclic trimers fully substituted by 2- and 4-pyridinoxy groups have almost the same steric crowdness as the phenoxy analogue, and no ring strain could successfully be induced to undergo ring-opening polymerization in a short period of reaction time at low temperatures.

Solution Polymerizaion of Hexakis(pyridinoxy)-cyclotriphosphazenes. To compare with the products of melt polymerization reactions of the fully substituted trimers (**1**, **2**, and **3**), poly[bis(pyridinoxy)phosphazenes] (**4**, **5**, and **6**) were also prepared by substitution of poly(dichlorophosphazene)[14] with pyridinoxide isomers. These substituted polymers are poorly soluble in most organic solvents, except for DMSO and DMF, but could be identified by ^{31}P NMR spectroscopy. GPC measurement of **4** in DMF gave a molecular weight $M_w = 6.1 \times 10^4$ and M_w/M_n ratio of 1.4, in agreement with the previous report.[14] However, polymers **5** and **6** were found to be not very soluble in most organic solvents, and consequently no GPC measurements could be performed. The ^{31}P chemical shifts of the substituted polymers referenced to triphenyl phosphate given in Table 1 show that the ^{31}P resonance of the polymers shifted upfield relative to the corresponding trimer, which is a general phenomenon of the other phospazenes.[19,21,22]

Solution polymerization reactions of the fully substituted trimers (**1**, **2**, and **3**) were attempted at 200 °C in 1,2,4-trichlorobenzene (bp 213.5 °C), as described in the Experimental Section. Thermal reaction of **2** among these trimers in solution gave rise to an insoluble polymeric product within 5 h, which was obtained in 80% yield after reaction for 4 days. This precipitated polymer was characterized by ^{31}P NMR and IR spectroscopies. Unlike the melt polymerization, the solution polymerization of **2** in 1,2,4-trichlorobenzene yielded a linear polymer, which is nearly the same as the polymer **5** obtained by substitution of the chloropolymer with **2**, as shown in Figure 2e. However, the same thermal solution reaction of **1** and **3** gave no polymeric product after reaction for 4 days, and in order to affect polymerization of **3** in solution, it seems necessary to employ a different solvent with higher boiling point.

Thermal Properties vs Polymerizability. To find whether there is any relationship between thermal properties and thermal polymerizability of the cyclic trimers, we have performed DSC analysis on the fully substituted trimers, which exhibit interesting thermal behaviors as shown in Figure 3. Each endothermic peak of the DSC curves corresponds to the melting point of each compound, but we have found that the exothermic properties of the trimers are closely related with their thermal polymerizability. In other words, the trimers **2** and **3** showed their exothermic peaks at 179.4 and 224.1 °C, respectively, but **1** did not show any exothermic peak in the measured temperature range. Furthermore, no detectable weight loss was observed from TGA in the temperature range of the exothermic peaks of **2** and **3**. Such exothermic behaviors are in accord with the fact that, as mentioned in the previous section, trimers **2** and **3** undergo direct melt polymerization reaction above at 150 and 200 °C, respectively, while no polymerization occurs for **1** even at 300 °C.

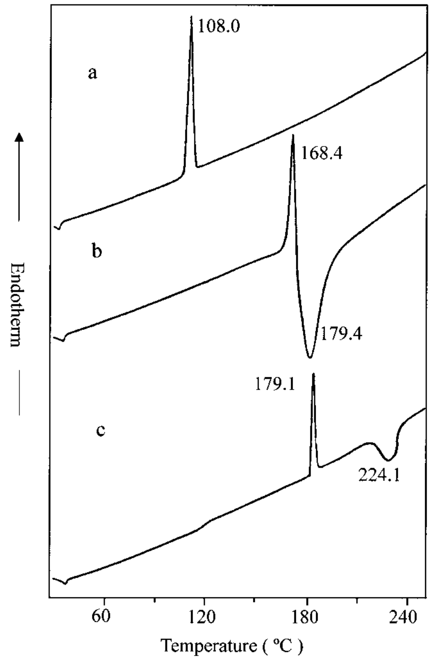


Figure 3. DSC thermograms of **1** (a), **2** (b), and **3** (c).

In the case of $(NPCl_2)_3$, the exothermic curve starts around at 170 °C, but its overall exothermic peak is broad and weak as shown in Figure 4. It was reported that $(NPCl_2)_3$ is thermally polymerized over a wide range of temperatures at a relatively slow rate, which is in accord with its observed thermal properties. It is generally known that the exothermic peak of the DSC curve represents the enthalpy change associated with a chemical change of the compound, and the height of the curve is directly proportional to the rate of the chemical change.[25] Therefore, from consideration of the above-mentioned thermal behaviors in conjunction with the results of thermal conductivity measurement of the trimers which will be discussed in the following section, it may be presumed that the exothermic peak is related to ionization properties of the trimers. In other words, since trimer **2** has a remarkably sharper exothermic peak at a lower temperature compared with $(NPCl_2)_3$, it seems that the melt polymerization of **2** proceeds much faster due to higher rate of ionization of the pyridinoxy group from the phosphazene ring compared with $(NPCl_2)_3$ and results in branched polymers as is seen from its complicated broad ^{31}P NMR spectra in Figure 2. However, the figure shows that thermal

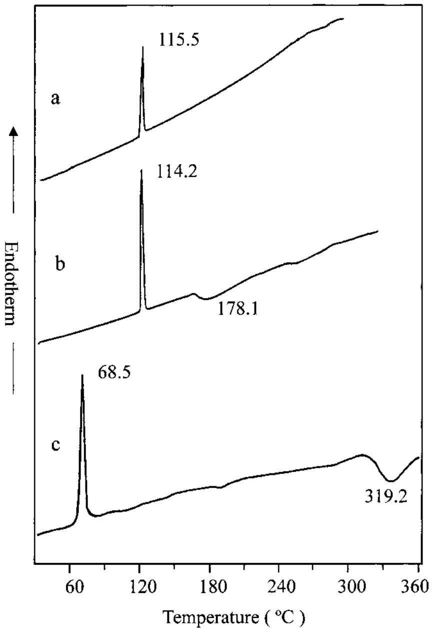


Figure 4. DSC thermograms of $[NP(OPh)_2]_3$ (a), $(NPCl_2)_3$ (b), and $N_3P_3(OPh)_5Cl$ (c).

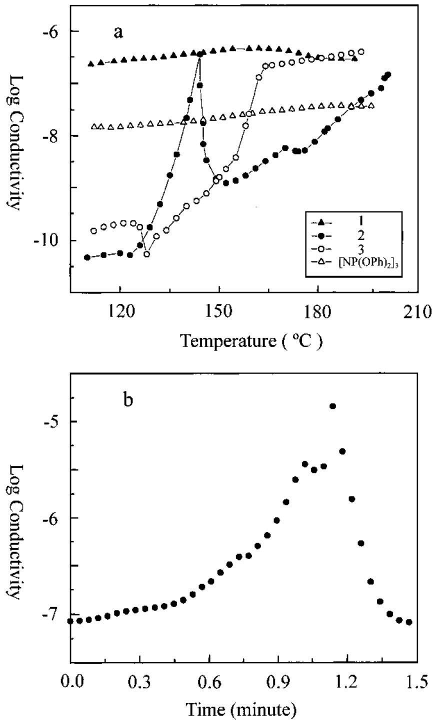


Figure 5. Temperature-dependent conductivity of **1**, **2**, **3**, and $[NP(OPh)_2]_3$ (a) and time-dependent conductivity at 150 °C of **2** (b). All data points are the average values of two repeated measurements.

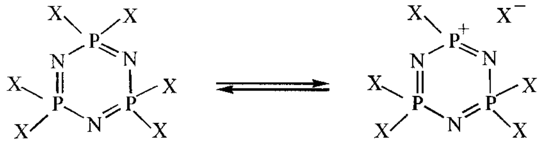
polymerization of **2** performed slowly in solution yields a linear polymer that is almost identical with the polymer **5** obtained by substitution of the chloropolymer with 4-pyridinoxide in solution. Thus, the cyclic trimers fully substituted with 2- and 4-pyridinoxy groups bearing no ring strain undergo a ring-opening polymerization without any catalyst at unusually low temperatures compared to that of tris(*o*-phenylenedioxy)cyclotriphosphazene (300 °C)[11] and that of $N_3P_3(OCH_2CF_3)_4(\eta^5\text{-}C_5H_4)_2Fe$ (250 °C).[10] To confirm such a relationship of the exothermic peak with polymerizability, DSC analyses were also performed for other known cyclic trimers, $[NP(OCH_2CF_3)_2]_3$, $[NP(OPh)_2]_3$, $[NP(OPhNO_2\text{-}p)_2]_3$, and $N_3P_3(OPh)_5Cl$. As was expected, no exothermic peak was observed for $[NP(OCH_2CF_3)_2]_3$, $[NP(OPh)_2]_3$, and $[NP(OPhNO_2\text{-}p)_2]_3$ which are not thermally polymerized. However, $N_3P_3(OPh)_5Cl$ exhibited an exothermic peak at 319 °C as shown in Figure 4c, and as a matter of fact, this trimer has been found to undergo easily polymerization at 320 °C within 3 h. The ^{31}P NMR spectrum of the melt polymerization product of $N_3P_3(OPh)_5Cl$ is shown in Figure 2d, which shows a singlet at 5.2 ppm in the region of polymers.[21,22] It is known that when the phosphazene backbone contains both $NP(OR)_2$ and NP(OR)Cl units and if the Cl content is minor, the ^{31}P resonance appears as a singlet.[13] Therefore, it may be concluded that both thermal polymerizability and the polymerization temperature range of the phosphazene trimers may be predicted from the presence and the temperature range of an exothermic peak on their respective DSC curve.

Conductivity Measurements. The crystals of hexakis(pyridinoxy)cyclotriphosphazenes were pressed into pellets, and the conventional four-point probe method[15] was used to obtain their dc electrical conductivity. The variation of the dc electrical conductivity with temperature for these trimers are shown in Figure 5a along with that of hexakis(phenoxy)cyclotriphosphazene for comparison. The figure shows that the conductivity of hexakis(phenoxy)cyclotriphosphazene and **1**, which do not polymerize, did not change as the temperature was raised to 200 °C. On the other hand, the conductivity of **2** rose rapidly from around 145 °C and then fell drastically and increased steadily to 200 °C. Trimer **3** had a little different profile as its conductivity increased continuously from 150 to 200 °C. Such results are agreed satisfactorily with the aforementioned observations of DSC analysis and the results of the direct polymerization. According to the literature,[18] the increased conductivity of $(NPCl_2)_3$ at high temperature is due to the release of chloride ion as the charge carriers, which means that ionization into charge-carrying species occurs concurrently with polymerization. The abovementioned results are also consistent with the increased conductivity during polymerization. However, it is impossible to conclude from the results whether this conductivity could be either electronic or ionic in nature because of the dc measurement. Therefore, variation of conductivity was measured with time at constant temperature (150 °C) for **2**. As shown in Figure 5b, the conductivity at 150 °C rose rapidly at the start but immediately fell, which suggests that such a drastic decrease is due to polarization effects under direct current. Thus, it is clear that the conductivity increase is attributed to the presence of ions as the charge carriers, which is most readily explained in terms of ionic conductivity. Such results strongly support that 4- and 2-pyridinoxy groups are readily ionized from the cyclic trimers, resulting in increasing conductivity, which can afford the polymerization process.

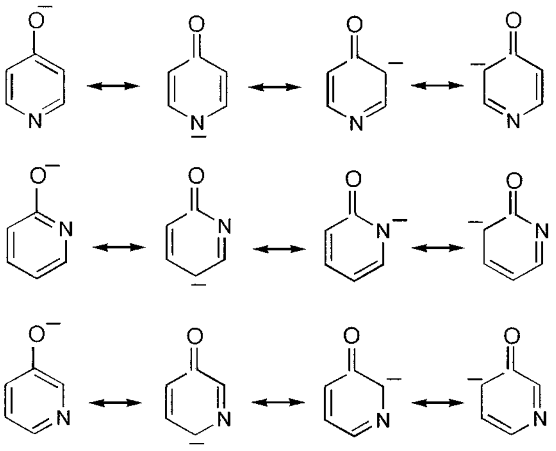
Mechanism of Polymerization. The initiation of the polymerization of phosphazene trimers has been generally accepted as ionization of a halide (or pseudohalide) ion from a phosphorus atom (Scheme 2).[1,18,26]

The results of our conductivity measurements and DSC analysis described above clearly support this ionic mechanism. Thus, the polymerizability of phosphazene trimers is determined by dissociation and relative stability of the anion X. From the results of conductivity

Scheme 2



Scheme 3



measurements, the difference in the polymerizability of **2** and **3** from **1** may be explained in the terms of resonance theory: the anion of 4- or 2-pyridinoxide is more resonance stabilized than 3-pyridinoxide or phenoxide analogues due to the negative charge delocalized by the 2- and 4-positioned nitrogen atom (Scheme 3), which are reflected by their pK_a values of 2-hydroxypyridine (1.25), 4-hydroxypyridine (3.23), 3-hydroxypyridine (4.80), and phenol (9.99).[27] Thus, the anion stability of the substituent of the phosphazene trimer seems to play a critical role in the polymerization of the substituted phosphazene trimer.

In conclusion, among the fully substituted trimers, 4-pyridinoxy (**2**)- and 2-pyridinoxy (**3**)-substituted trimeric isomers easily undergo ring-opening polymerization while the 3-pyridinoxy-substituted trimer (**1**) does not, although the three pyridinoxy-substituted trimers have the similar phosphazene ring structure without ring strain. Such a difference in polymerizability of these trimeric isomers, therefore, seems to be ascribed to a purely electronic difference, which may be explicable in terms of the resonance theory of the substituents. Furthermore, it has been found that polymerizability of the substituted trimers is closely related to their thermal properties and can be predicted from their DSC analysis: appearance and the temperature range of an exothermic peak are indicative of polymerizability and polymerization temperature range of the trimers.

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Supporting Information Available: For **1**, tables of details of crystallographic data, atomic coordinates, and equivalent isotropic displacement parameters, selected bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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