

It is likely that the diimine complex prepared in this work has a N-racemic conformation.

In conclusion, the oxidative dehydrogenation of $[\text{Ni}(\text{A})]^{2+}$ in the presence of nitric acid produces the N-racemic isomer of $[\text{Ni}(\text{B})]^{2+}$. This work shows that the axial coordination of the hydroxyl group in the complex $[\text{Ni}(\text{A})]^{2+}$ makes the oxidation to the nickel(III) state easier and then accelerates the reaction. Most interestingly, the hydroxyl groups of the unsaturated complex $[\text{Ni}(\text{B})]^{2+}$ are not involved in coordination.

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Melt Polymerization of Hexachlorocyclotriphosphazene in the Presence of Aluminum Trichloride and Diethyltin(IV) Dichloride

Yangha Cho, Hyounggee Baek, Ok-Sang Jung, Moo-Jin Jun[†], and Youn Soo Sohn*

*Inorganic Chemistry Laboratory,
Korea Institute of Science and Technology,
Seoul 136-791, Korea*

[†]*Department of Chemistry, Yonsei University,
Seoul 120-749, Korea*

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It is well known that the thermal polymerization of hexachlorocyclotriphosphazene is very sensitive to impurities of reactant and reaction conditions,¹⁻³ and thus the yield of the linear polyphosphazene and gel formation by cross-linking are unpredictable. Thermal polymerization of hexachlorocyclotriphosphazene is usually stopped when the melted reactant ceases to flow, since cross-linking reaction is accelerated beyond this point.² In fact, when polymerization of purified hexachlorocyclotriphosphazene at 250 °C was stopped after 11 h where the reactant ceased to flow, approximately 40% yield of the linear polymer was obtained without gel formation, but extension of the reaction time to 15 h lowered the yield of the linear polymer to 11% with cross-linked gel formation up to more than half of the reactant.⁴ To overcome this drawback, various kinds of Lewis acid catalysts were reported to improve both production yield and reaction time, but most catalytic polymerizations result in lower molecular weight polymers.⁵⁻¹²

In our previous report, organotin(IV) chlorides were shown to act as inhibitor delaying remarkably the rate of polymerization with prominent improvements in both the molecular weight and the yield of the linear polymer in contrast to most Lewis acids.⁴ On the other hand, using excess amounts (>2 wt.%) of aluminum trichloride as catalyst, low molecular weight poly(dichlorophosphazene) ($M_w = 10^4$ - 10^5) was easily prepared in almost quantitative yield.¹³

Herein we report high conversion of hexachlorocyclotriphosphazene to high molecular weight polymers in the presence of mixed catalysts of aluminum trichloride and diethyltin(IV) dichloride.

Experimental

Materials. Hexachlorocyclotriphosphazene, $(\text{NPCl}_2)_3$ pur-

chased from Aldrich was used after purification by sublimation at 55 °C under vacuum (~0.1 mmHg). Diethyltin(IV) dichloride and aluminum trichloride were purchased from Alfa and Aldrich, respectively. Trifluoroethanol from Aldrich was dried over molecular sieves just before use. Solvents such as benzene and tetrahydrofuran were dried before use by refluxing over sodium-benzophenone and calcium hydride, followed by distillation.

Measurements. IR spectra were recorded on an Analyt FX-6160 FT-IR spectrophotometer in thin film between KBr disks. ¹H- and ³¹P NMR spectra were measured using Varian Gemini 300 spectrometer operating at 300.00 MHz (¹H) and 121.44 MHz (³¹P) in pulse mode with Fourier transform. The chemical shifts were relative to SiMe₄ (¹H) and triphenylphosphate (³¹P) as internal and external references, respectively, for the indicated nuclei. Viscosity measurements were made with a Cannon-Ubbelohde type 526 viscometer at 30 °C (±0.1°) using acetone containing 0.1% *n*-Bu₄NBr. Molecular weight was determined by using a Waters Model 590 gel permeation chromatograph equipped with a Waters 410 differential refractometer. The samples were eluted with a tetrahydrofuran solution containing 0.1% *n*-Bu₄NBr through two Waters ultrastaygel linear columns. Sample concentrations were approximately 0.5% by weight, a typical injection volume being 100 μL, and a flow rate of 1.2 mL/min was used. Molecular weight calibration was performed by using polystyrene standards with narrow molecular weight distribution (Waters Associates). The weight-average (\bar{M}_w) and number-average (\bar{M}_n) molecular weights were calculated by using the Waters Maxima 820 data analysis system. Thermogravimetric analysis was performed using a Perkin-Elmer TGA-2 with a heating rate of 20 °C/min. Elemental analyses were performed at the Chemical Analysis Center at KIST.

Polymerization of (NPCl₂)₃. Pyrex glass tubes (23 mm o.d. and 10 cm length) were soaked for 24 h in chromic acid solution, followed by washing more than 10 times with distilled water and then drying at 140 °C. The dried tube was attached to a vacuum line, evacuated, and then flamed out. The cooled tube was loaded in a dry box filled with argon gas with the trimer (5.0 g, 14.4 mmol) and appropriate amounts of aluminum trichloride and diethyltin dichloride as mixed catalysts. The tube was evacuated for 1 h under ice bath and then sealed under vacuum. The sealed tube was heated at the required temperature in a specially designed reaction oven in which a metal axle holding the tubes was rotating with 1 rpm to stir the melted reactant. After polymerization was carried out for a desired time period, the tube was cooled and then moved to the dry box. The

Table 1. Melt Polymerizations of (NPCl₂)₃ in the Presence of 0.2 wt.% AlCl₃

Temperature °C	Time h	Yield %	[η]* dl/g
230	15	78	0.42
240	8	85	0.72
250	4	85	0.61

*Intrinsic viscosity measured in acetone containing 0.1% *n*-Bu₄NBr.

Table 2. Yields of Polydichlorophosphazenes Depending on the Amounts of Catalysts at 240 °C

Time h	Blank ^a	0.2% AlCl ₃	0.2% AlCl ₃ + 0.2% Et ₂ SnCl ₂	0.2% AlCl ₃ + 0.4% Et ₂ SnCl ₂	0.2% AlCl ₃ + 1.0% Et ₂ SnCl ₂
4	25	72	73	84	75
5	30	75	75	84	84
6	28	82	86	85	85
7	CL ^b	85	88	92	92
8	CL	85	85	93	93
9	CL	CL	CL	CL	95

^aMelt polymerized without catalyst at 255 °C. ^bCL: cross-linked.

tube was broken and the entire reaction mixture was dissolved in benzene and then subjected to a substitution reaction with sodium trifluoroethoxide for characterization.

[NP(OCH₂CF₃)₂]_n. Poly(dichlorophosphazene) was converted to the trifluoroethoxide derivative by the literature procedure.¹ The derivatized product obtained from the acetone/*n*-hexane solvent pair was reprecipitated twice from acetone into benzene. Anal. calcd for a typical polyphosphazene [NP(OCH₂CF₃)₂]_n: C, 19.77; H, 1.66; N, 5.76; P, 12.74; F, 46.90. Found: C, 19.80; H, 1.62; N, 5.75; P, 13.00; F, 46.8. ³¹P NMR (acetone-d₆): 11.7 ppm.

Results and Discussion

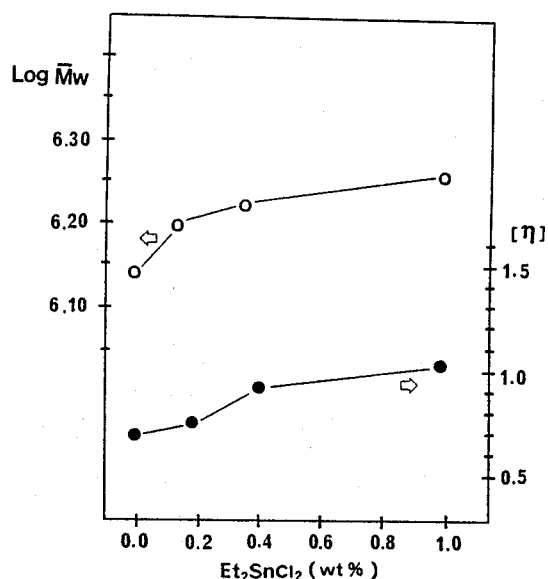
In order to optimize the reaction temperature in the presence of a catalytic amount of aluminum trichloride (0.2 wt.% of hexachlorocyclotriphosphazene), polymerization reactions were attempted at various temperatures around 240 °C, which has been known as the general temperature range in the polymerization (Table 1). The reaction at 240 °C was found to be suitable for the polymerization in view of the yield and viscosity of the resultant polymers. Thus melt polymerizations of hexachlorocyclotriphosphazene were performed at this temperature with changing amounts of diethyltin dichloride in addition to a constant amount of aluminum trichloride (0.2%) as well as with variation of the reaction time (4-9 h). Table 2 lists yields of the polymer products depending on the content of diethyltin dichloride and the reaction time. It is seen in the table that the polymer yield is considerably improved as the reaction time increases at this reaction temperature regardless of the combination of the catalysts, but cross-linking starts beyond the reaction time of 5 or 6 h in the presence of no or low content (<0.2%) of diethyltin dichloride. However, larger content (>0.4%) of diethyltin dichloride seems to delay cross-linking reaction resulting in higher polymer yield. As a matter of fact, extending the reaction time beyond 9 h the reactants containing no or small amounts of diethyltin dichloride became mostly cross-linked gel, but in the presence of larger amount (>1.0%) of diethyltin dichloride no cross-linking reaction was observed leading to almost quantitative conversion of the phosphazene trimer to the polymer.

Furthermore, the molecular weight and thermal stability of the polymers listed in Table 3 exhibit that the polymers prepared in the presence of diethyltin dichloride have equivalent or even higher molecular weights ($\bar{M}_w > 10^6$) and cor-

Table 3. Molecular Weights and Thermal Properties of Polydichlorophosphazene^a Depending on the Amounts of Catalysts

Catalysts	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n	T_{10}^b (°C)
Blank ^c	167	34	4.9	395
0.2% AlCl ₃	138	43	3.2	388
0.2% AlCl ₃ +	162	48	3.4	391
0.2% Et ₂ SnCl ₂				
0.2% AlCl ₃ +	164	43	3.8	395
0.4% Et ₂ SnCl ₂				
0.2% AlCl ₃ +	183	44	4.2	400
1.0% Et ₂ SnCl ₂				

^aMelt polymerized at 240 °C for 7 h. ^bT₁₀: Temperature of 10% degradation from TGA. ^cMelt polymerized without catalyst at 255 °C for 5 h.

**Figure 1.** Molecular weights and intrinsic viscosities of polyphosphazenes depending on the contents of Et₂SnCl₂.

responding thermal stability compared with the blank polymer prepared without catalyst. Also, all the chromatograms of the polymers formed in the presence of the catalysts have shown a monomodal and narrow molecular weight distribution in contrast to the well-known bimodal molecular weight distribution of the blank polymer. Figure 1 shows that the molecular weight and the intrinsic viscosity of the polymers are slightly increasing as the content of diethyltin dichloride increases.

Organotin(IV) compounds have already been demonstrated by the authors to act as a negative catalyst by inhibiting effectively the cross-linking reactions during the thermal polymerization reaction of the phosphazene trimers.⁴ It is generally known that Lewis acids such as boron and aluminum trihalides acting as initiation catalyst for ring-opening polymerization of the phosphazene trimer accelerate the polymerization reaction, but beyond a certain degree of polymerization cross-linking reaction is also induced resulting in limited product yields.^{5,11} However, addition of a relatively large amount of diethyltin dichloride seems to inhibit such a cross-

linking reaction allowing the chain-growing reaction to proceed for a enough period of time until high molecular weight is attained.

In conclusion, the catalytic melt polymerization of the phosphazene trimer using a combined catalytic system of aluminum trichloride and diethyltin dichloride affords high molecular weight poly(dichlorophosphazene) ($\bar{M}_w > 10^6$) in high yield (>90%). The molecular weights of the polymers are approximately proportional to the content of diethyltin dichloride in the catalytic system.

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Deoxygenation and Decomposition of Cyclic Ethers by Molybdenum Atoms

Sock Sung Yun*, Seung Ho Yeon, Yun Dong Choi†, and In Soon Chang†

Department of Chemistry,
Chungnam National University,
Taejon 305-764, Korea

†Korea Advanced Energy Research Institute,
Taejon 305-353, Korea

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Metal atoms have been utilized to effect insertion of a metal atom into carbon-hydrogen^{1,2} and carbon-carbon bonds.¹ The reactivity of metal atoms has also been studied for