# Studies on the mechanism of phosphazene ring-opening polymerization (ROP)

**Selen BİLGE**

*Ankara University, Faculty of Science, Department of Chemistry,*
*06100 Tandoğan, Ankara-TURKEY*
*e-mail: sbilge@science.ankara.edu.tr*

In this study, the ring-opening polymerization (ROP) of cyclic trimer $N_3P_3Cl_6$ catalyzed by $[Et_3Si(N_3P_3Cl_6)][CHB_{11}H_5Br_6]$ (**3**) obtained from the reaction of $N_3P_3Cl_6$ (**1**) and $Et_3Si(CHB_{11}H_5Br_6)$ (**2**) at room temperature was investigated. This provided a unique opportunity to explore the polymerization mechanism. The coordinatively unsaturated cation $[N_3P_3Cl_5]^+$ is responsible for the ROP of $N_3P_3Cl_6$, and is formed by the intramolecular elimination of $Et_3SiCl$ from **3**. The detection of $Et_3SiCl$ by ^{1}H-NMR as the catalysis proceeded offers new evidence for the formation of $[N_3P_3Cl_5]^+$. The progress of the catalysis was followed using ^{31}P-NMR and revealed the build-up of a polymer. Cyclic phosphazenes with rings larger than that of $N_3P_3Cl_6$ $[(Cl_2P=N)_n$ (n = 4-7)] were observed fairly early in the course of the ROP. The propagation of that polymerization at room temperature proceeded via a living cationic mechanism.

**Key Words:** ROP, polyphosphazenes, carboranes, spectroscopy

## Introduction

The term "polyorganophosphazenes" refers to an important class of polymers used in a wide range of alternative industrial applications in such areas as flame retardants,[1] high performance elastomers,[2] rechargeable lithium batteries,[3] and biomedical materials, including synthetic bones,[4] biomedical membranes,[5] and polymer electrolytes.[6] The general structure of polyorganophosphazenes, $[R_2P=N]_n$, includes an inorganic backbone formed by nitrogen and phosphorus atoms and 2 side groups (R), such as alkoxy,[7] aryloxy,[8] alkyl,[9] aryl,[10] amine,[11] carboranyl,[12] metallocenyl,[13]$\eta^6$-arenyl,[14] and organosilicon[15] groups, attached to each phosphorus atom. Through the variation of the side groups, polyorganophosphazenes can be tailor-made to meet a variety of functional needs. The scientific interest in poly(dichlorophosphazene) $[Cl_2P=N]_n$ originated with the synthesis of a rubbery crosslinked polymer by Stokes in 1897 by heating cyclic trimer $[(Cl_2P=N)_3, N_3P_3Cl_6]$ at high

temperatures.[16] This polymer received little interest over the next 60 years, probably due to its insolubility in all solvents and its sensitivity to hydrolysis. Moreover, the hydrolysis of the polymer released phosphate, ammonia, and hydrochloric acid when the polymer was exposed to the atmosphere. In 1965, Allcock et al. obtained the first soluble linear poly(dichlorophosphazene), i.e., a precursor polymer, using the thermal ring-opening polymerization (ROP) when melting highly purified $N_3P_3Cl_6$ at 250 °C in a sealed evacuated glass tube; additionally, polyorganophosphazenes were synthesized via chlorine substitution from poly(dichlorophosphazene) with nucleophiles.[11,17,18] Since then, subsequent developments using the thermal ROP and several other synthetic routes have yielded more than 700 different polyorganophosphazenes with different side groups and skeletal architectures, resulting in an extensive range of physical and chemical properties.[19−24] However, the thermal ROP of cyclic trimers is still the most widely used synthetic approach. This process must be terminated before an approximately 70% conversion of the cyclic trimer to yield an uncrosslinked and soluble poly(dichlorophosphazene). Only further heating of the poly(dichlorophosphazene) rapidly causes crosslinks to create the insoluble inorganic rubber. Therefore, isolated yields of the soluble polymer are often 40%.[23] Certain Lewis acids, such as $BCl_3$[25] or $AlCl_3$,[26] catalyze the thermal ROP, allowing the process temperature to be reduced to approximately 200 °C. A typical uncatalyzed or catalyzed ROP at high temperatures provides no appreciable molecular weight control and produces high molecular weight polymers with a broad molecular weight distribution.[27−29] The difficulties and drawbacks associated with performing ROP of a cyclic trimer either with or without a catalyst at high temperatures should be investigated and compared to that of the reaction at ambient temperatures. The first ambient temperature ROP of a cyclic trimer using initiators $[R_3Si(N_3P_3Cl_6)][HCB_{11}R_5X_6]$ based on carborane anions $\{[HCB_{11}R_5X_6]^-$, R=H, Me, Cl; X=Cl, Br; R=Me, Et$\}$ and N-silylated phosphazene cations $\{[R_3Si(N_3P_3Cl_6)]^+$, R=Me, Et$\}$[30] was recently reported by Reed and Manners.[31] This approach is an important method in the sense that polymerization takes place at ambient temperatures via a living polymerization mechanism that allows for the control of the molecular weight of the polymer; moreover, the chain transfer and chain termination steps lead to polymers with narrow polydispersity.[31] The ROP reaction has been extensively studied, and several mechanisms have been proposed as being radical,[32] anionic,[33] or cationic.[23,34,35] This article describes an endeavor to elucidate the mechanism of this new ROP of cyclic trimer $N_3P_3Cl_6$ catalyzed by $[Et_3Si(N_3P_3Cl_6)][HCB_{11}H_5Br_6]$ (**3**) obtained from the reaction of $N_3P_3Cl_6$ (**1**) and $Et_3Si(CHB_{11}H_5Br_6)$ (**2**) at room temperature (Scheme 1). The ring-opening mechanism is discussed using information obtained from $^1$H- and $^{31}$P-NMR studies.

## Experimental

**General:** All of the ROP experiments were carried out in a glovebox from Vacuum Atmospheres Company ($O_2$, $H_2O$ < 2 ppm), and air sensitive solids were handled in the glovebox. All of the reactions outside of the glovebox were done in Schlenk tubes with Teflon stopcocks. The solvents were purchased from Acros and dried following procedures detailed in the literature,[36] distilled under argon, and stored over 4-Å molecular sieves in the glovebox. All carborane reagents used in the experiments were freshly prepared. Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (Aldrich, 99.99%), was further purified via sublimation. The sublimation was carried out on a high vacuum line at approximately 60 °C. The sublimate was collected in the glovebox and stored in an amber vial in the glovebox until it was used. $^1$H- and $^{31}$P-NMR spectra were recorded on a Bruker AVANCE
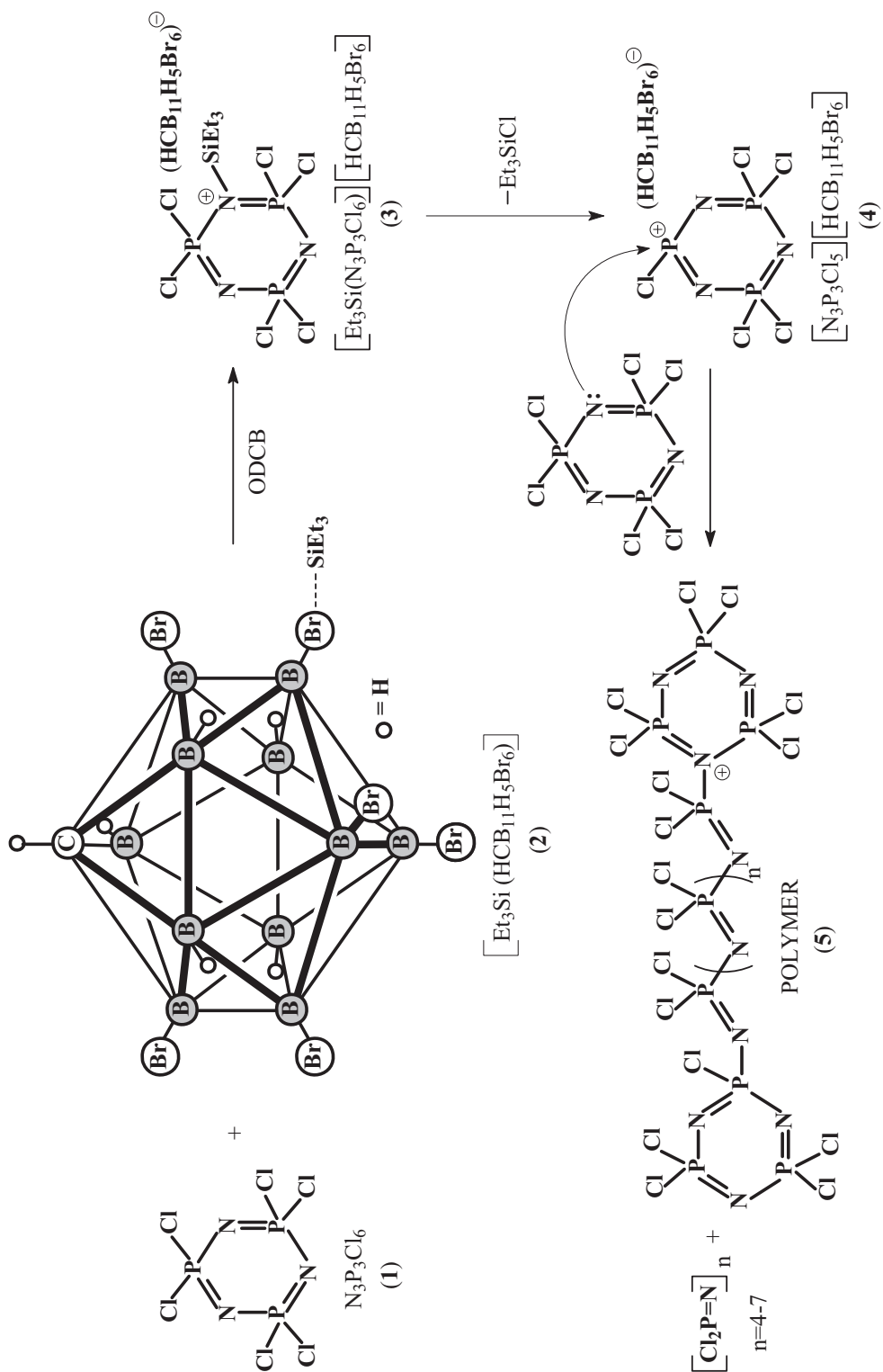
**Scheme 1.**

600 NMR spectrometer. All NMR experiments were performed in *o*-dichlorobenzene (ODCB).

**Triethylsilylcarborane [Et$_3$Si(CHB$_{11}$H$_5$Br$_6$)] (2):** Prepared by literature procedure.[37]

**N-silylated phosphazene precatalyst [Et$_3$Si(N$_3$P$_3$Cl$_6$)][CHB$_{11}$H$_5$Br$_6$] (3):** Synthesized by treating N$_3$P$_3$Cl$_6$ (**1**) with the freshly prepared and strongly electrophilic silyl carborane reagent Et$_3$Si(HCB$_{11}$H$_5$Br$_6$) (**2**) in dry ODCB according to the literature method.[30]

**Ambient-temperature ROP reactions:** Performed by using 5 equivalents of N$_3$P$_3$Cl$_6$ (**1**) (157 mg, 0.45 mmol) and 1 equivalent of [Et$_3$Si(N$_3$P$_3$Cl$_6$)][CHB$_{11}$H$_5$Br$_6$] (**3**) (98 mg, 0.09 mmol) dissolved in 1.0-M and 0.5-M concentrations of N$_3$P$_3$Cl$_6$ (**1**) with 0.5 mL and 1.0 mL, respectively, of dry ODCB, and 3 equivalents of **1** (104 mg, 0.30 mmol) and 1 equivalent of **3** (108 mg, 0.10 mmol) dissolved in a 1-M concentration of **1** with 0.3 mL of dry ODCB at room temperature in an inert-atmosphere dry box (Scheme 1). The solution was magnetically stirred, and the formation of the polymer (**5**) was monitored by $^{31}$P{$^1$H}-NMR spectroscopy at 242.94 MHz at 30-min intervals in an NMR tube (Figure 1). The conversion percentage was plotted against polymerization time (Figure 2). The $^1$H-NMR spectra of Et$_3$SiCl, precatalyst **3**, and the polymer mixture in ODCB were also recorded at 600.13 MHz to show the formation of Et$_3$SiCl in the ROP (Figure 3).
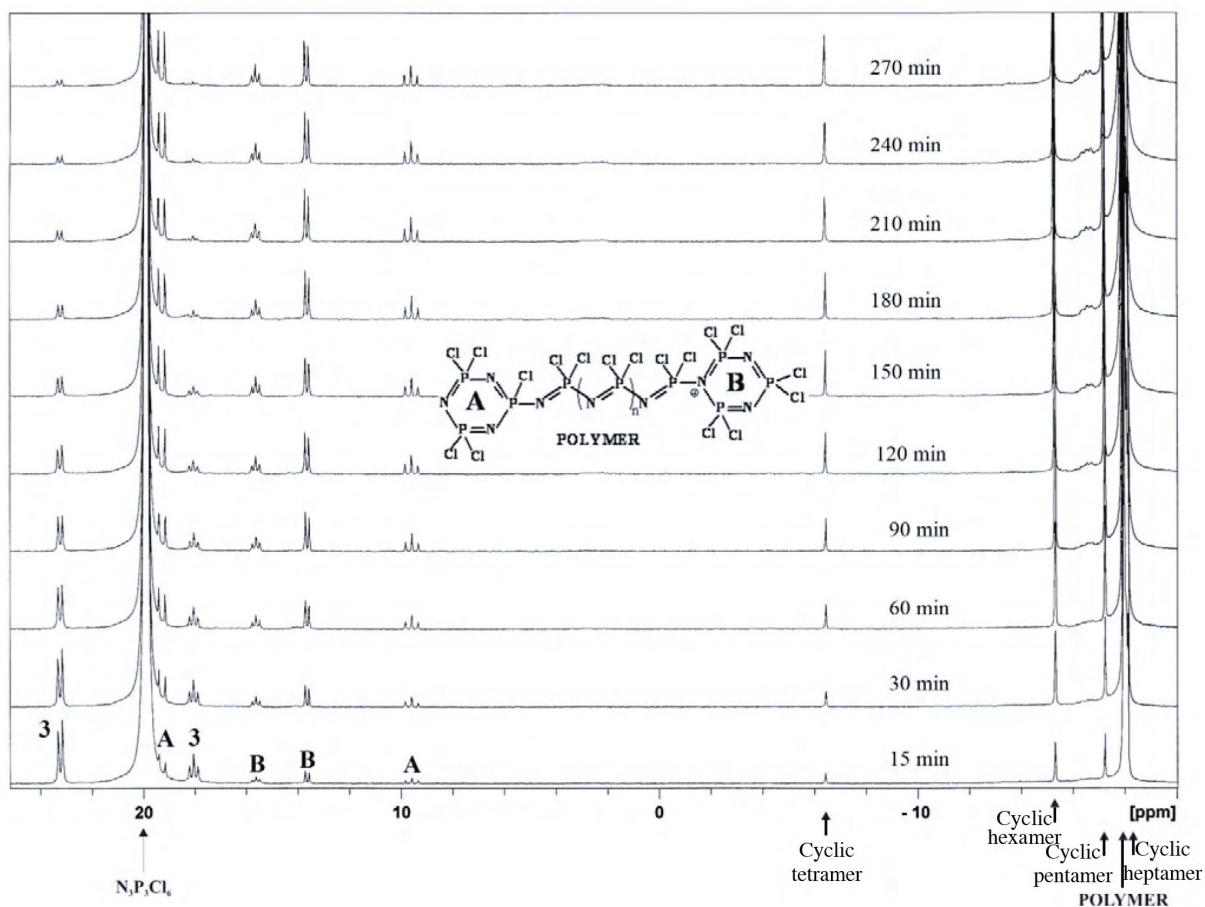


**Figure 1.** $^{31}$P-NMR spectra with the reaction monitored for 270 min at 30-min intervals, showing the progress (from bottom to top) of polymerization of 1 M of N$_3$P$_3$Cl$_6$ in ODCB catalyzed by **3** in the NMR tube.

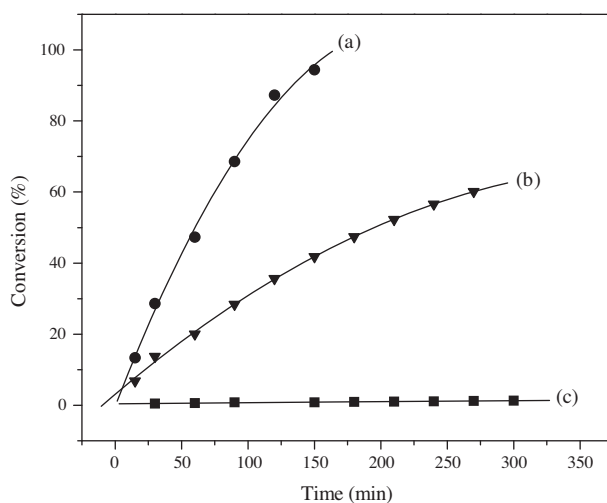**Figure 2.** Plot of polymer conversion (%) according to $N_3P_3Cl_6$ versus time for the reaction of 1 equivalent of precatalyst **3** with (a) 3 equivalents and (b) 5 equivalents of $N_3P_3Cl_6$ dissolved in a 1-M concentration of $N_3P_3Cl_6$ with ODCB, and (c) 5 equivalents of $N_3P_3Cl_6$ dissolved in a 0.5-M concentration of $N_3P_3Cl_6$ with ODCB. These are ^{31}P-NMR data with the reaction monitored with samples taken at 30-min intervals in the NMR tube at room temperature.

# Results and discussion

Although the mechanism of the ROP is still not clearly understood, 2 different mechanisms for the ROP of $N_3P_3Cl_6$ were proposed by Emsley[38] and Allcock[19,23] (Scheme 2). In Emsley's mechanism (Scheme 2a),[38] the nitrogen on $N_3P_3Cl_6$ gets protonated in the first step. The protonation weakens and breaks the bond between the nitrogen and a neighboring phosphorous, which opens the ring, leaving the lone pair of electrons on the nitrogen and creating a phosphazenium cation. The lone pair on the nitrogen attacks a phosphorous on another $N_3P_3Cl_6$, thereby starting the polymerization. On the other hand, the mechanism proposed by Allcock (Scheme 2b)[19,23] is the more commonly accepted mechanism, speculating that the ROP of $N_3P_3Cl_6$ proceeds through cationic intermediates. The initiating step in this cationic mechanism is the heterolytic dissociation of the phosphorus-chloride bond to form coordinatively unsaturated and highly reactive phosphazenium cation $[N_3P_3Cl_5]^+$. This step could be achieved by heating $N_3P_3Cl_6$ at 250 °C or with Lewis acids, which could act as a chloride abstractor (Scheme 2b). Propagation occurs via an electrophilic attack of $[N_3P_3Cl_5]^+$ by another molecule of $N_3P_3Cl_6$ to produce a cationic cyclolinear species, which can subsequently be attached to another molecule of $N_3P_3Cl_6$, thereby resulting in continued chain propagation. This hypothesis is supported by a synthesis route of poly(dichlorophosphazene) $[Cl_2P=N]_n$ in which the addition of Lewis acids, such as $BCl_3$[25] or $AlCl_3$,[26] reduces the ROP temperature to approximately 200 °C as compared to the uncatalyzed ROP temperature of 250 °C. Therefore, we must understand the interaction of $N_3P_3Cl_6$ with Lewis acids. Presumably, coordinatively unsaturated phosphazenium cation $[N_3P_3Cl_5]^+$ acts as the key intermediate in the ROP. The nitrogen atoms on $N_3P_3Cl_6$ are very poor bases ($pK_a = -6$ in nitrobenzene),[39] and very strong Lewis or Bronsted acids are needed to abstract a chloride ion or to achieve either protonation or coordination.[40−43]

Therefore, the isolation of the $[N_3P_3Cl_5]^+$ cation from $N_3P_3Cl_6$ is very important in phosphazene polymer chemistry. Various attempts have been made to abstract a chloride ion from $N_3P_3Cl_6$ to generate and isolate $[N_3P_3Cl_5]^+$ and also to prove the existence of $[N_3P_3Cl_5]^+$ through the reaction of **1** with a variety of chloride acceptors.[40−43] To date, however, no direct evidence for the coordinatively unsaturated phosphazenium cation $[N_3P_3Cl_5]^+$ has been described in the literature.
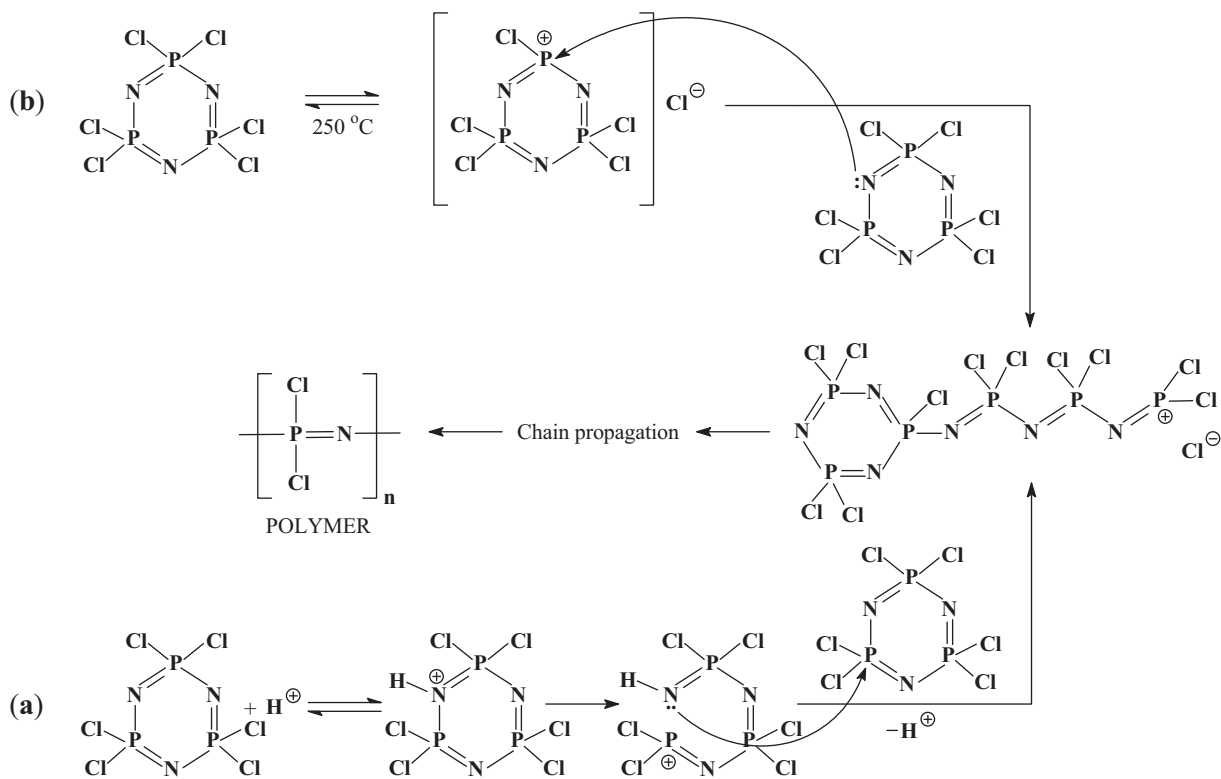


**Scheme 2.**

Owing to the fact that the icosahedral $CB_{11}$ carborane anions are among the least coordinating and the most inert anions to allow the isolation of coordinatively unsaturated cations, some have thought that these anions have a highly electrophilic character as developed in Reed's laboratory,[30] which may solve the problem. Manners and Reed recently investigated strong electrophilic silyl carborane reagents $\{[R_3Si(N_3P_3Cl_6)][HCB_{11}R_5X_6]$ R=H, Me, Cl; X=Cl, Br; R=Me, Et$\}$[30] for the ROP of $N_3P_3Cl_6$.[31] They found that the N-silylated phosphazene cation $[Et_3Si(N_3P_3Cl_6)]^+$ that is stabilized with a carborane counteranion, $[HCB_{11}H_5Br_6]^-$, is a very effective catalyst for the ROP reaction of $N_3P_3Cl_6$ at room temperature.[31] In this article, the N-silylated phosphazene precatalyst, $[Et_3Si(N_3P_3Cl_6)][CHB_{11}H_5Br_6]$ (**3**), was prepared by treating $N_3P_3Cl_6$ (**1**) with the silyl carborane reagent $Et_3Si(HCB_{11}H_5Br_6)$ (**2**)[37] in ODCB according to the literature method[30] and was used for the ROP of $N_3P_3Cl_6$ at room temperature.

All of the experimental observations that were obtained from the NMR results were used to better understand the polymerization mechanism and characterize the intermediate $[N_3P_3Cl_5]^+$. $[Et_3Si(N_3P_3Cl_6)][CHB_{11}H_5Br_6]$ (**3**) is a soluble homogenous catalyst at room temperature for the ROP reaction of $N_3P_3Cl_6$, so following the kinetic progress of the polymerization with NMR spectroscopy is very useful. Over the course of time,

the formation of the polymer was monitored by proton-decoupled $^{31}$P-NMR [$^{31}$P{$^{1}$H}] at 30-min intervals, and shortly after the beginning of the reaction, the polymerization had just started. The $^{31}$P-NMR signals that were recorded for each polymerization experiment are the same in terms of both chemical shift values and signal patterns. Therefore, the $^{31}$P-NMR spectra obtained from the reaction between 5 equivalents of $N_3P_3Cl_6$ and 1 equivalent of precatalyst **3** dissolved in a 1-M concentration of $N_3P_3Cl_6$ with ODCB are given as an example in Figure 1. All of the signals were labeled in the $^{31}$P-NMR spectra. The $N_3P_3Cl_6$ monomer showed up at $\delta$P = 19.9 ppm, and its corresponding polymer (**5**) appeared as a large signal at $\delta$P = –17.9 ppm. The reported $^{31}$P-NMR data for $N_3P_3Cl_6$ and its polymer are in accordance with the corresponding values obtained from the thermal ROP reactions in the literature.[11,17,18] On the other hand, the doublet and triplet at $\delta$P = 18.04 and 23.35 ppm ($^2J_{PP}$ = 39.4 Hz), respectively, correspond to the precatalyst (**3**). As can be seen from Figure 1, while the intensities of the signal for precatalyst **3** and $N_3P_3Cl_6$ decrease as the reaction proceeds, the intensity of the signal increases for the polymer (**5**). Moreover, 2 new sets of triplets and doublets with equal integration grow. They can possibly be assigned to unsymmetrical phosphazene rings (marked **A** and **B**) at either end of the growing polymer chains (Figure 1). While the doublet and triplet of ring **A** appeared at $\delta$P = 18.7 and 9.0 ppm ($^2J_{PP}$ = 59.8 Hz), respectively, the doublet and triplet of ring **B** were observed at $\delta$P = 13.5 and 16.3 ppm ($^2J_{PP}$ = 36.2 Hz), respectively. Furthermore, the peaks between $\delta$P = –7.0 and –18.7 ppm, with the exception of that at –17.9 ppm, support of the existence of cyclic phosphazenes with rings larger than that of the $N_3P_3Cl_6$, the cyclic tetramer [$(PCl_2=N)_4$, $\delta$P = –7.0 ppm], the cyclic pentamer [$(PCl_2=N)_5$, $\delta$P = –17.8 ppm], the cyclic hexamer [$(PCl_2=N)_6$, $\delta$P = –15.8 ppm], and the cyclic heptamer [$(PCl_2=N)_7$, $\delta$P = –18.7 ppm]. These higher-molecular-weight cyclic species are observed fairly early in the time course of the ROP, and the signals of these species increase with time. Similar cyclic compounds are formed in addition to poly(dichlorophosphazene) in the thermal polymerization of $N_3P_3Cl_6$ when melting at 250 °C.[19]

The conversion percentage of $N_3P_3Cl_6$ to the polymer was calculated from the following equation: [integral polymer/(integral $N_3P_3Cl_6$ + integral polymer)] × 100. Additionally, the conversion percentage for $N_3P_3Cl_6$ was plotted against polymerization time (Figure 2). When comparing the 1.0-M and 0.5-M concentrations of $N_3P_3Cl_6$ (Figure 2, lines b and c, respectively; and Table), the lower concentrations of $N_3P_3Cl_6$ led to the slow formation of the polymer as expected.

The nitrogen coordination rather than the chloride abstraction was obtained from the reaction of **1** and silyl carborane reagent **2**.[30] The resulting cation [$Et_3Si(N_3P_3Cl_6)$]$^+$ in precatalyst **3** is a potential precursor to coordinatively unsaturated cation [$N_3P_3Cl_5$]$^+$ and may provide an insight into the ROP of $N_3P_3Cl_6$. The suggested ROP mechanism of $N_3P_3Cl_6$ is given in Scheme 3. In the mechanism, polymerization is induced by [$N_3P_3Cl_5$]$^+$, which is responsible for the ROP of $N_3P_3Cl_6$ as the true catalyst. Therefore, the formation of $Et_3SiCl$ is required to initiate the ROP reaction. The triethylsilylation on a N atom provides coordinatively unsaturated intermediate [$N_3P_3Cl_5$]$^+$ via intramolecular elimination reaction of $Et_3SiCl$ from precatalyst **3**. The evidence for this intermolecular elimination comes from the $^1$H-NMR identification of free $Et_3SiCl$ in the reaction mixture as catalysis proceeds (Figure 3). The detection of $Et_3SiCl$ from the $^1$H-NMR is new evidence for the formation of coordinatively unsaturated cation [$N_3P_3Cl_5$]$^+$. A comparison of the $CH_3$ and $CH_2$ proton signals of $Et_3SiCl$, precatalyst **3**, and the polymer mixture in Figure 3 (lines a-c, respectively) shows that the $^1$H-NMR spectrum of the polymer mixture has $CH_2$ and $CH_3$ signals at $\delta$ = 0.81 and 1.06 ppm, respectively, belonging to free $Et_3SiCl$ produced in the reaction. Therefore, coordinatively unsaturated cation [$N_3P_3Cl_5$]$^+$

**Table.** The data of polymer conversion percentage according to $N_3P_3Cl_6$ versus time.*

| Time (min) | Conversion percentage of $N_3P_3Cl_6$ to polymer $[Et_3Si(N_3P_3Cl_6)][CHB_{11}H_5Br_6]$ (**3**) + x $N_3P_3Cl_6$ | | |
|---|---|---|---|
| | x = 5 | | x = 3 |
| | 1 M | 0.5 M | 1 M |
| 15 | 6.85 | - | 13.36 |
| 30 | 13.74 | 0.48 | 28.60 |
| 60 | 20.02 | 0.59 | 47.33 |
| 90 | 28.38 | 0.80 | 68.59 |
| 120 | 35.63 | - | 87.28 |
| 150 | 41.79 | 0.84 | 94.41 |
| 180 | 47.44 | 0.95 | - |
| 210 | 52.30 | 1.02 | - |
| 240 | 56.64 | 1.09 | - |
| 270 | 60.14 | 1.23 | - |
| 300 | - | 1.30 | - |

*The estimations were made using the integral ratio of the ^{31}P-NMR signals.
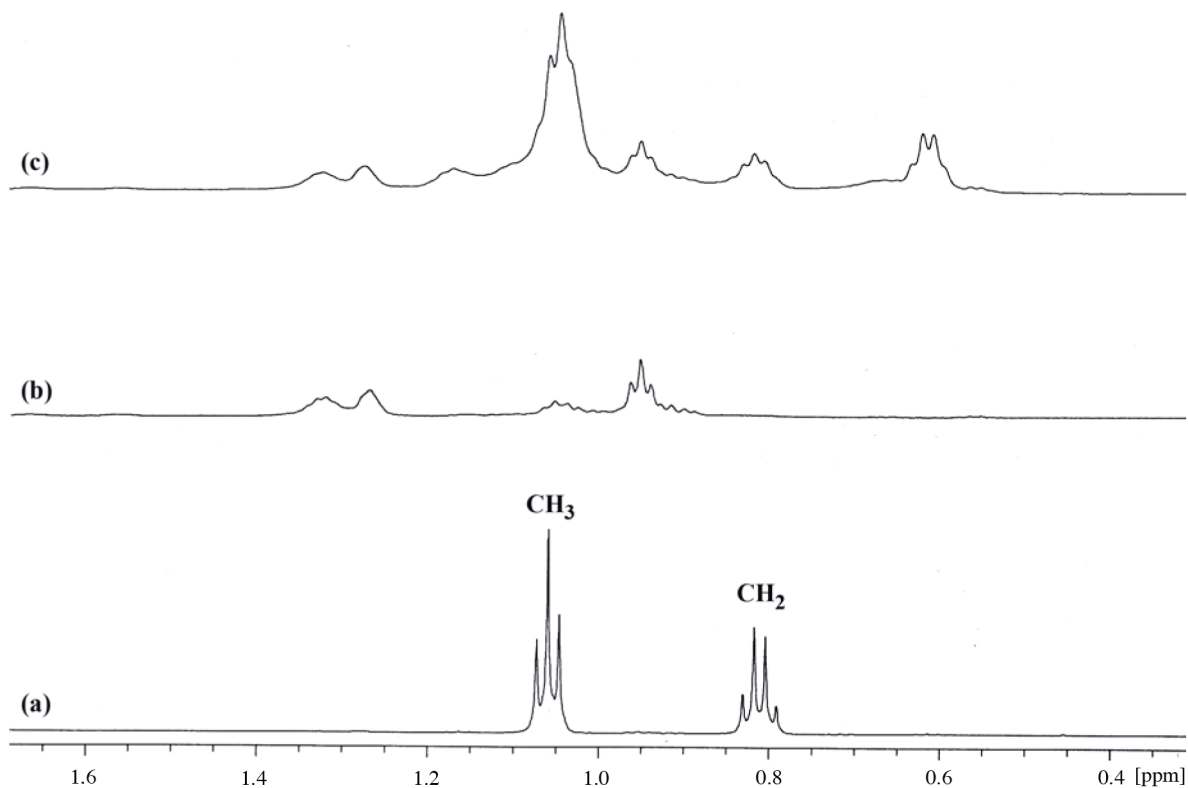


**Figure 3.** ^{1}H-NMR spectra of (a) $Et_3SiCl$, (b) precatalyst **3**, and (c) any polymer mixture in ODCB at room temperature.
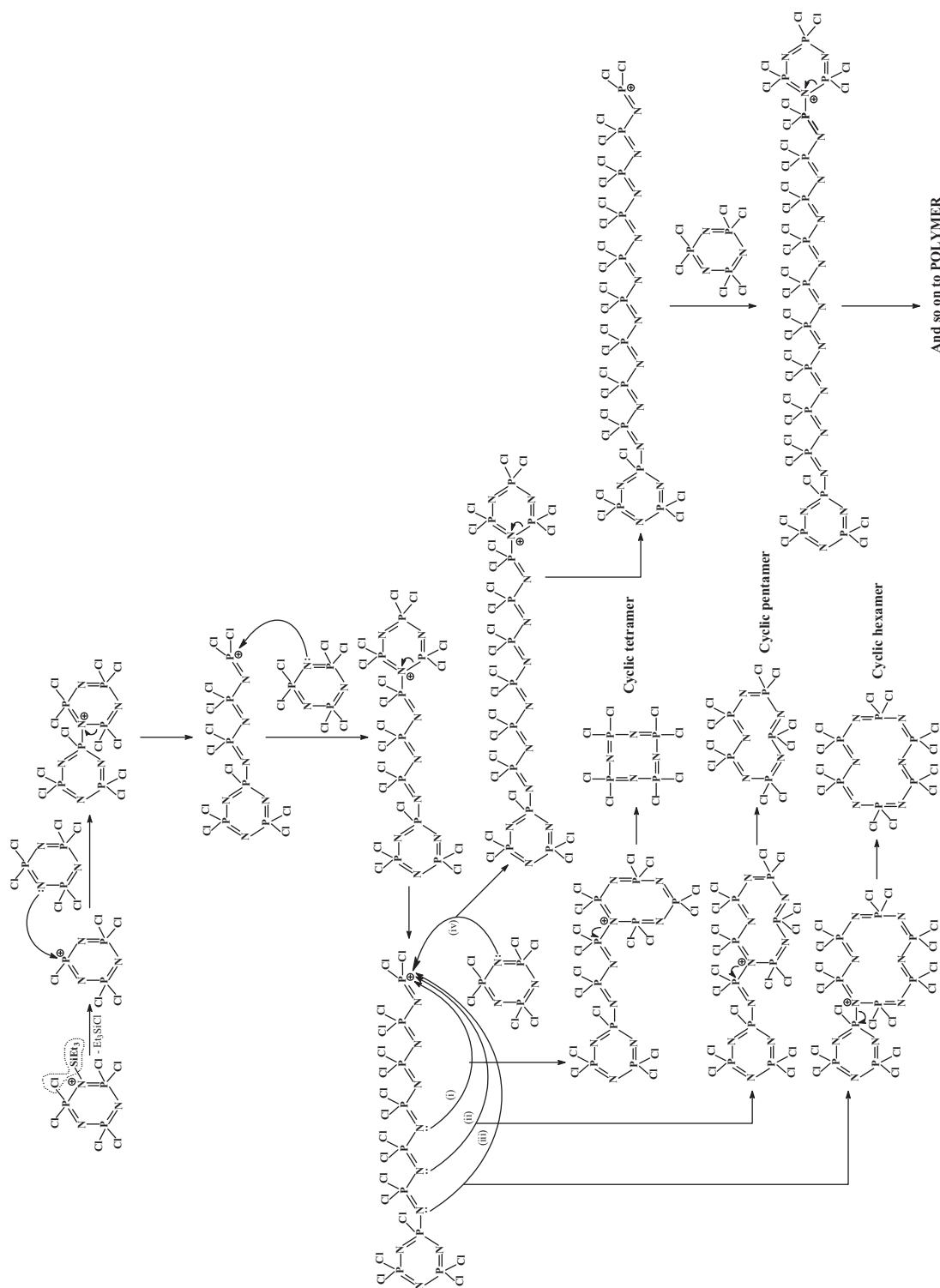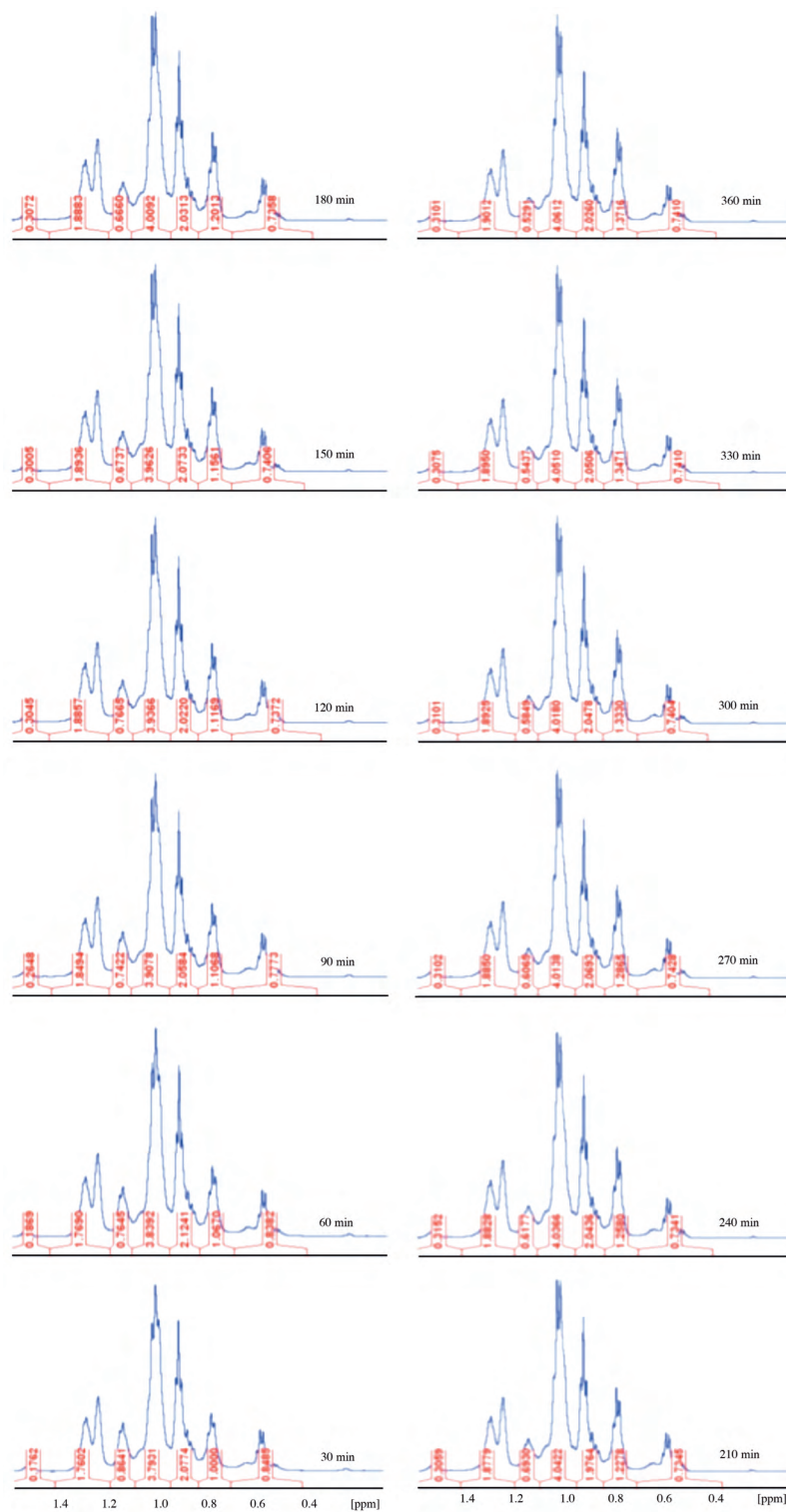
**Scheme 3.**

**Figure 4.** Signals at $\delta = 1.6\text{-}0.4$ ppm showing integral ratio of $CH_3$ and $CH_2$ proton signals.

in $[N_3P_3Cl_5][CHB_{11}H_5Br_6]$ (**4**) is most likely being produced in situ. Although there is no direct evidence of coordinatively unsaturated phosphazenium cation $[N_3P_3Cl_5]^+$, detection of $Et_3SiCl$ as a byproduct suggests the existence of the cation. The cation is a very reactive electrophile, so it is very difficult to discover the signal of the cation in $^{31}P$-NMR spectroscopy. In addition, the $^1H$-NMR spectrum of the reaction between 1 equivalent of precatalyst **3** and 5 equivalents of $N_3P_3Cl_6$ dissolved in a 0.5-M concentration of $N_3P_3Cl_6$ with ODCB was recorded and the signals were carefully examined between $\delta = 1.6$ and 0.4 ppm (Figure 4). This was used to see if integrations of the $CH_3$ and $CH_2$ proton signals of $Et_3SiCl$ became larger over the course of time. Growth of the integral ratio of the $CH_2$ and $CH_3$ proton signals of $Et_3SiCl$ for the polymer mixtures at $\delta = 0.81$ and 1.06 ppm, respectively, even once, confirms the formation of $Et_3SiCl$ under the ROP conditions by intramolecular elimination from precatalyst **3**, which also supports the formation of coordinatively unsaturated cation $[N_3P_3Cl_5]^+$.

On the other hand, the propagation step involves the coordinatively unsaturated cation $[N_3P_3Cl_5]^+$ acting as a cationic initiator by attacking the skeletal nitrogen atom of an $N_3P_3Cl_6$ molecule, inducing ring-opening and chain propagation by a cationic mechanism. This step cleaves the attacked $N_3P_3Cl_6$ and transfers the cationic charge to the terminal phosphorus. As a result, it is possible to see growing polymer chains and end-groups on the chains, and the polymerization study of $N_3P_3Cl_6$ in ODCB in the presence of **3** as a catalyst confirms that, at room temperature, the propagation in that polymerization proceeds via a living cationic mechanism.

# Acknowledgement

## References

1. Prange, R.; Reeves, S. D.; Allcock, H. R. *Macromolecules* **2000**, *33*, 5763-5765.

2. Allcock, H. R.; Napierala, M. E.; Cameron, C. G.; O'Connor, S. J. M. *Macromolecules* **1996**, *29*, 1951-1956.

3. Xu, G.; Lu, Q.; Yu, B.; Wen, L. *Solid State Ion.* **2006**, *177*, 305-309.

4. Greish, Y. E.; Bender, J. D.; Lakshmi, S.; Brown, P. W.; Allcock, H. R.; Laurencin, C. T. *Biomaterials* **2005**, *26*, 1-9.

5. Singh, A.; Krogman, N. R.; Sethurman, S.; Nair, L. S.; Sturgeon, J. L.; Brown, P. W.; Laurencin, C. T.; Allcock, H. R. *Biomacromolecules* **2006**, *7*, 914-918.

6. Langone, F.; Lora, S.; Veronese, F. M.; Caliceti, P.; Parnigotto, P. P.; Palma, G. *Biomaterials* **1995**, *16*, 347-353.

7. Bolonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854-6855.

8. Allcock, H. R.; Turner, M. L. *Macromolecules* **1993**, *26*, 3-10.

9. Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Macromolecules* **1979**, *12*, 1014-1015.

10. Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377-382.

11. Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716-1718.

12. Scopelianos, A. G.; O'Brien, J. P.; Allcock, H. R. *J. Chem. Soc. Chem. Commun.* **1980**, *4*, 198-199.

13. Allcock, H. R.; Riding, G. H.; Lavin, K. D. *Macromolecules* **1987**, *20*, 6-10.

14. Allcock, H. R.; Dembek, A. A.; Klingenberg, E. H. *Macromolecules* **1991**, *24*, 5208-5214.

15. Allcock, H. R.; Brennan, D. J. *J. Organomet. Chem.* **1988**, *341*, 231-239.

16. Stokes, H. N. *Am. Chem. J.* **1897**, *19*, 782-796.

17. Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965,** *87*, 4216-4217.

18. Allcock, H. R.; Kugel, R. L; Valen, K. J. *Inorg. Chem.* **1966,** *5*, 1709-1715.

19. Allcock, H. R. *Phosphorus-Nitrogen Compounds*, Academic Press, New York, 1972.

20. Gleria, M.; De Jaeger, R., Eds. *Phosphazenes: A Worldwide Insight*, Nova Science Publishers, Inc., New York, 2004.

21. Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*, 2nd ed., Oxford University Press, Inc., New York, 2005.

22. Blackstone, V.; Presa Soto, A.; Manners, I. *Dalton Trans.* **2008**, 1-9.

23. Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*, John Wiley & Sons, Inc., New Jersey, 2003.

24. Gleria, M.; De Jaeger, R. *Top. Curr. Chem.* **2005**, *250*, 165-251.

25. Sennett, M. S.; Hagnauer, G. L.; Singler, R. E.; Davis, G. *Macromolecules* **1986**, *19*, 959-964.

26. Sohn, Y. S.; Cho, Y. H.; Baek, H.; Jung, O. S. *Macromolecules* **1995**, *28*, 7566-7568.

27. Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541-562.

28. D'Halluin, G.; De Jaeger, R.; Chambrette, J. P.; Potin, P. *Macromolecules* **1992**, *25*, 1254-1258.

29. Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848-2849.

30. Zhang, Y.; Tham, F. S.; Reed, C. A. *Inorg. Chem.* **2006**, *45*, 10446-10448.

31. Zhang, Y.; Huynh, K.; Manners, I.; Reed, C. A. *Chem. Commun.* **2008**, 494-496.

32. Patat, F.; Kollinski, F. *Macromol. Chem. Phys.* **1951**, *6*, 292-317.

33. Gimblett, F. G. R. *J. Polym. Sci.* **1962**, *60*, S29-S31.

34. Allcock, H. R. *Polymer* **1980**, *21*, 673-683.

35. Gleria, M.; Audisio, G.; Daolio, S.; Tralde, P.; Vecchi, E. *Macromolecules* **1984**, *17*, 1230-1233.

36. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed., Pergamon Press Ltd., Sydney, 1980.

37. Reed, C. A.; Kim, K. C.; Stoyanov, E.; Stasko, D.; Tham, F. S.; Mueller, L. J.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2003**, *125*, 1796-1804.

38. Emsley, J.; Udy, P. B. *Polymer* **1972**, *13*, 593-594.

39. Feakins, D.; Last, W. A.; Neemuchwala, N.; Shaw, R. A. *J. Chem. Soc.* **1965**, 2804-2811.

40. Macdonald, A. L.; Trotter, J. *Can. J. Chem.* **1974**, *52*, 734-737.

41. Heston, A. J.; Panzner, M.; Youngs, W. J.; Tessier, C. A. *Phosph. Sulf. Silicon* **2004**, *179*, 831-837.

42. Heston, A. J.; Panzner, M.; Youngs, W. J.; Tessier, C. A. *Inorg. Chem.* **2005**, *44*, 6518-6520.

43. Gonsior, M.; Antonijevic, S.; Krossing, I. *Chem. Eur. J.* **2006**, *12*, 1997-2008.