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^{31}P MAS NMR Spectroscopy of Hexachlorocyclotriphosphazene at Different Stages During Thermal Ring-Opening Polymerization

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Abstract Thermal ring-opening polymerization of hexachlorocyclotriphosphazene was probed using ^{31}P magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The spectrum of unreacted hexachlorocyclotriphosphazene was compared with the spectra of a reaction mixture at 3, 8 and 17.5 h of polymerization. Signals from trimer, oligomer, polymer and hydrolysis products were identified in the spectra and used to observe changes in the mixture during polymerization. The signal of poly(dichlorophosphazene) exhibits a complex behavior where ten individual components were observed and analyzed by deconvolution. These lines were preliminarily assigned to species with differing chain lengths based on their chemical shifts and relative intensities. This work shows that ^{31}P MAS NMR has the potential to provide quantitative information about the rates of chain propagation and cross-linking during thermal ring-opening polymerization.

Keywords MAS NMR · Solid-state nuclear magnetic resonance · Ring-opening polymerization · Hexachlorocyclotriphosphazene · Poly(dichlorophosphazene)

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1 Introduction

Polyphosphazenes are a class of inorganic polymers that has drawn much research attention due to their extremely useful properties and wide range of applications. The pioneer of polyphosphazene synthesis and research is Allcock, who primarily developed and characterized this class of polymers since the 1960s [1, 2]. Polyphosphazenes are composed of a backbone of alternating phosphorous and nitrogen atoms, with two side groups attached to each phosphorous atom (Fig. 1).

The polymeric precursor poly(dichlorophosphazene) can be functionalized [2] through the direct nucleophilic substitution of the chlorine side groups. To date over 700 derivatives have been reported [3]. This broad array of polyphosphazenes has found remarkable utility for applications such as: electric insulators and conductors, non-linear optics, lubricants, membranes, flame-resistant and flame-retardant films and coatings, solid polymer electrolytes, photosensitive materials, artificial bone grafts, soft tissue prostheses, chemotherapeutic models and drug delivery systems—to name just a few [4]. A general schematic of nucleophilic substitution is shown in Fig. 2.

Poly(dichlorophosphazene) is commonly obtained via either thermal ring-opening polymerization (ROP) of hexachlorocyclotriphosphazene $(NPCl_2)_3$, [2] thermal condensation of $Cl_3P = NP(O)Cl_2$ [5, 6] or ambient living cationic polymerization of phosphoranimine $Cl_3P = NSiMe_3$ in the presence of catalytic PCl_5 [7].

Ring-opening polymerization proceeds at 250–300 °C, as seen in Fig. 3.

The ring-opening approach is rather complicated and somewhat unpredictable due to a lack of complete understanding and control over the polymerization process [8]. The polymers produced are high molecular weight

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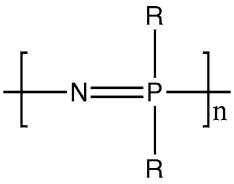

Fig. 1 A general structure of a polyphosphazene repeating unit (R = NHR, NHAr, OR, OAr, Ar)

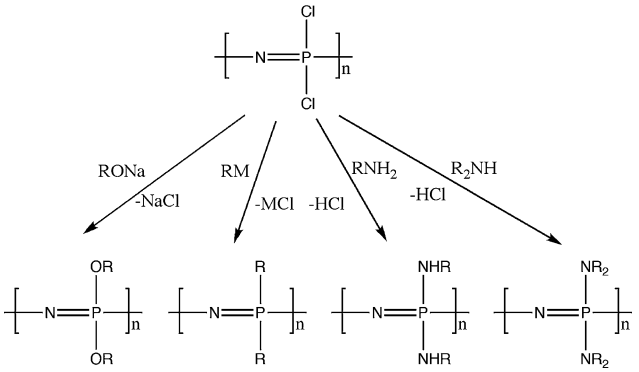

Fig. 2 Polyphosphazene derivatives obtained via nucleophilic substitution of side-chains in poly(dichlorophosphazene)

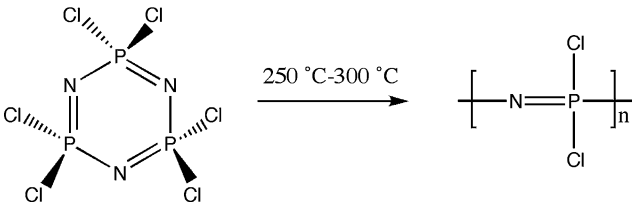

Fig. 3 Synthesis of poly(dichlorophosphazene) via thermal ring-opening polymerization of hexachlorocyclotriphosphazene

($M_w > 2 \times 10^5$), but may differ largely in M_w distribution and macromolecular arrangements even when prepared under similar conditions. This results in very high polydispersity indices ($M_w/M_n > 10$). Another difficulty associated with thermal ring-opening polymerization, which is believed to proceed by a cationic chain mechanism, is the formation of 'inorganic rubbers' due to cross-linking. The mechanism for this reaction is still uncertain; however, it has been suggested that cross-linking may occur at later stages of polymerization when most of the cyclic trimer species are depleted [8]. Formation of the cross-linked polymer matrix can also occur if the hydrolytically unstable poly(dichlorophosphazene) is exposed to trace moisture, in which it undergoes rapid hydrolysis of P–Cl segments, and branching between polymer chains then occurs via formation of P–O–P bonds [8].

Solid-state NMR is a very powerful and versatile spectroscopic method that has found a broad range of applications in the study of polymers [9]. It can provide valuable insight into structure, dynamics and morphology, giving information at the atomic level, often inaccessible by other conventional techniques commonly used for polymer characterization [10, 11]. Despite its usefulness and accessibility, relatively little work on hexachlorocyclotriphosphazene and poly(dichlorophosphazene) involving solid-state NMR has been done in the past [12–15]. In this work, the ^{31}P MAS NMR spectra of hexachlorocyclotriphosphazene at various stages during the thermal ring-opening polymerization will be presented, providing direct observation of the polymerization process as it proceeds.

2 Results and Discussion

Figure 4 depicts spectra of the unreacted hexachlorocyclotriphosphazene and the product mixtures after 3, 8 and 17.5 h of thermal ring-opening polymerization.

The spectrum of unreacted $(NPCl_2)_3$, at the bottom of Fig. 4, contains a side-band pattern centered about 19 ppm which is assigned to cyclic six and eight membered species [8]. The inhomogeneous broadening of the signal is caused in part by disorder in the trimer ring, and by residual couplings to $^{35/37}$Cl known to exist [15]. Two peaks found at 0.8 and −11 ppm correspond to the partially polymerized cyclic species and to the hydrolysis products, respectively [12]. The intensities of these signals are overemphasized due to their much shorter T_1's (as determined by a saturation-recovery experiment) than that of the trimer, as the latter's spins are not allowed to return to equilibrium between successive scans.

After 3 h of reaction at 250 °C, a sharp line arises at −17 ppm, which represents the superposition of signals from linear high molecular weight poly(dichlorophosphazene) of

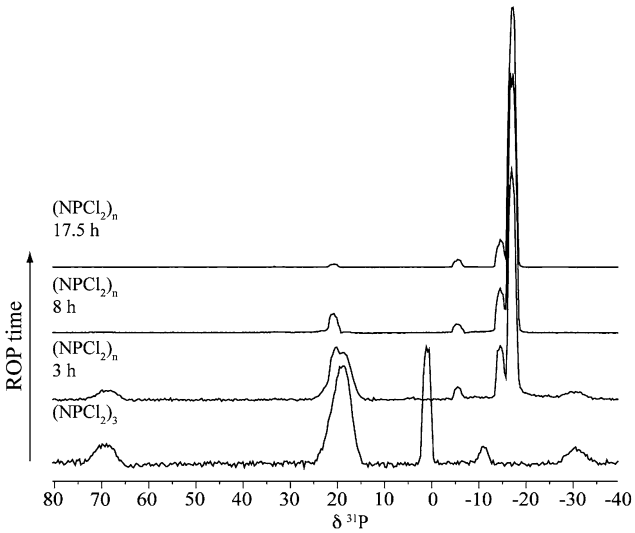

Fig. 4 One-dimensional 202 MHz ^{31}P MAS NMR spectra of the reaction mixture during different stages of the thermal ring-opening polymerization of hexachlorocyclotriphosphazene. (MAS rate = 10 kHz)

differing chain lengths [12]. The signal is significantly more narrow than that of trimer indicating that the residual coupling to $^{35/37}$Cl is averaged out by increased mobility in the polymer backbone [12]. A signal at −6 ppm emerges at the same time which corresponds to cyclic $(NPCl_2)_n$, where n can be as high as 8 [16]. Low molecular weight oligomers, with chain lengths that are much shorter than those typical of the polymer, have signals that are shifted down-field appearing near −15 ppm [16]. Furthermore, the peaks at 0.8 and −11 ppm disappear altogether. Depletion of the trimer and tetramer starting materials is reflected by a lower intensity of the signal at 19 ppm.

This pattern of behavior continues as seen in the spectrum at 8 h of ROP. The ratio between absolute intensities of $(NPCl_2)_n$ and $(NPCl_2)_3$ increases further, and the intensity of the signal at −6 ppm remains unchanged. The latter indicates that ROP leads to chain propagation without producing additional cyclic phosphazenes.

At 17.5 h the polymerization is essentially complete as indicated by the very low intensity of the signal at 19 ppm due to only trace amounts of cyclic trimer and tetramer species present in the reaction mixture. Meanwhile, the intensity of the signal at −6 ppm does not increase which confirms that most of the starting material has been converted to high molecular weight poly(dichlorophosphazene) chains.

The signals near −17 ppm reveal complex structure with several components contributing to the overall shape of the peak. Assuming that any remaining $^{35/37}$Cl residual coupling is not responsible for the fine structure observed, [15] it should then result from differences in chains lengths. Changes in the distribution of these components would reflect corresponding changes in the chain length distribution and hence give insight into the rate of chain propagation. Alternatively, if the residual $^{35/37}$Cl coupling cannot be ruled out, it would likely be only partially responsible for the fine structure in the signal, where the remainder would be attributed to differences in chain lengths.

Preliminary results of the deconvolution analyses are shown in Fig. 5 and are tabulated in Table 1. A total of ten components are suggested for samples at 3, 8 and 17.5 h. Differences in the distribution of linewidths and intensities between the three samples are due in part to uncertainty in the deconvolution method; however, they also reflect changes occurring in the reaction mixture as the polymerization time increases. As such, one can readily appreciate that the intensities of lines at about −15 ppm decrease with polymerization time, which corroborates their assignment to lower molecular weight oligomers, as increased reaction time leads to a greater conversion to higher molecular weight species. Similarly, components corresponding to a high molecular weight polymer increase in areas according to polymerization time.

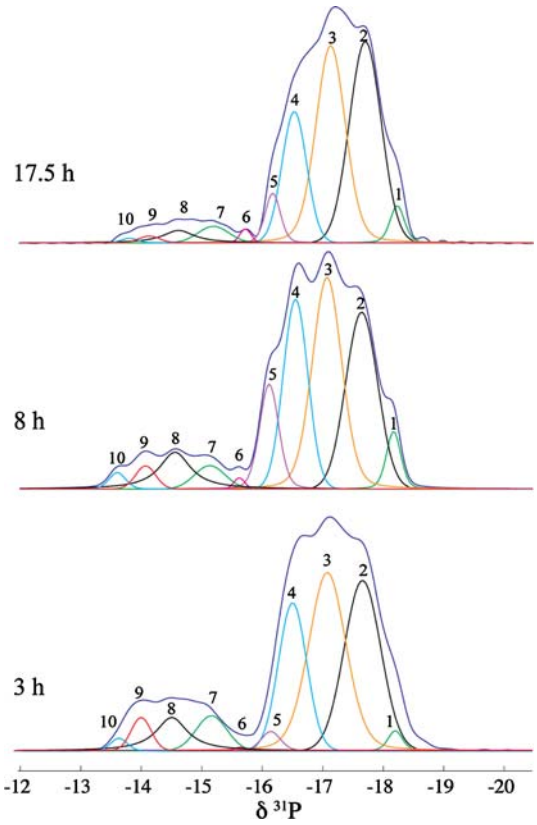

Fig. 5 Deconvolution analyses of the ^{31}P MAS NMR spectra of the reaction mixture taken at 3, 8 and 17.5 h during thermal ring-opening polymerization of hexachlorocyclotriphosphazene. MAS rate 10 kHz

3 Conclusions

It was demonstrated that ^{31}P MAS NMR spectroscopy can be readily used to follow the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at different stages during the process. Signals from the trimer, oligomer, polymer and hydrolysis products were identified in the spectra and used to observe the changes in the sample composition during the polymerization process. Despite the inhomogeneous line broadening caused by disorder of the trimer ring, as well as by residual coupling to $^{35/37}$Cl, spectral resolution was sufficient for the purposes of this study. The distribution between signals in the spectra at various stages of the polymerization were reconcilable with those to be expected over time during the polymerization process.

The resolution of the polymer signals was significantly improved over the trimer and was seen to contain several contributions. These signals were subjected to deconvolution analyses, from which information about their chemical shifts, widths and intensities was extracted. Changes in the contribution of the components in each signal were observed with reaction time. These components were

Table 1 Results of the deconvolution analyses of the ^{31}P MAS NMR spectra of the reaction mixture taken at 3, 8 and 17.5 h during thermal ring-opening polymerization of hexachlorocyclotriphosphazene

Peak	3 h			8 h			17.5 h		
	δ[a] (ppm)	Width[b] (Hz)	Area[c] (a.u.)	δ (ppm)	Width (Hz)	Area (a.u.)	δ (ppm)	Width (Hz)	Area (a.u.)
1	−18.05	58.60	8.815e5	−18.08	56.56	1.647e6	−18.04	50.51	1.044e7
2	−17.55	159.6	4.377e7	−17.55	125.3	3.930e7	−17.51	139.4	4.348e7
3	−16.94	129.5	4.452e7	−16.97	117.2	4.694e7	−16.92	117.1	4.187e7
4	−16.38	103.0	3.565e7	−16.45	96.96	3.277e7	−16.49	87.75	3.248e7
5	−16.01	73.61	8.277e5	−16.01	74.73	2.520e7	−16.01	72.61	1.527e7
6	−15.54	44.33	1.267e4	−15.52	44.34	8.703e5	−15.53	45.51	1.117e6
7	−15.02	119.2	1.861e7	−15.03	119.2	5.057e6	−15.02	119.2	4.818e6
8	−14.45	125.1	1.632e7	−14.45	125.3	1.149e7	−14.44	125.1	3.209e6
9	−13.93	91.05	1.012e7	−13.93	90.91	4.402e6	−13.93	91.8	8.927e5
10	−13.49	65.17	8.432e5	−13.49	64.65	2.083e6	−13.49	64.89	7.077e5

[a] Referenced externally to H_3PO_4 (85%)

[b] Full width at half height (FWHH)

[c] Total area under the peak as determined by absolute intensity and FWHH. Areas are directly comparable as the spectra have equal number of scans

preliminarily assigned to polymer and oligomer species of differing chain lengths. Definitive conclusions regarding their spectral assignment will become more apparent with improved resolution, which presumably could be achieved using the appropriate $^{35/37}Cl$ decoupling sequences that would have to be developed for this application [17, 18]. With improved resolution comes a promise of obtaining a better insight into the thermal ring-opening polymerization of hexachlorocyclotriphosphazene.

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