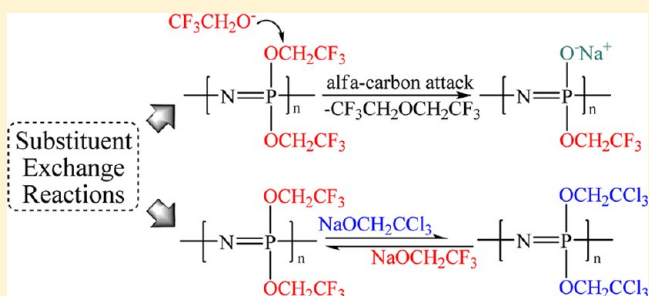


Substituent Exchange Reactions with High Polymeric Organophosphazenes

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ABSTRACT: Side group exchange reactions have been studied for linear high polymeric organophosphazenes, $[N=P(OR_2)]_n$ ($n \sim 15\,000$). Specifically, the exchange behavior of polymers was examined where $OR = OCH_2CF_3$, $OCH_2CF_2CF_2CF_2CF_2H$, OCH_2Cl , OC_6H_4CHO -*p*, OC_6H_4CN -*p*, and $OC_6H_4NO_2$ -*p* with sodium trifluoroethoxide. No aryloxy group replacement by trifluoroethoxy was detected, probably due to the well-protected reactive sites of the polyphosphazenes shielded by aryloxy side groups. For the exchange behavior of $[N=P(OCH_2CF_3)_2]_n$ and $[N=P(OCH_2CF_2CF_2CF_2CF_2H)_2]_n$ with $NaOCH_2CF_2CF_2CF_2CF_2H$ and $NaOCH_2CF_3$, partial substituent exchange was achieved for both reactions. Furthermore, under conditions with excess nucleophile these side group exchange reactions are followed by reactions that introduce sodium–oxo groups attached to phosphorus in place of organic substituents, and this is a mechanism for subsequent hydrolysis and molecular weight decline in the presence of water. Thus, the relative instability of high polymeric $[N=P(OCH_2CF_3)_2]_n$ in the presence of excess $NaOCH_2CF_3$ emerged as an explanation for problems with the synthesis of $[NP(OCH_2CF_3)_2]_n$ and $[NP(OCH_2CF_3)_x(OCH_2(CF_2)_mCF_2H)_{2-x}]_n$ polymers that have attracted wide fundamental and practical interest. However, substituent exchange reactions do appear to be an alternative synthetic approach for the synthesis of some polyphosphazenes, especially mixed-substituted elastomers and the recently reported trichloroethoxy/trifluoroethoxy-containing cosubstituted polyphosphazenes.



INTRODUCTION

High molecular weight polyphosphazenes are inorganic backbone polymers with an essentially linear backbone of alternating phosphorus and nitrogen atoms and two organic or organometallic side groups linked to each phosphorus atom.^{1–4} A distinctive feature of polyphosphazenes is the ease with which the polymer properties can be precisely tailored through changes in the side groups to optimize properties for specific uses, such as in bone regeneration scaffolds,^{5–7} fire resistance and retardance,^{8,9} low-temperature elastomers,¹⁰ fuel cell membranes,^{11–13} and solid or gel polymer lithium ion conductors.^{14,15}

Most of the classical high molecular weight linear polyphosphazenes have been prepared via a ring-opening polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, to high polymeric poly(dichlorophosphazene), $(NPCl_2)_n$ followed by replacement of the labile chlorine atoms in this macromolecular intermediate by organic groups, such as alkoxy, aryloxy, or amino units^{4,16} as shown in Scheme 1. In addition, cosubstituted poly(organophosphazenes) can be synthesized by the sequential or simultaneous reaction of different nucleophiles with poly(dichlorophosphazene) to obtain materials with tunable properties controlled by the side group ratios (Scheme 1).

Alternatively, cosubstituted polyphosphazenes could in principle be prepared through the replacement of organic side groups already linked to a phosphazene chain by other

groups^{16–18} (Scheme 1). This appealing alternative offers the prospect that single-substituent poly(organophosphazenes) can be converted readily to mixed-substituent materials that are of broad interest. More important, from a practical point of view, most poly(organophosphazenes) are much more stable reaction intermediates than poly(dichlorophosphazene) and might be used as specialized macromolecular intermediates for the preparation of other poly(organophosphazenes) with adjustable properties.¹⁷

Poly[bis(2,2,2-trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$, was one of the first stable phosphazene polymers synthesized.^{2,3,19–21} Since that time numerous studies have been conducted on this polymer. However, its synthesis by the reaction of poly(dichlorophosphazene) with sodium trifluoroethoxide in an etheric solvent such as THF, while straightforward to perform in the hands of most investigators, has nevertheless proved curiously challenging in some laboratories. Attempts to scale up this process from the normal 100–200 g scale to, for example, a kilogram level occasionally yielded no substituted high polymer at all, even in laboratories where no problems had been encountered at a smaller scale.

A clue to the explanation was initially provided by Ferrar at Eastman Kodak, who reported²² that the properties of the fully

Received: October 4, 2012

Revised: November 2, 2012

Published: November 13, 2012



Scheme 1. Synthesis of Cosubstituted Poly(organophosphazenes) by Sequential or Simultaneous Addition of Nucleophiles to $(\text{NPCl}_2)_n$ or by Side Group Exchange Reactions

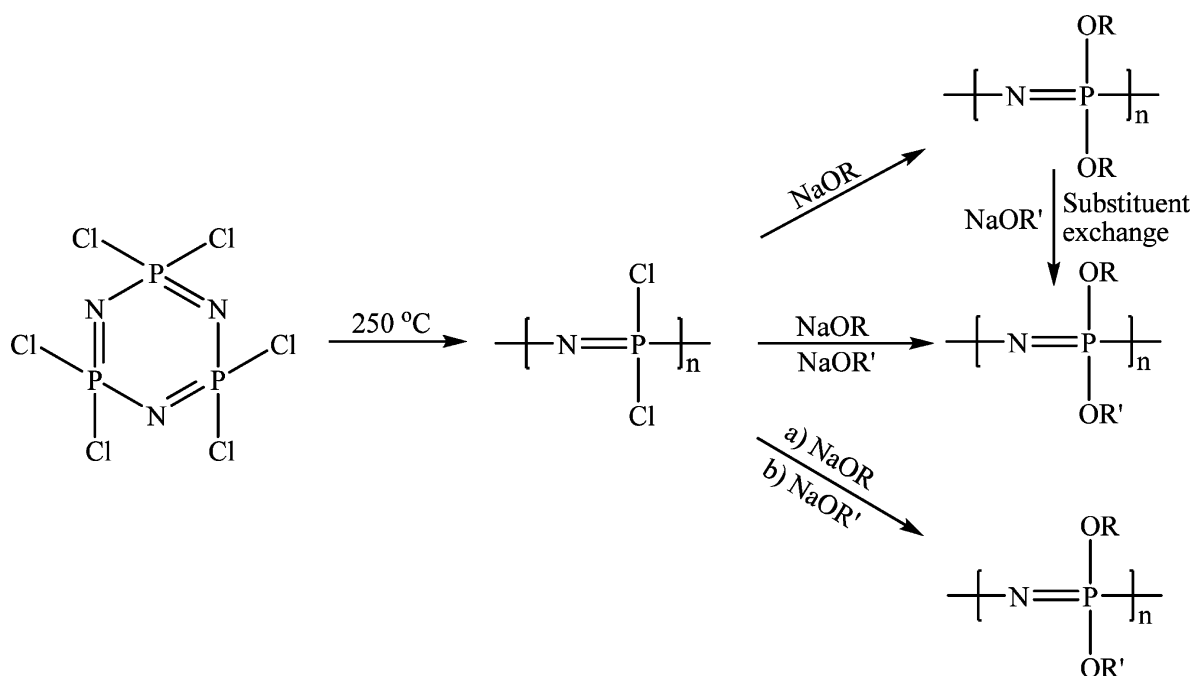


Table 1. Characterization Data for Polymeric Organophosphazenes

compd	side group	repeating units	T_g ($^{\circ}\text{C}$) ^a	T_m ($^{\circ}\text{C}$) ^a	M_n ^b	PDI	yield (%)
1 ³	OC_6H_5	3800	0.95	143.4	890 000	1.78	88.3
2 ²⁸	$\text{OC}_6\text{H}_4\text{CHO-}p$	— ^c	46.5	160.0	—	—	89.5
3 ²⁹	$\text{OC}_6\text{H}_4\text{CN-}p$	—	79.7	245.5	—	—	76.6
4 ²⁹	$\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$	—	84.3	268.0	—	—	85.6
5 ³	OCH_2CF_3	2270	−64	230	550 000	1.4	84.3
6 ¹⁹	$\text{OCH}_2(\text{CF}_3)_4\text{H}$	4680	−20.52	—	2 400 000	2.33	80.3
7 ³⁰	OCH_2CCl_3	4200	12.4	132.5	1 500 000	2.37	51.2

^aMeasured by differential scanning calorimetry. ^bMeasured by GPC calibrated by linear polystyrene standards. ^cPolymers 2–4 cannot dissolve in THF.

substituted polymer varied with the presence of excess sodium trifluoroethoxide, a condition often employed to ensure the replacement of all the chlorine atoms in $(\text{NPCl}_2)_n$. Ferrar and co-workers found that excess nucleophile ($\text{NaOCH}_2\text{CF}_3$) can attack fully substituted poly[bis(2,2,2-trifluoroethoxy)-phosphazene] and bring about changes in the polymer morphology, such as transformation of a crystalline polymer to an amorphous one.²² However, according to their observations, chemical analyses of the polymers did not detect a difference in the materials before and after the treatment with $\text{NaOCH}_2\text{CF}_3$ despite large changes in the polymer physical properties.²² Later, Kolich and co-workers invented a surface treatment of mixed-substituent polyphosphazene fluoroelastomers with sodium trifluoroethoxide to produce a material having enhanced solvent resistance by a side group exchange reaction.²³

Our earlier work with the organic side group exchange processes carried out on small molecule cyclic or linear phosphazene oligomers^{24–26} revealed a possible explanation. These studies showed that side group displacements by organic nucleophiles such as sodium 2,2,2-trifluoroethoxide are sometimes accompanied by side reactions such as α -carbon attack by excess of the nucleophile.^{3,22,24} Hence, a part of this present

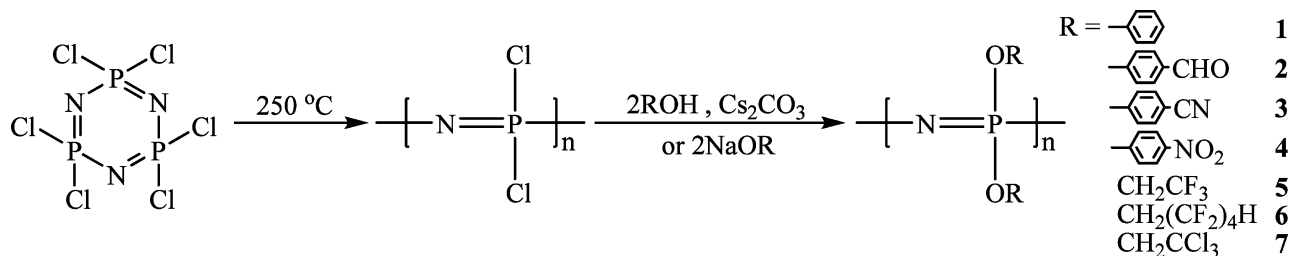
study was devoted to examine the reaction of high molecular weight $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ with sodium trifluoroethoxide.

Two related issues are discussed in this paper. First, we consider the possibility that a useful means for diversifying the structure of poly(organophosphazenes) is by organic side group exchange reactions. Possible starting materials are either aryloxy or fluoroalkoxy-substituted polymers. Second, we provide an explanation for a few puzzling reports involving problems with the synthesis of poly[bis(2,2,2-trifluoroethoxy)phosphazene] by the reactions of poly(dichlorophosphazene) with sodium trifluoroethoxide. Furthermore, as an example of the potential synthetic utility of the exchange process, the substituent exchange reaction has been applied to the synthesis of trichloroethoxy/trifluoroethoxy cosubstituent polyphosphazenes.

EXPERIMENTAL SECTION

Materials. All reactions were carried out under an atmosphere of dry argon using standard Schlenk line techniques. Tetrahydrofuran (EMD) was dried using solvent purification columns.²⁷ 2,2,2-Trifluoroethanol (Aldrich) was purified by vacuum distillation from CaH_2 (Aldrich). Phenol (Aldrich) was purified by sublimation. 4-Nitrophenol was recrystallized twice from toluene. Hexachlorocyclotriphosphazene, $(\text{NPCl}_2)_3$ (from various sources including Fushimi

Scheme 2. Synthesis and Characterization of Polymeric Aryloxy and Alkoxyphosphazenes



Pharmaceutical Co., Japan, and Ningbo Chemical, China), was purified by recrystallization from hexanes and by vacuum sublimation at 50 °C. High molecular weight poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of recrystallized and sublimed hexachlorocyclotriphosphazene in evacuated Pyrex tubes at 250 °C.³

Equipment. ¹H and ³¹P NMR spectra were obtained using a Bruker AMX-360 NMR spectrometer, operated at 360 and 146 MHz, respectively. ¹H NMR spectra were referenced to tetramethylsilane signals while ³¹P NMR chemical shifts were referenced to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. All chemical shifts are reported in ppm. Molecular weight distribution data were obtained using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with two Phenomenex Phenogel linear 10 columns and a Hewlett-Packard 1047A refractive index detector. The samples were eluted at 1.0 mL/min with a 10 mM solution of tetra-*n*-butylammonium nitrate in THF. The elution times were calibrated with polystyrene standards. Glass transition temperatures were determined by differential scanning calorimetry (DSC) with a TA Instruments Q10 and a heating rate of 10 °C/min and a sample size of ca. 10 mg.

Synthesis of High Polymers 1–7. Polymers 1–7 were synthesized according to procedures reported previously^{3,19,28–30} (Table 1). A typical synthetic procedure for polymeric aryloxyphosphazenes derivatives is as follows: A THF solution (150 mL) of poly(dichlorophosphazene) (3.0 g, 25.9 mmol) was added to a THF (150 mL) suspension of cesium carbonate (21.1 g, 64.7 mmol) and phenol (6.09 g, 64.7 mmol). The reaction solution was stirred for 48 h at reflux. The polymer solution was concentrated by rotary evaporation, and the residue was poured into water to precipitate the polymeric product, which was further purified by repeated precipitation three times into both water and hexanes. The pure product was dried under vacuum to yield a white solid 1. Yield: 74.5%. The other poly(organophosphazene)s were synthesized in a similar manner by using different alkoxy or aryloxy nucleophiles as shown in Scheme 2. The characterization data of 1–7 are listed in Table 1.

Substituent Exchange Reactions for Polymers 1–7 with Nucleophiles. All the substituent exchange reactions were carried out in a similar manner. Generally, 1 equiv of polymer side group was exposed to 2 equiv of nucleophiles under reflux in THF. The following is a typical procedure. A solution of 1 (1 g, 4.33 mmol) in THF (10 mL) was added dropwise to a stirred solution of sodium 2,2,2-trifluoroethoxide, prepared from 2,2,2-trifluoroethanol (1.91 g, 17.3 mmol) and sodium hydride (0.42 g, 17.3 mmol) in THF (90 mL). The mixture was stirred at reflux in THF. At timed intervals, starting after the first day, samples were taken and the reaction progress was monitored by ³¹P NMR, mass spectrometry, and GPC. The presence of etheric side products was established by mass spectrometric analysis of the reaction mixtures.

RESULTS AND DISCUSSION

Exchange Reactions of 1–4 with NaOCH₂CF₃. No substituent exchange was detected with high polymers 1–4 when exposed to NaOCH₂CF₃. Similar results were obtained in an earlier study,¹⁶ where no substituent exchange occurred between [NP(OPh)₂]_n and sodium trifluoroethoxide due to the severe steric hindrance caused by phenoxy groups. A possible

Table 2. Exchange Reaction of Polymer 5 with NaOCH₂(CF₂)₄H

	0 day	1 day	3 days	6 days
<i>M_n</i>	550 000	660 000	680 000	290 000
% of replacement	0	61.3	59.3	52.1

explanation is that side group steric hindrance by the aryloxy groups shields access to the backbone and to the P–O–C side linkages. Aryloxy group replacement can be achieved in cyclotriphosphazenes, cyclotetraphosphazenes, and linear oligomers with no more than 20 repeating units.^{24–26} With the linear short chain species side group exchange reactions occur preferentially at the end units once the number of repeating units reach 40. Considering the much more significant shielding effect at the high polymer level due to chain coiling, it is perhaps understandable that no substituent replacement of aryloxy groups was detected with 1–4. The resistance of the longest chain aryloxy-substituted linear oligomers and polymers to side group exchange suggests that these species may be more resistant to degradative side reactions than their alkoxy-substituted counterparts.

Exchange Reactions of 5 and 6 with NaOCH₂(CF₂)₄H and NaOCH₂CF₃. High-performance elastomers based on fluoroalkoxyphosphazenes are the basis of some of the most promising applications of polyphosphazenes. The idealized structure is [N=P(OCH₂CF₃)(OCH₂(CF₂)₄H)]_n, where the presence of two or more different side groups markedly reduces the tendency for crystallinity.^{19,31,32} The elastomeric properties of the final products are highly dependent on both the ratio of the side groups and the distribution sequence along the polymer chain. Therefore, a study of possible substituent exchange reactions during synthesis is an important aspect of this field. In addition, the possibility of α -carbon attack to generate etheric side products as detected for cyclic or oligomeric phosphazenes^{25,26} raises the possibility that hydrolytically sensitive sites may be introduced which would be detrimental to the properties of these high polymeric polyphosphazenes.

Exchange Reaction of 5 with NaOCH₂(CF₂)₄H. It was found that substituent exchange reactions occur when a ratio of 1:4 was used between the side groups in 5 and NaOCH₂(CF₂)₄H at reflux temperature in THF. Roughly 61% of the OCH₂CF₃ groups were replaced by OCH₂(CF₂)₄H units after one day reaction, as determined by ¹H NMR spectrometry. The theoretical value of the molecular weight *M_n* of the resulting polymer after 1 day of reaction should be 920 000, calculated by the molecular weight difference between OCH₂CF₃ and OCH₂(CF₂)₄H side groups. However, this value is different from the one measured by GPC, which is 660 000 in Table 2. A possible explanation for the discrepancy may be the change of hydrodynamic radius of the resulting polymer after

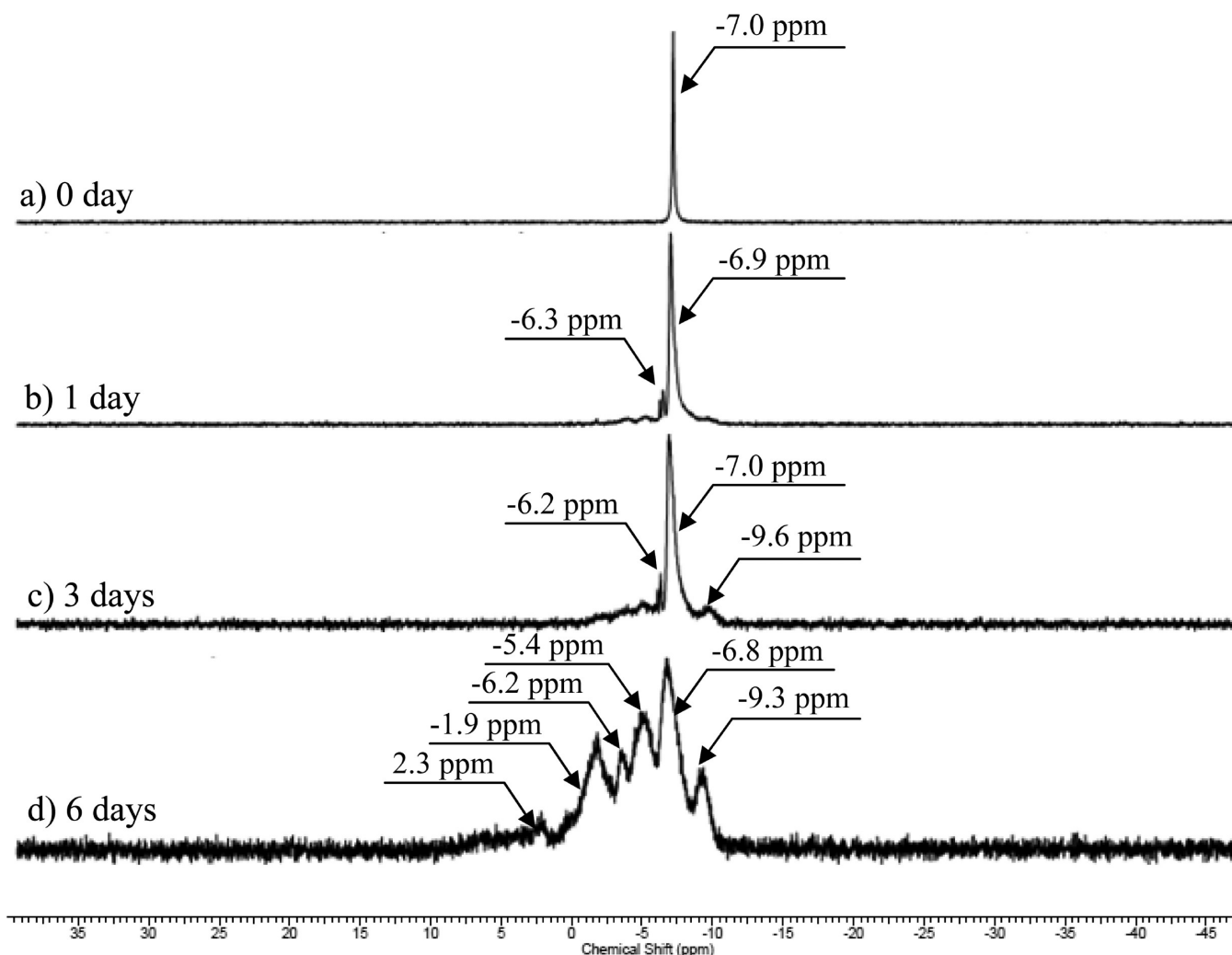


Figure 1. ^{31}P NMR spectra for substituent exchange reaction between **5** and $\text{NaOCH}_2(\text{CF}_2)_4\text{H}$ (1:4, reflux in THF) for (a) 0, (b) 1, (c) 3, and (d) 6 days.

Table 3. Exchange Reaction of **6** with $\text{NaOCH}_2\text{CF}_3$

	0 day	1 day	3 days	6 days
M_n	2 400 000	330 000	340 000	130 000
% of replacement	0	69.7	72.6	64.4

more than half of the side groups in **5** have been replaced. After 3 days of reaction, the molecular weight and replacement percentage remained almost the same as at day 1, $M_n = 680\,000$, and the percent of replacement was 59.3%. However, after 6 days of reaction both M_n and the replacement percentage decreased. M_n declined from 680 000 to 290 000, while the first appearance of the etheric side product $\text{CF}_3\text{CH}_2\text{OCH}_2(\text{CF}_2)_4\text{H}$ was detected by mass spectrometry. The results suggested that the significant decrease of M_n after 6 days is mainly the result of the introduction of hydrolytically sensitive $\text{P}-\text{O}^-\text{Na}^+$ sites, on the polymer backbone by α -carbon attack. Isolation and purification of the polymer involves exposure to aqueous media which brings about the chain cleavage process. This attack may also occur within the first 3 days of reaction, although no etheric side product was detected, and it was not significant enough to lead to an obvious molecular weight decline.

These results were also supported by ^{31}P NMR spectrometry as shown in Figure 1. No significant change was detected during the first 3 days (Figures 1a–c). In contrast, multiple peaks appeared and became broader after 6 days of reaction, which indicated the occurrence of α -carbon attack on polymer backbone.

Exchange Reaction of **6 with $\text{NaOCH}_2\text{CF}_3$.** The similar exchange reaction between **6** and $\text{NaOCH}_2\text{CF}_3$ was detected throughout 6 days of reaction. The replacement percentage was 69.7% after 1 day and did not show a significantly change within 6 days (Table 3). The apparent decline of molecular weight from 2 400 000 to 330 000 was detected in the first day reaction, which is significantly lower than the theoretical value of the molecular weight, 1 500 000, calculated from the molecular weight difference between OCH_2CF_3 and $\text{OCH}_2(\text{CF}_2)_4\text{H}$. This discrepancy may be the result of the change of hydrodynamic radius of the resulting polymer. After 6 days of reaction, the α -carbon attack on polymer backbone became significant and led to the second molecular weight decline as in the exchange reaction between **5** and $\text{NaOCH}_2(\text{CF}_2)_4\text{H}$.

Stability of Poly[bis(2,2,2-trifluorophosphazene)] in the Presence of Nucleophiles. According to the exchange reactions discussed above, fluoroalkoxyphosphazenes showed

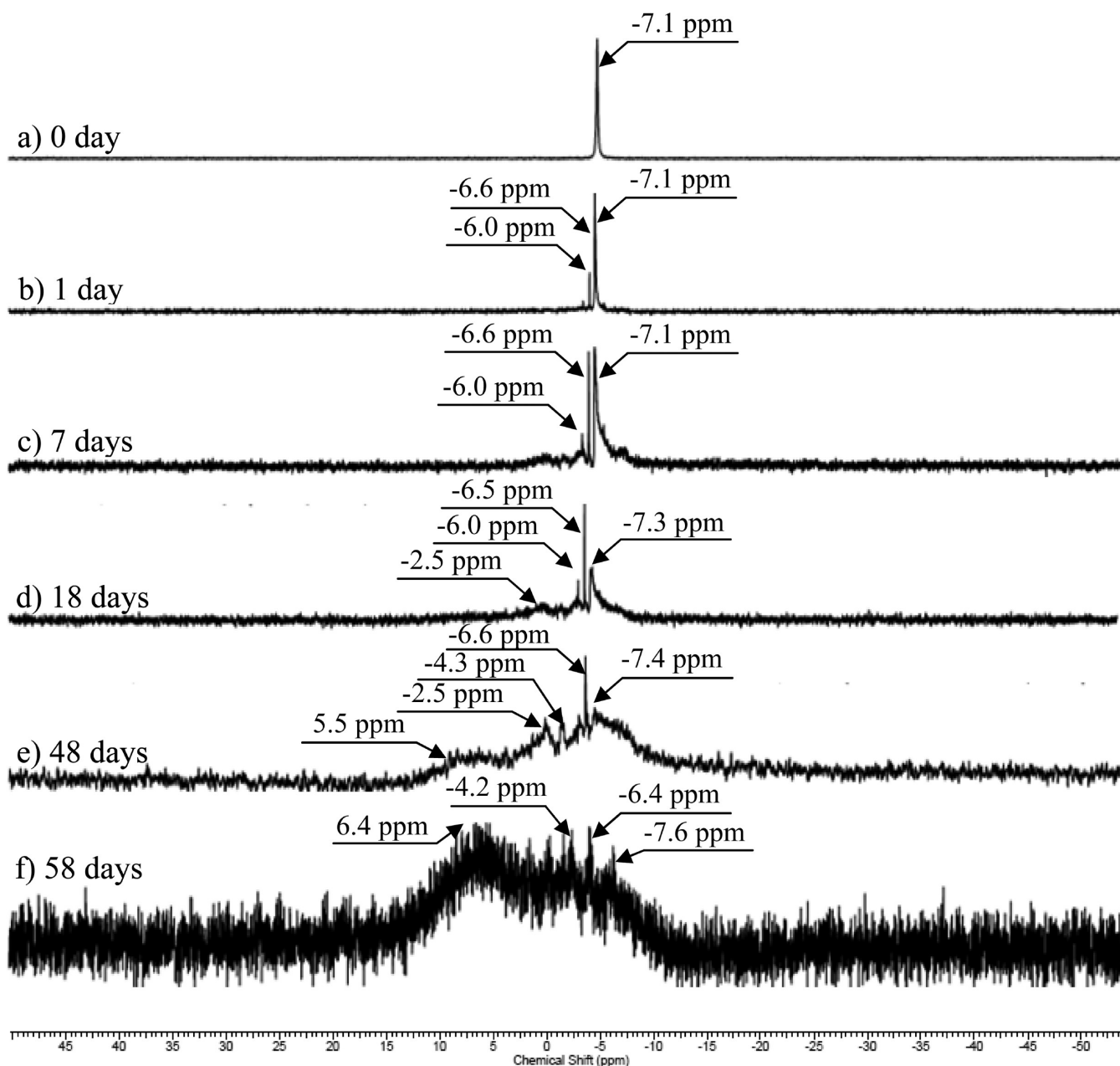


Figure 2. ^{31}P NMR spectra for substituent exchange reaction between polymer **5** and sodium trifluoroethoxide (1:4, reflux in THF) for (a) 0, (b) 1, (c) 7, (d) 18, (e) 48, and (f) 58 days.

Table 4. Exchange Reaction of Polymer **5** with $\text{NaOCH}_2\text{CF}_3$

	0 day	1 day	1 week	2 weeks
M_n	700 000	160 000	58 000	— ^a

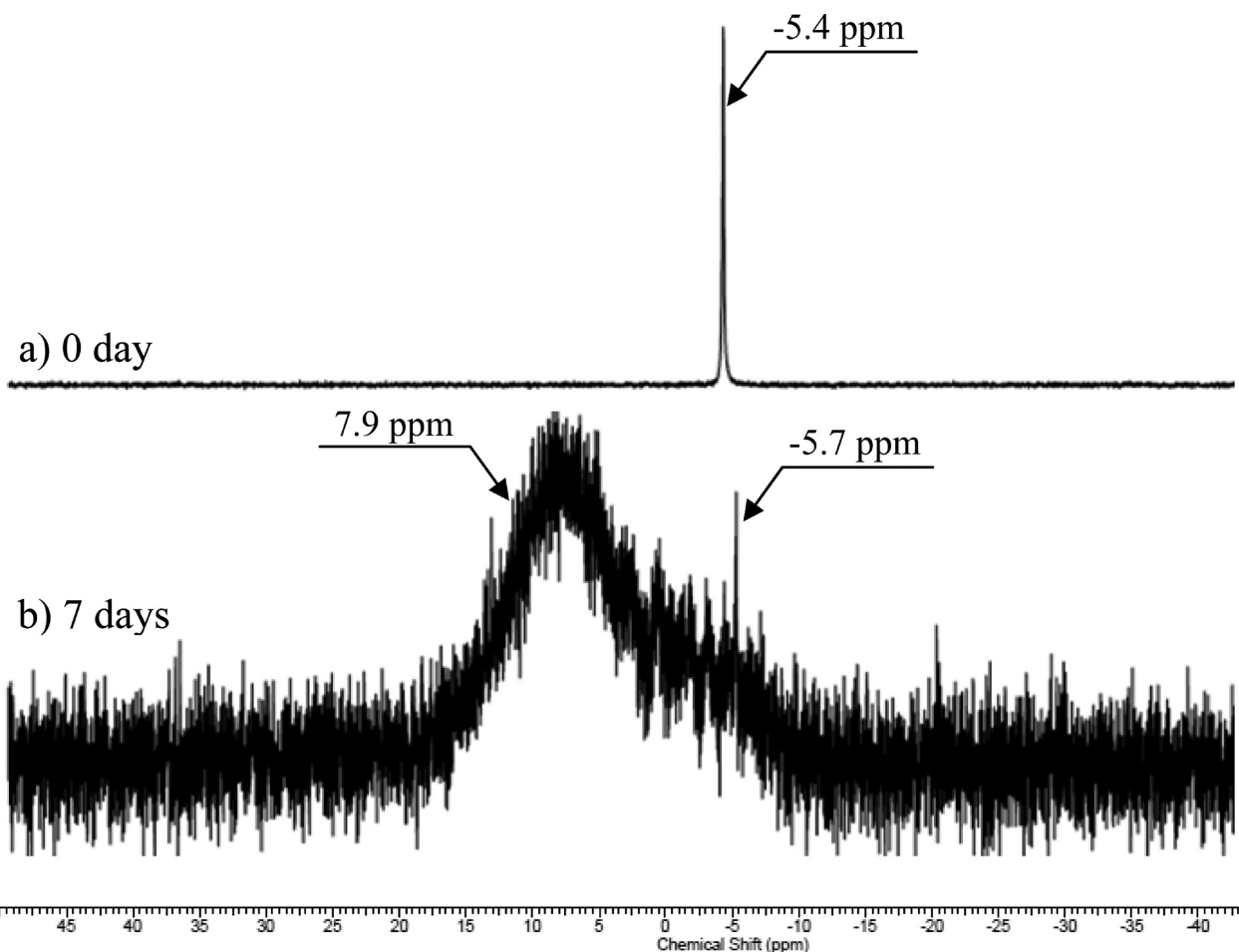
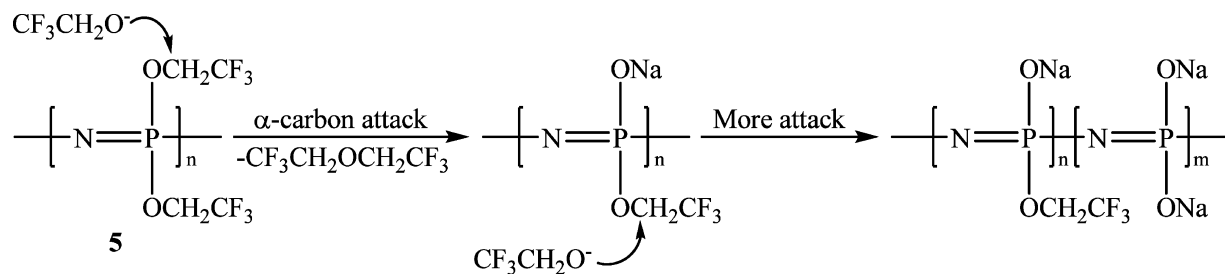
^aCannot precipitate from acidic deionized water; no GPC data.

some instability in the presence of excess nucleophiles in this reaction system, and this resulted in a molecular weight decline following purification. In this current study, poly[bis(2,2,2-trifluoroethoxyphosphazene)] (**5**) was treated with an excess of sodium trifluoroethoxide with a more extended reaction time (58 days) than in the literature²² (14 days) in order to detect possible changes by ^{31}P NMR, GPC, and mass spectrometry to study the reaction process in detail.

In this investigation, poly[bis(2,2,2-trifluoroethoxyphosphazene)] (**5**) showed a long-term instability in the presence of

excess nucleophiles. As illustrated in Figure 2, after 1 day of reaction, a single sharp ^{31}P NMR peak at -6.6 ppm appeared beside the major peak at -7.1 ppm from **5**. The relative intensity of these two peaks changed as the reaction proceeded. The major peak at -7.1 ppm became broader after 7 days, while small broad peaks at -2.5 and -10.1 ppm were detected in the ^{31}P NMR spectrum. In addition, a decline in molecular weight was also detected within the first 2 weeks, as shown in Table 4. Indeed, the molecular weight declined from the original 700 000 to 160 000 after 1 day reaction. This was followed by a further decrease to 57 000 after 1 week. However, GPC data could not be obtained after 2 weeks because the polymer could not be isolated by precipitation from the reaction solution during isolation. Furthermore, the major peak at -7.1 ppm broadened continuously with increasing reaction time. After 48 days, a new broad peak at $+6.4$ ppm was

Scheme 3. Substituent Exchange Reaction Process of 5 with Sodium Trifluoroethoxide

Figure 3. ^{31}P NMR spectra for substituent exchange reaction between 5 and sodium trifluoroethoxide (1:15, reflux in THF) for (a) 0 and (b) 7 days.Table 5. Substituent Exchange between 7 and $\text{NaOCH}_2\text{CF}_3$

	$\text{NaOCH}_2\text{CF}_3$	reaction time (day)	replacement (%)	M_n
7	1:2	1	57.4	730 000
7	1:3	1	71.8	920 000
7	1:4	1	100	830 000

detected, the intensity of which increased during the following 10 days. Bis(trifluoroethyl) ether was detected by mass spectrometry from the exchange reaction between 5 and sodium trifluoroethoxide, which indicated that the cleavage reaction from α -carbon attack by excess nucleophile also occurred in this exchange reaction process.

Therefore, we propose the reaction mechanism shown in Scheme 3 between 5 and sodium trifluoroethoxide. Initially, the α -carbon attack by excess sodium trifluoroethoxide occurred,

even during the first day of reaction, although neither bis(trifluoroethyl) ether nor a significant change in ^{31}P NMR was detected. But some hydrolytically sensitive ONa sites had been introduced along the polymer backbone, which served as chain cleavage sites during the subsequent purification via aqueous media. This led to a serious decline in molecular weight (from 700 000 to 160 000) following precipitation into acidic water. As the exchange reaction proceeded, more and more ONa sites were introduced until after 2 weeks 5 could not be isolated by precipitation. In the end, after 58 days most of the trifluoroethoxy side groups on the polymer had been replaced by ONa units and chain cleavage as indicated by the presence of a broad peak at +6.4 ppm, an indication of the degradation. In order to confirm that the chain cleavage is the result of an attack by excess $\text{NaOCH}_2\text{CF}_3$, and not from trace amounts of water or free alcohol in the reaction system, two

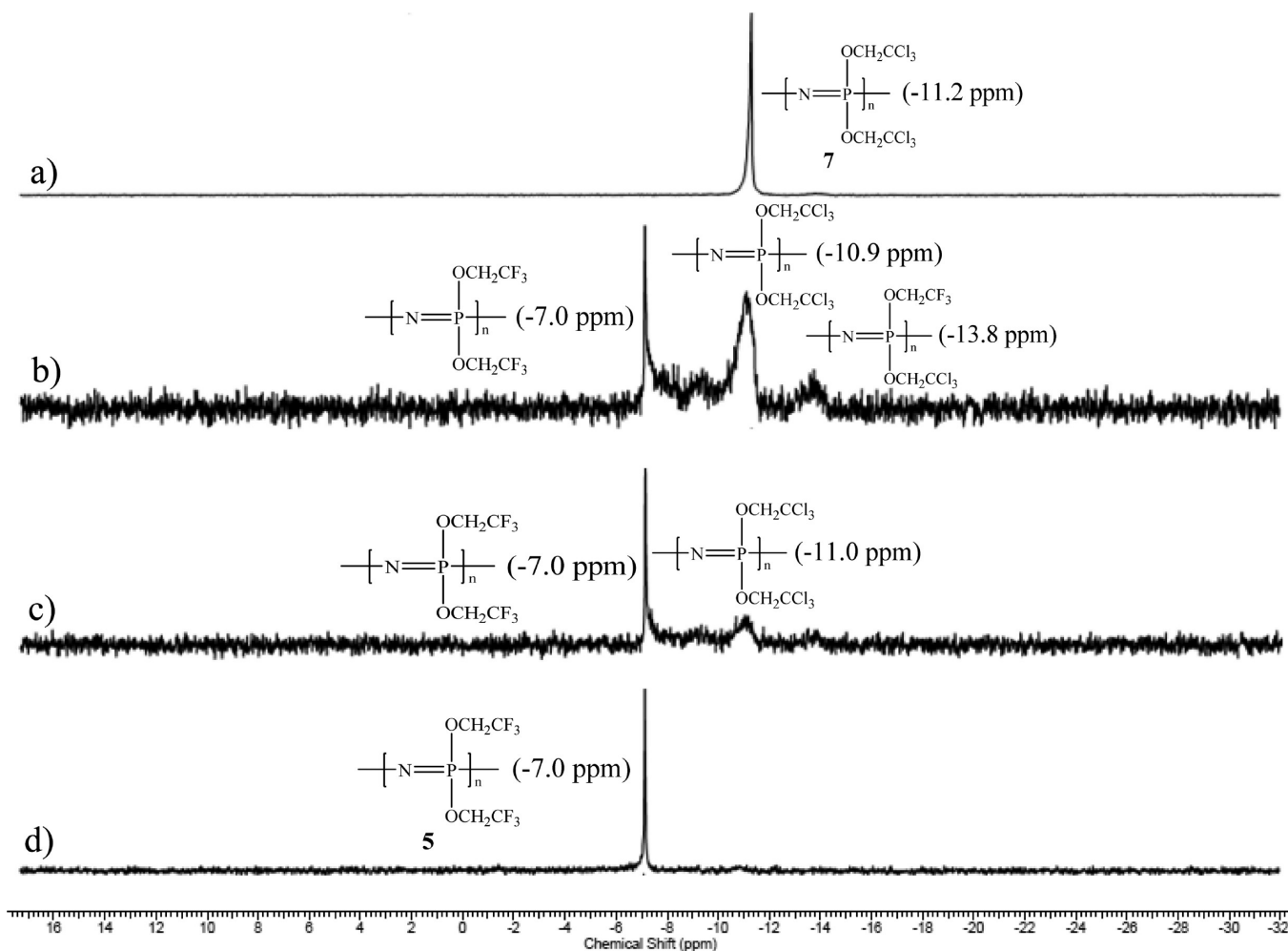


Figure 4. ^{31}P NMR spectra for substituent exchange reaction 1 day reflux in THF between **7** and $\text{NaOCH}_2\text{CF}_3$ in the ratio of (a) 1:0, (b) 1:2, (c) 1:3, and (d) 1:4.

Table 6. Substituent Exchange between **5** and $\text{NaOCH}_2\text{CCl}_3$

	$\text{NaOCH}_2\text{CCl}_3$	reaction time (days)	replacement (%)	M_n
5	1:4	4	20	670 000
5	1:8	4	24	130 000
5	1:12	4	25	— ^a

^aCannot precipitate from acidic deionized water; no GPC data.

reference reactions were conducted by refluxing **5** in THF, either with or without HOCH_2CF_3 . Both experiments showed no change in either the ^{31}P NMR spectrum or the mass spectrum after 1 month of treatment. Consequently, the presence of $\text{NaOCH}_2\text{CF}_3$ is crucial for the α -carbon attack. Moreover, the effect of increasing the excess nucleophile, $\text{NaOCH}_2\text{CF}_3$, on the cleavage reaction was also studied by using a 1:15 ratio of **5** to $\text{NaOCH}_2\text{CF}_3$, rather than the original ratio of 1:4. The presence of a larger excess of $\text{NaOCH}_2\text{CF}_3$ led to a faster cleavage reaction, as shown in Figure 3. After 7 days, almost no ^{31}P peak at -7.1 ppm could be detected. Instead, a prominent broad peak appeared at $+6$ ppm, attributed to a much faster cleavage reaction. Therefore, based on this work, in the synthesis of poly[bis(2,2,2-trifluoroethoxy)phosphazene], the amount of $\text{NaOCH}_2\text{CF}_3$ should be strictly controlled to not only achieve complete substitution but also avoid the introduction of hydrolytically sensitive sites on the polymer backbone due to the α -carbon attack.

Application of the Exchange Reaction to the Synthesis of Polyphosphazenes Containing Trichloroethoxy Units. Recently, a new class of polyphosphazenes containing trichloroethoxy units was synthesized in our laboratory by the reactions of poly(dichlorophosphazene) with sodium trichloroethoxide.³⁰ The homosubstituted poly[bis(2,2,2-trichloroethoxy)phosphazene] (**7**) had only limited solubility in common organic solvents, probably due to its high crystallinity.³⁰ This resulted in poor processability and limited its prospective applications. However, the cosubstituted derivatives with trifluoroethoxy units showed much improved solubility in common organic solvents, together with excellent film-forming properties and potential fire-resistant application.³⁰ As mentioned above, the substituent exchange reaction is an alternative synthetic approach that allows access to cosubstituted polyphosphazenes, starting from a more stable homosubstituted precursor rather than $(\text{NPCL}_2)_n$. Therefore, the feasibility of synthesis of cosubstituted polyphosphazenes containing trichloroethoxy/trifluoroethoxy units by substituent exchange reaction was examined.

In general, this study showed that the fully substituted poly[bis(2,2,2-trifluoroethoxy)phosphazene] can be obtained by an exchange reaction between **7** and $\text{NaOCH}_2\text{CF}_3$ within 1 day. By contrast, only a maximum of 25% replacement could be achieved between **5** and $\text{NaOCH}_2\text{CCl}_3$, even though a large excess nucleophile (12 equiv) was used.

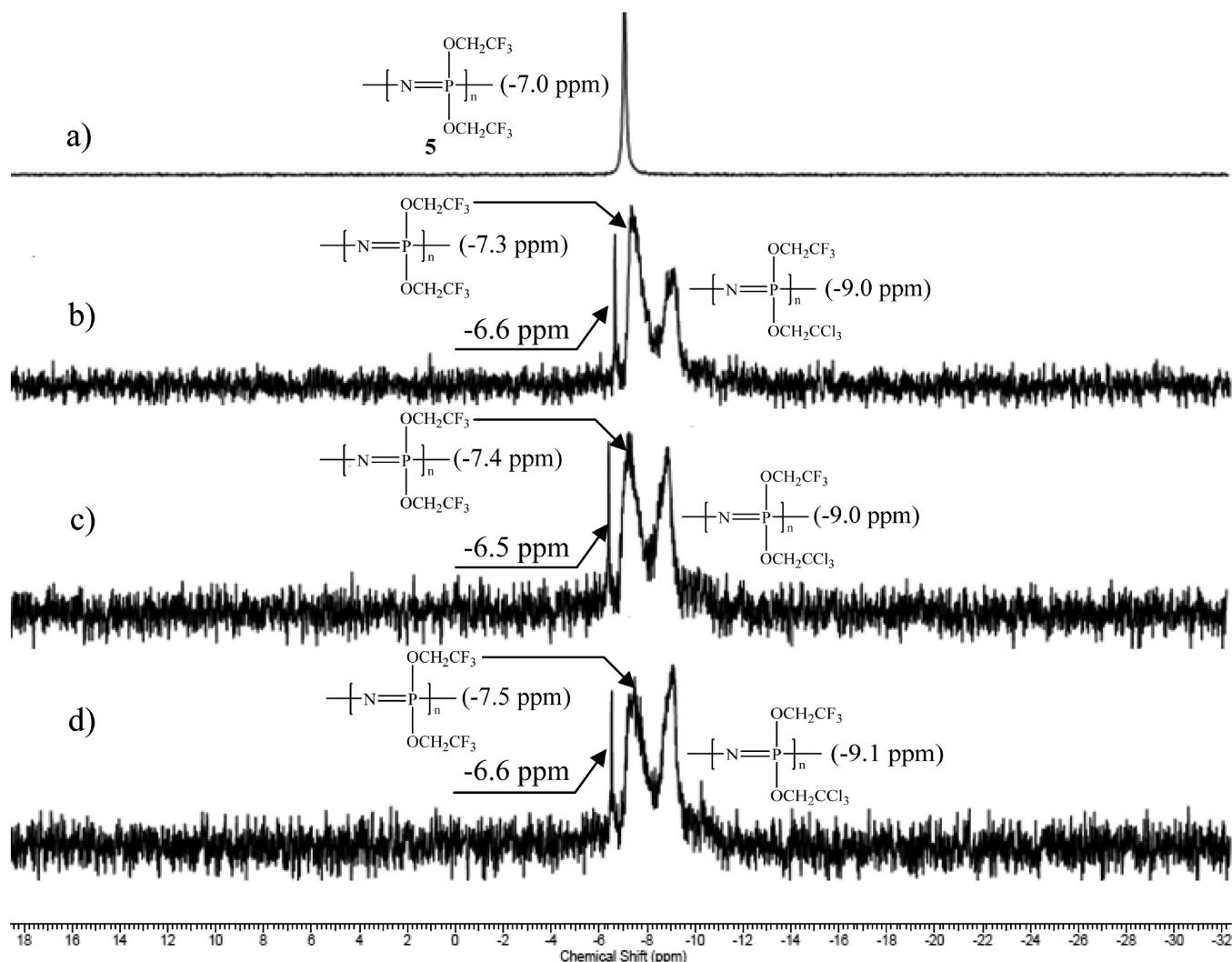
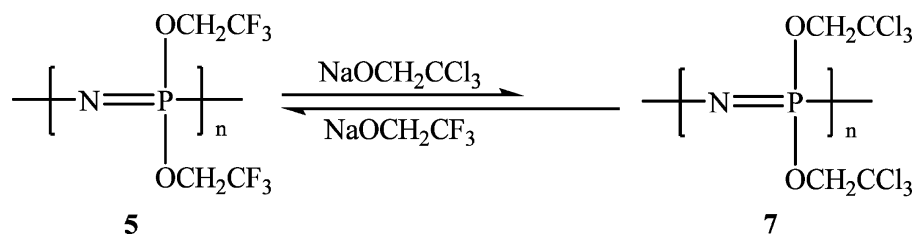


Figure 5. ^{31}P NMR spectra for substituent exchange reaction 4 days reflux in THF between **5** and sodium trichloroethoxide in the ratio of (a) 1:0, (b) 1:4, (c) 1:8, and (d) 1:12.

Scheme 4. Reversible Substituent Exchange Reaction between **5 and **7****



The substituent exchange reaction data for the reaction of **7** with $\text{NaOCH}_2\text{CF}_3$ are listed in Table 5. Replacement percentages as high as 57.4% and 71.8% can be achieved within 1 day by using a ratio of 1 to 2 or 1 to 3 of repeating units of **7** and $\text{NaOCH}_2\text{CF}_3$. No further change was detected by ^{31}P NMR with longer reaction times. In addition, 100% replacement of trichloroethoxy by trifluoroethoxy occurred, as the ratio was increased to 1:4 as shown in Figure 4. More important, the resultant products retained relatively high molecular weights with trichloroethoxy as the nucleophile, which indicated a greater resistance to α -carbon attack and molecular weight decline if the reaction time was controlled within 1 day.

On the other hand, complete replacement of trifluoroethoxy by trichloroethoxy could not be achieved via the exchange reaction between **5** and $\text{NaOCH}_2\text{CCl}_3$, even with 12 equiv of nucleophile and an extended reaction time of 4 days. The results are shown in Table 6. The maximum replacement was only 25% (Figure 5). Moreover, in this case, serious polymer breakdown occurred due to severe α -carbon attack by the excess nucleophile after an extended reaction time of 4 days.

Therefore, it is plausible to presume a reversible reaction equilibrium between **5** and **7** in the presence of nucleophiles, where this equilibrium lies strongly on the side of **7** as illustrated in Scheme 4. A possible driving force for this process may be the release of steric hindrance generated by the

replacement of the more bulky trichloroethoxy side groups by the less bulky trifluoroethoxy unit. Furthermore, the electron-withdrawing ability of the trichloroethoxy side group may also play an important role in determining the degree of substitution. Unlike general alkoxy or fluoroalkoxy polyphosphazenes, the ^{31}P NMR chemical shift of **7** is at -11.5 ppm rather than ~ -7 ppm as in other alkoxy or fluoroalkoxy polyphosphazenes. This indicates the unusual electron-withdrawing effect of the trichloroethoxy group.³⁰ This is the first time that a reversible substituent exchange equilibrium has been detected in polyphosphazene reactions.

The results from this study are important with respect to the synthesis of soluble and processable cosubstituted polyphosphazenes that bear both trichloroethoxy and trifluoroethoxy units. First, this study showed that the order of addition of the different nucleophiles is crucial for determining the composition and resultant properties of the final products. This is because of the greater ease of replacement of trichloroethoxy units by sodium trifluoroethoxide. Second, a targeted product with a specific composition can also be synthesized by the exchange reaction between **7** and $\text{NaOCH}_2\text{CF}_3$. Thus, the more stable intermediate poly[bis(2,2,2-trichloroethoxy)-phosphazene] (**7**) rather than the moisture-sensitive poly-(dichlorophosphazene) could be the starting point for the synthesis of mixed trifluoroethoxy/trichloroethoxy substituted polyphosphazenes. Moreover, the composition of the final products can be finely tuned by varying the amount of $\text{NaOCH}_2\text{CF}_3$.

CONCLUSIONS

The most important conclusion from this work is that large excess amounts of fluoroalkoxide nucleophiles should be avoided in the synthesis of fluoroalkoxy phosphazene polymers from poly(dichlorophosphazene) or during the side group exchange processes. No exchange reactions were detected between polymeric aryloxyphosphazenes and $\text{NaOCH}_2\text{CF}_3$, probably due to protection of the reaction sites by the steric hindrance of the aryloxy side groups. By contrast, the side group replacement between $[\text{N}=\text{P}(\text{OCH}_2\text{CF}_3)_2]_n$ and $\text{NaOCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$ or $[\text{N}=\text{P}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H})_2]_n$ and $\text{NaOCH}_2\text{CF}_3$ revealed that only partial substituent exchange can be achieved for both reactions. Moreover, these side group exchange reactions are also followed by the formation of sodium-oxo groups at phosphorus in place of the organic substituents, especially when an excess of the attacking nucleophile is present. This leads to subsequent hydrolysis and molecular weight decline after exposure to water during isolation and purification. Thus, an explanation for the variation of properties of poly[bis(2,2,2-trifluoroethoxy)-phosphazene] was formed, based on its exposure to excess sodium trifluoroethoxide by a situation that leads to the formation of bis(trifluoroethyl) ether from α -carbon attack. The introduced P-ONa units then serve as hydrolytically sensitive sites, and in the presence of water, these can be sites for chain cleavage. Thus, in the synthesis reactions in which trifluoroethoxy groups are introduced the amount of sodium trifluoroethoxide nucleophile should be well controlled to ensure the complete replacement of chlorine atoms and to avoid the introduction of hydrolytically sensitive sites. Achieving this balance is the key to the synthesis of stable high polymers. Finally, the substituent exchange process provides a method for the synthesis of cosubstituted polyphosphazenes with both trichloroethoxy and trifluoro-

thoxy side units. By using poly[bis(2,2,2-trichloroethoxy)-phosphazene] as a starting stable intermediate, the ratio between the two different side groups can be finely tuned by controlling the amount of sodium trifluoroethoxide in the reaction mixture.

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; Wiley-Interscience: Hoboken, NJ, 2003.
- (2) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216–4217.
- (3) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709–1715.
- (4) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716–1718.
- (5) Weikel, A. L.; Cho, S. Y.; Morozowich, N. L.; Nair, L. S.; Laurencin, C. T.; Allcock, H. R. *Polym. Chem.* **2010**, *1*, 1459–1466.
- (6) Deng, M.; Nair, L. S.; Nukavarapu, S. P.; Kumbar, S. G.; Jiang, T.; Weikel, A. L.; Krogman, N. R.; Allcock, H. R.; Laurencin, C. T. *Adv. Funct. Mater.* **2010**, *20*, 2794–2806.
- (7) Deng, M.; Nair, L. S.; Nukavarapu, S. R.; Jiang, T.; Kanner, W. A.; Li, X. D.; Kumbar, S. G.; Weikel, A. L.; Krogman, N. R.; Allcock, H. R.; Laurencin, C. T. *Biomaterials* **2010**, *31*, 4898–4908.
- (8) Reed, C. S.; Taylor, J. P.; Guigley, K. S.; Coleman, M. M.; Allcock, H. R. *Polym. Eng. Sci.* **2000**, *40*, 465–472.
- (9) Allcock, H. R.; Taylor, J. P. *Polym. Eng. Sci.* **2000**, *40*, 1177–1189.
- (10) Allcock, H. R. *Adv. Mater.* **1994**, *6*, 106–115.
- (11) Fei, S. T.; Wood, R. M.; Lee, D. K.; Stone, D. A.; Chang, H. L.; Allcock, H. R. *J. Membr. Sci.* **2008**, *320*, 206–214.
- (12) Fu, J. W.; Xu, Q.; Chen, J. F.; Chen, Z. M.; Huang, X. B.; Tang, X. Z. *Chem. Commun.* **2010**, *46*, 6563–6565.
- (13) Tsang, E. M. W.; Zhang, Z. B.; Yang, A. C. C.; Shi, Z. Q.; Peckham, T. J.; Narimani, R.; Frisken, B. J.; Holdcroft, S. *Macromolecules* **2009**, *42*, 9467–9480.
- (14) Lee, D. K.; Allcock, H. R. *Solid State Ionics* **2010**, *181*, 1721–1726.
- (15) Thielen, J.; Meyer, W. H.; Landfester, K. *Chem. Mater.* **2011**, *23*, 2120–2129.
- (16) Allcock, H. R.; Kim, Y. B. *Macromolecules* **1994**, *27*, 3933–3942.
- (17) Allcock, H. R.; Maher, A. E.; Ambler, C. M. *Macromolecules* **2003**, *36*, 5566–5572.
- (18) Allcock, H. R.; Connolly, M. S.; Harris, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 2482–2490.
- (19) Rose, S. H. *J. Polym. Sci., Ser B* **1968**, *6*, 837–839.
- (20) Allcock, H. R.; Rutt, J. S.; Fitzpatrick, R. J. *Chem. Mater.* **1991**, *3*, 442–449.
- (21) Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.* **1991**, *3*, 450–454.
- (22) Ferrar, W. T.; Marshall, A. S.; Whitefield, J. *Macromolecules* **1987**, *20*, 317–322.
- (23) Kolich, C. H.; Klobucar, W. D. U.S. Patent 4,945,139, 1990.
- (24) Allcock, H. R.; Smeltz, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 4143–4149.
- (25) Liu, X.; Breon, J. P.; Chen, C.; Allcock, H. R. *J. Chem. Soc., Dalton Trans.* **2012**, *41*, 2100–2109.
- (26) Liu, X.; Breon, J. P.; Chen, C.; Allcock, H. R. *Inorg. Chem.* **2012**, *51*, 11910–11916.
- (27) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
- (28) Allcock, H. R.; Austin, P. E. *Macromolecules* **1981**, *14*, 1616–1622.

- (29) Carriedo, G. A.; Alonso, F. J. G.; Gonzalez, P. A. *Macromol. Rapid Commun.* **1997**, *18*, 371–377.
- (30) Chen, C.; Allcock, H. R. *Macromolecules* **2012**, DOI: 10.1021/ma301822m.
- (31) Rose, S. H.; Cable, J. U.S. Govt. Res. Rept. AD-693-289, 1969.
- (32) Rose, S. H. U.S. Patent 3,515,688, 1970.