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Substituent Exchange Reactions of Linear Oligomeric Aryloxyphosphazenes with Sodium 2,2,2-Trifluoroethoxide

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ABSTRACT: Side-group-exchange reactions have been studied for short-chain linear oligomeric phosphazenes, $(RO)_4P[N{=}P(OR_2)]_nOR$ (n = 6, 10, 20, and 40) as models for the corresponding linear high polymers ($n \sim 15000$). Specifically, the exchange behavior of oligomers where OR = OCH_2CF_3, OC_6H_5, OC_6H_4CHO-p, OC_6H_4CN-p, and $OC_6H_4NO_2$-p with sodium trifluoroethoxide was examined. The ease of aryloxy group replacement by trifluoroethoxy increased with the electron-withdrawing character in the order OR = $OC_6H_5 \ll OC_6H_4CHO$-p < OC_6H_4CN-p < $OC_6H_4NO_2$-p, but the reaction was efficient only if the phosphazene contained no more than 20 repeating units. However, attempts to force slower reactions by the use of excess sodium trifluoroethoxide induced secondary reactions at the trifluoroethoxy units already introduced to produce $CF_3CH_2OCH_2CF_3$ and generate $-O^-Na^+$ units in their place. The longest chain model underwent side-group-exchange reactions preferentially at the end units. These results are significant for the synthesis of phosphazene high polymers with fluoroalkoxy and aryloxy side groups.

INTRODUCTION

The reactions of phosphazene linear high polymers, $[N{=}PR_2]_n$ (where $n \sim 15000$),[1−4] are crucial for the synthesis of a wide variety of materials that are of interest in biomedicine,[5−7] energy storage,[8−12] and aerospace applications.[13−15] However, some of these reactions are complicated, and experimental conditions often have to be optimized by studies of small-molecule model systems. Phosphazene cyclic trimers and tetramers, $[N{=}PR_2]_{3\text{ or }4}$, have traditionally been used as models for the high polymers, but their rigid skeletal structures and their reactivities differ in important ways from the behavior of their linear high polymeric counterparts. Short-chain linear phosphazenes are alternative small-molecule models because their general architecture is more reminiscent of the high polymers. The use of a living cationic condensation method has provided reliable access to linear phosphazene oligomers with precisely tailored chain lengths, and this presents new opportunities to examine model reactions.[16,17] The only disadvantage of these linear models is the higher ratio of end- to-middle units in the oligomers than in the high polymers, but this is less serious for species that contain more than five or six middle units.

One of the potentially useful reactions under development for polyphosphazenes involves the exchange reactions of one organic side group by another.[18−20] This is an alternative technique to the normal synthesis procedure in which the chlorine atoms in high-molecular-weight poly(dichlorophosphazene), $(NPCl_2)_n$, are replaced by organic nucleophiles.[3,18] Because the chlorophosphazene high polymer is hydrolytically sensitive, it must be stored and handled under anhydrous conditions. Most organophosphazenes are water-stable. Hence, the use of an organophosphazene high polymer as a starting point for the introduction of other side groups has considerable appeal, particularly for the synthesis of mixed-substituent derivatives. In earlier studies, we examined the side-group exchange reactions of organophosphazene cyclic trimers and tetramers in some detail,[21,22] but the behavior of linear oligomers has not been reported. Here we describe the similarities and differences between the cyclic and linear oligomeric systems in the exchange process.

In the following text, the codes used are as follows: side groups in the linear oligomers are denoted by numerals 1 = phenoxy, 2 = formylphenoxy, 3 = cyanophenoxy, and 4 = nitrophenoxy, whereas the chain-length repeating units are indicated by letters, where a is n = 6, b is n = 10, c is n = 20, and d is n = 40. The number of repeating units, n, in the linear oligomers is defined as shown in Scheme 1. Note that, in the discussion of the end-group influence, both the $P(OR)_4$ and $P(OR)_3$ sites are important.

Scheme 1. Structures of Cyclic (i and ii), Linear Oligomeric (iii), and High Polymeric (iv) Systems

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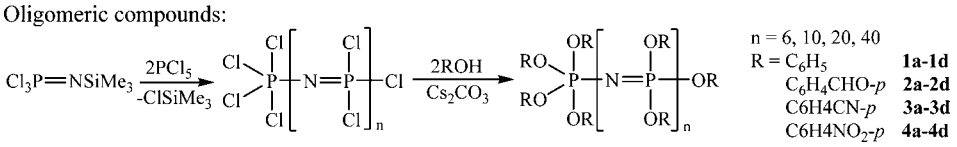
Scheme 2. Synthesis and Characterization of Oligomeric Aryloxyphosphazenes



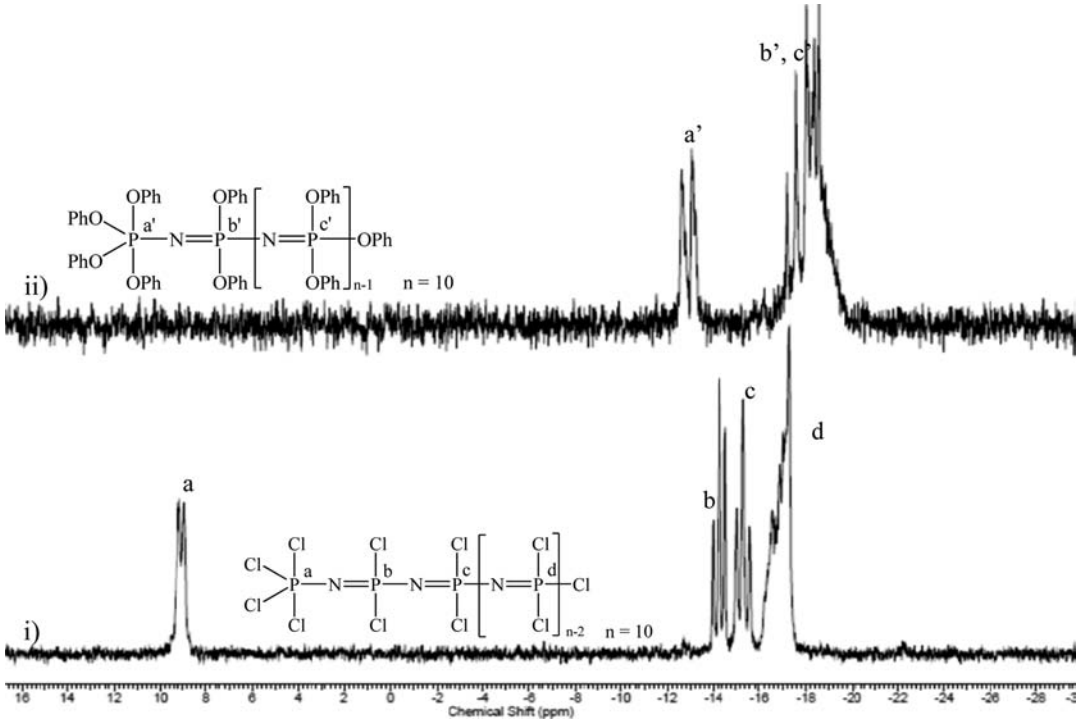


Figure 1. (i) ^{31}P NMR spectrum of oligo(dichlorophosphazene) with n = 10. (ii) ^{31}P NMR spectrum of **1b**.

EXPERIMENTAL SECTION

Materials. All reactions were carried out under an atmosphere of dry argon using standard Schlenk-line techniques. Tetrahydrofuran (THF; EMD) was dried using solvent purification columns.[23] 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. Sulfuryl chloride (Aldrich) and phosphorus trichloride (Aldrich) were purified by distillation. Phosphorus pentachloride (Aldrich) was purified by sublimation under vacuum before use. Lithium bis(trimethylsilyl)-amide (Aldrich) and other reagents were used as received.

Equipment. ^{1}H and ^{31}P NMR spectra were obtained using a Bruker AMX-360 NMR spectrometer, operated at 360 and 146 MHz, respectively. ^{1}H NMR spectra were referenced to tetramethylsilane signals, while ^{31}P 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 with a heating rate of 10 °C/min and a sample size of ca. 10 mg.

Synthesis of Chlorophosphoranimine, Cl_3P═$NSiMe_3$. The synthesis of the chlorophosphoranimine monomer followed a previously reported procedure with some modifications.[16,24,25] Briefly, PCl_3 (46.25 g, 0.33 mol) was added dropwise to $LiN(SiMe_3)_2$ (56.93 g, 0.33 mol) in ether (500 mL) at 0 °C over 30 min. The mixture was allowed to remain at 0 °C and was stirred for another 1 h. Sulfuryl chloride (45.22 g, 0.33 mmol) was then added slowly over 30 min, and the reaction mixture was stirred at 0 °C for 2 h. After completion of the reaction, the insoluble salt was removed by filtration. The crude product was condensed to one-third of its original volume by removing the ether and was purified by vacuum distillation at room temperature to yield a colorless liquid. Yield: 63%. ^{1}H NMR ($CDCl_3$): δ 0.16 (s, 9H). ^{31}P NMR ($CDCl_3$): δ −57.08.

Synthesis of Linear Oligomeric Compounds. A typical synthetic procedure for oligomeric aryloxyphosphazene derivatives is as follows: For the synthesis of the 20 repeating unit oligo-(phenoxyphosphazene), a 25 mL portion of a methylene chloride solution of PCl_5 (0.36 g, 1.72 mmol) was stirred at room temperature for 2 h to dissolve PCl_5. To this solution was added Cl_3P═$NSiMe_3$ (4.00 g, 17.18 mmol), and the mixture was stirred at room temperature for 4 h. The progress of the reaction was monitored using ^{31}P NMR spectroscopy until complete conversion of Cl_3P═$NSiMe_3$ to oligo(dichlorophosphazene) had occurred. The solvent was removed under reduced pressure to yield a viscous liquid. The product was redissolved in THF (50 mL) and was treated with an excess of phenol (4.2 g, 44.67 mmol) and cesium carbonate (14.55 g, 44.67 mmol). The reaction mixture was stirred at reflux for 1 day, followed by concentration of the solution under reduced pressure and then precipitation of the oligomer three times into water and hexanes to isolate a white product **1c**. Yield: 60.5%. The other oligomeric aryloxyphosphazenes were synthesized in a similar manner by varying the ratio of PCl_5 to Cl_3P═$NSiMe_3$ to control the number of repeating units, followed by substitution with aryloxy nucleophiles, as shown in Scheme 2.

Substituent Exchange Reactions by Sodium 2,2,2-Trifluoroethoxide. All of the substituent exchange reactions were carried out

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in a similar manner. Generally, 1 equiv of aryloxy side groups reacted with 2 equiv of sodium trifluoroethoxide under reflux in THF. The following is a typical procedure: A solution of **1a** (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 ^{31}P NMR, mass spectrometry, and gel permeation chromatography (GPC). The presence of etheric side products was established by mass spectrometric analysis of the reaction mixtures.

RESULTS AND DISCUSSION

Synthesis of Starting Oligomers 1−6. The starting materials with chlorine substituents were synthesized by a living cationic polymerization.[16,24] The chlorine atoms were then replaced by nucleophilic substitution to yield oligo(organophosphazenes). The number of repeating units in the oligomeric species was controlled by the ratio of PCl_5 to $Cl_3P{=}NSiMe_3$ in a solution of PCl_5 in dichloromethane (DCM). Under these conditions, the oligomerization proceeded quantitatively without side reactions.[17] Each oligomeric dichlorophosphazene was then treated with various aromatic nucleophiles in the presence of cesium carbonate. The cesium carbonate synthetic route[26] resulted a significantly higher substitution efficiency than the use of sodium aryloxide. However, the degree of polymerization (DP) calculated from GPC data was different from the targeted value. The discrepancy may be the result of the differences of the hydrodynamic radius between oligomers and polystyrene, which is used to calibrate GPC. Figure 1 shows typical ^{31}P NMR spectra of the synthesis of a phenoxy oligomer with 10 repeating units (**1b**), as reported in previous literature.[17]

Role of Solubility and Crystallinity in the Synthesis of Oligomeric Aryloxyphosphazenes. Aryloxyphosphazenes with electron-withdrawing functional groups like formyl, cyano, or nitro on the aromatic ring are only sparingly soluble in common organic solvents. For example, the cyclic trimers hexakis(4-cyanophenoxy)cyclotriphosphazene and hexakis(4-nitrophenoxy)cyclotriphosphazene and their cyclic tetrameric counterparts dissolve only in hot dimethyl sulfoxide (DMSO) or *N*,*N*-dimethylformamide,[27,28] while high polymeric poly[bis(4-cyanophenoxy)phosphazene] and poly[bis(4-nitrophenoxy)phosphazene] are almost insoluble in any organic solvent.[27] This insolubility is attributed to both the extended rigid structure and the high polarity of the side chains. Both factors may induce extensive side-group stacking in the solid state and thus lead to microcrystallinity and, consequently, to insolubility.[29,30] Similar behavior was found for polyphosphazenes that possess a donor−acceptor substitution pattern within the mesogenic group in side-chain liquid-crystalline polyphosphazenes.[29] Microcrystallite formation and its role in causing the precipitation of partly substituted products complicate the reaction chemistry by necessitating forcing reaction conditions to bring about complete chlorine replacement.

This study showed that the solubility of the aryloxy oligomers decreased as the number of repeating units increased. Thus, the oligomers with 6 and 10 repeating units were more soluble in common organic solvents than the oligomers with 20 and 40 repeating units. Table 2 illustrates the solubility of aryloxyphosphazenes with varied skeletal chain lengths. Specifically, most of the oligomers were soluble in DMSO either at room temperature or when heated, and all of the oligomers with 6 or 10 repeating units were also soluble in common organic solvents such as THF, DCM, and acetone. For these species, the molecular weights of oligomers with 6 and 10 repeating units could be estimated by GPC, as shown in Figure 2, and the data are shown in Table 1. However, the

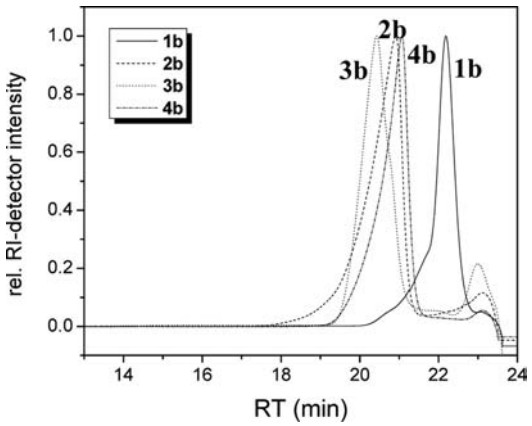

Figure 2. GPC traces of **1b**, **2b**, **3b**, and **4b**.

solubility decreased significantly as the number of repeating units exceeded 10, as illustrated in Table 2, and this limited the characterization by GPC.

Thermal Transitions. The thermal properties of the oligomers were studied by DSC analysis. The appearance of glass-like transitions in the DSC curves of short-chain linear oligomers is perhaps surprising. However, these transitions were detected at progressively higher temperatures from 0.2 to 46.5 °C with the increase in the number of repeating units probably because of the lower mobility of the oligomer chains as the chain length increased from **2a** to **2d**. Melting transitions (T_m) were also detected for **2c**, **3c**, and **4c** as the repeating units reached 20, which provided evidence for crystallinity. Typical examples are shown in Figure 3 for **2a**−**2d**. However, oligomers **2a** and **2b** with 6 and 10 repeating units, respectively, showed no T_m transitions, and this is probably the reason for the good solubility in common organic solvents. By contrast, the solubility of **2c** and **2d** decreased dramatically with the appearance of T_m transitions at 105.3 and 157.9 °C. Although microcrystallinity was also detected for the phenoxyphosphazene oligomers, this was easily disrupted by common organic solvents such as THF or DCM because of the lower relative polarity of the aryl ring, making phenoxyphosphazene oligomers more soluble than other aryloxy oligomers.

Exchange Reactions of Linear Aryloxyphosphazene Oligomers 1a−1d with Sodium Trifluoroethoxide. Earlier preliminary studies demonstrated that phenoxy side groups on both cyclotriphosphazenes and cyclotetraphosphazenes can be replaced by sodium trifluoroethoxide to generate fully substituted trifluoroethoxycyclophosphazenes.[21,22,31] These reactions are followed by an attack by excess nucleophiles on the α-carbon of the 2,2,2-trifluoroethoxy groups linked to phosphorus to give a species in which one trifluoroethoxy group has been replaced by an $-O^-Na^+$ unit.[22] However, no substituent exchange was detected with high-molecular-weight poly(diphenoxyphosphazene), and a large excess of sodium trifluoroethoxide is required to replace the phenoxy groups in nongeminal cosubsituted high polymeric $[NP(OCH_2CF_3)(OPh)]_n$.[18] Side-group steric hindrance by the phenoxy groups

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Table 1. Characterization Data of Oligomeric Organophosphazenes

compound	side group	n^a	T_g (°C)^b	T_m (°C)^b	$M_n{}^c$	DP	PDI^c	yield (%)
1a	phenoxy	6	−15.8		828	3.4	1.11	15.1
1b	phenoxy	10	−11.6		876	3.8	1.06	20.3
1c	phenoxy	20	−7.68	29.6	8975	38.8	1.05	60.5
1d	phenoxy	40	−5.68	60.4	12834	55.5	1.09	73.6
2a	formylphenoxy	6	0.21		5461	19.0	1.17	11.2
2b	formylphenoxy	10	19.11		5963	20.8	1.27	13.8
2c	formylphenoxy	20	37.8	105.3				40.5
2d	formylphenoxy	40	42.2	157.9				39.9
3a	cyanophenoxy	6	1.35		6379	22.7	1.17	25.5
3b	cyanophenoxy	10	69.0		7010	25.0	1.11	21.7
3c	cyanophenoxy	20	76.8	185.8				33.2
3d	cyanophenoxy	40	77.5	229.3				40.4
4a	nitrophenoxy	6	47.48		4095	12.7	1.24	12.9
4b	nitrophenoxy	10	62.8		4078	12.7	1.19	13.2
4c	nitrophenoxy	20	75.1	210.7				44.5
4d	nitrophenoxy	40	82.9	253.3				35.7

^{a}Repeating units. ^{b}Measured by DSC. ^{c}Measured by GPC calibrated by linear polystyrene standards.

Table 2. Solubility of Different Aryloxyphosphazenes with Varied Chain Lengths

		THF		DCM		acetone		ethyl acetate		DMSO		nitrobenzene	
	n	rt^a	heat	rt	heat	rt	heat	rt	heat	rt	heat	rt	heat
2a	6	S^b	S	S	S	S	S	P	P	S	S	S	S
2b	10	S	S	P^c	P	S	S	P	P	S	S	S	S
2c	20	I^d	I	I	I	P	S	I	I	S	S	P	S
2d	40	I	I	I	I	I	P	I	I	S	S	I	P
3a	6	S	S	I	I	S	S	P	P	S	S	P	P
3b	10	S	S	I	I	S	S	I	P	P	S	I	I
3c	20	I	I	I	I	P	P	I	I	S	S	I	I
3d	40	I	I	I	I	I	I	I	I	P	S	I	I
4a	6	S	S	I	I	S	S	I	P	S	S	S	S
4b	10	I	P	I	I	S	S	I	I	P	S	P	P
4c	20	I	I	I	I	P	P	I	I	P	P	I	P
4d	40	I	I	I	I	I	P	I	I	I	P	I	I

^{a}Room temperature. ^{b}S: soluble. ^{c}P: partially soluble. ^{d}I: insoluble.

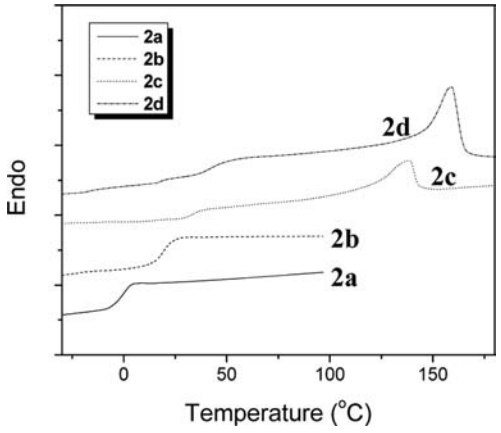

Figure 3. DSC analysis of **2a**−**2d**.

is one possible explanation for this phenomenon, in which the reactive site is well protected by the shielding effect of the phenoxy side units. Furthermore, as shown in Table 1, the T_g's of **1a**−**1d** increase from −15.8 to −5.68 °C, and the appearance of T_m when the number of repeating units reached 20 or more is also consistent with considerable steric hindrance associated with a decrease of the polymer backbone mobility and side-chain stacking. Therefore, it is reasonable that, as the molecular architecture changes from cyclotriphosphazene, cyclotetraphosphazene, and linear oligophosphazene to high-molecular-weight polyphosphazene, there may be a chain length beyond which no substituent exchange occurs because of the sequential buildup of steric hindrance by the side groups. In order to test this hypothesis, a series of exchange reactions were conducted between linear oligomeric phenoxyphosphazenes and sodium trifluoroethoxide.

In this investigation, it was found that substituent exchange reactions occur when a ratio of 1:4 was used between oligomeric phenoxyphosphazenes (**1a**−**1c**) and sodium trifluoroethoxide at reflux temperature (66 °C) in THF. As shown in Figure 4, the exchange reaction with oligomer **1a** was fast because more than 87.6% of the original phosphorus signals (−13.1 to −13.9 ppm, −18.1 to −19.1 ppm, and −22.3 to −23.0 ppm) from **1a** disappeared after 2 days of reaction. Concurrently, a new group of peaks appeared between +1.2 and −7.1 ppm from the replacement of phenoxy units by trifluoroethoxy units (Figure 4ii). However, the ^{31}P NMR spectra are too complicated to determine the exact percentage of replacement due to the multiple coupling of adjacent phosphorus atoms with different chemical environments and to their varying partially substituted patterns (geminal/non-

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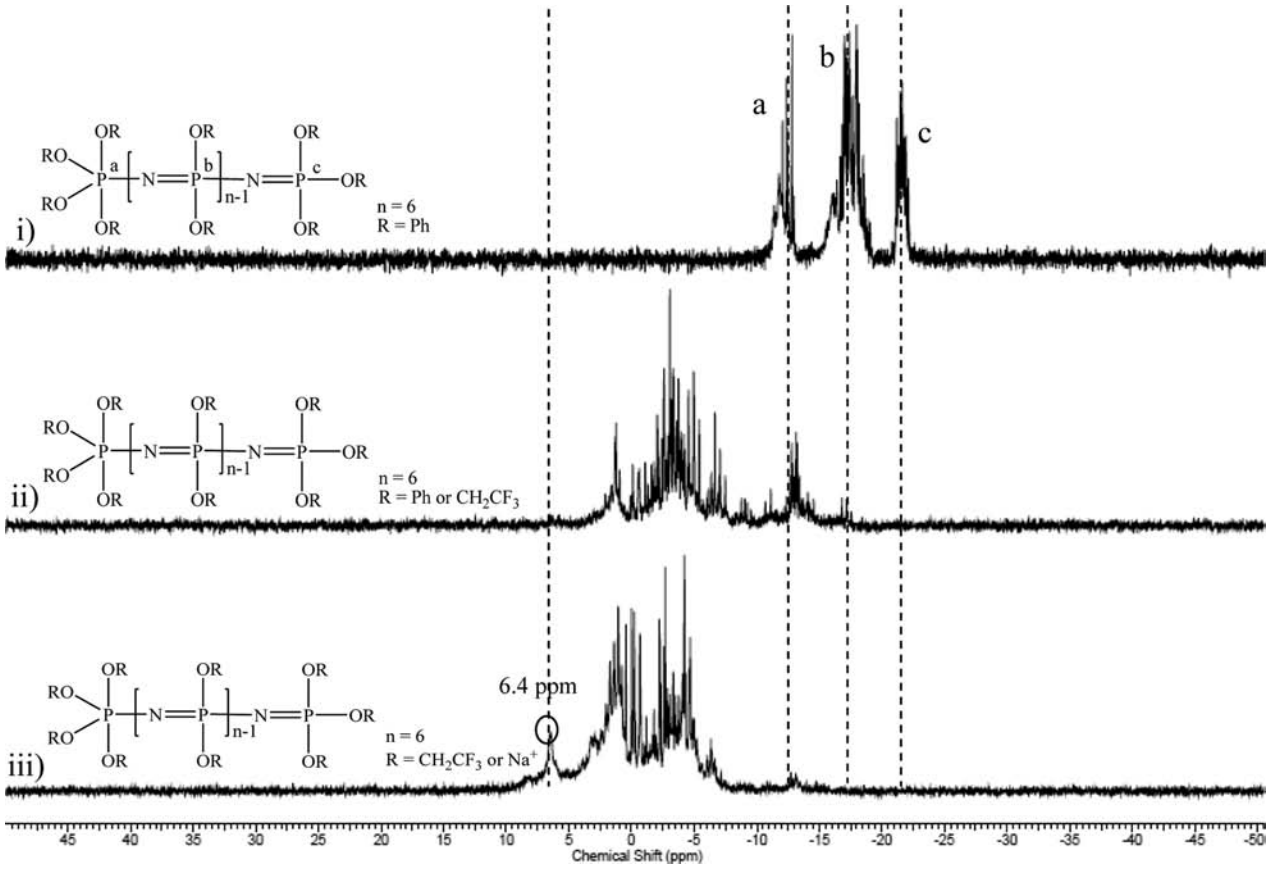

Figure 4. ^{31}P NMR spectra for the reaction between **1a** and sodium trifluoroethoxide (molar ratio 1:4): (i) 0 days; (ii) 2 days; (iii) 15 days.

geminal, cis, or trans). After 15 days of reaction, the original diphenoxyphosphazene peaks had almost completely disappeared but with the appearance of a new peak at +6.4 ppm (Figure 4iii).

Similar substituent exchange patterns were also detected from the reaction between **1b** and sodium trifluoroethoxide under the same reaction conditions. However, the substituent exchange reaction of **1c** was slightly different from that of **1a** and **1b**. For one thing, the exchange rate was slower. The original phosphorus signal could still be detected by ^{31}P NMR at −18.9 ppm after 15 days of reaction, a point when none of the P(OC_6H_5) signals remained for **1a** and **1b**. This slower substitution reaction rate may result from the gradually increasing steric hindrance as the chain length increased. Note that **1c** is the oligomer from which the first appearance of T_m was detected by DSC at 29.6 °C. Meanwhile, as in **1a**, a new peak near +6.4 ppm was also detected in the ^{31}P NMR spectra from both **1b** and **1c** after 15 days of reaction.

Influence of the End Units. In contrast to the substituent exchange reactions of **1a**−**1c**, an exchange reaction with **1d** was detected only for the end units, as shown in Figure 5. As illustrated in Figure 5i,ii, the doublet peaks (−12.4 and −12.8 ppm) originally assigned to the end units of **1d** had completely disappeared after 5 days of reaction, and new doublets appeared at −6.4 and −6.8 ppm, assigned to the trifluoroethoxy units after replacement of the phenoxy units. This preferred end-unit replacement process was not detected during the reactions of **1a**−**1c**, probably because the exchange rate at both the end and middle units occurs at the similar rates because of the weaker shielding effect of the side chains. As mentioned above, significant steric restriction is present in **1d**, as indicated by the elevated T_g (−5.68 °C) and T_m (60.4 °C), compared to **1a**−**1c**, a phenomenon clearly associated with the increased length of the chain.

The replacement rate differences between the end and middle units can be clearly differentiated in oligomer **1d**. In addition, with compounds **1a**−**1c**, as the reaction continued from 5 days (Figure 5ii) to 24 days (Figure 5iii), a new broad peak appeared at +6.8 ppm associated with the loss of trifluoroethoxy groups at the end units. This is probably the result of an attack by excess sodium trifluoroethoxide on the α-carbon of the terminal trifluoroethoxide groups. In earlier studies, this cleavage reaction was detected with both hexaphenoxycyclotriphosphazene and octaphenoxycyclotetraphosphazene.[22] In fact, the etheric side product $CF_3CH_2OCH_2CF_3$ was identified by mass spectrometry (mass = 163.01) in those reaction mixtures, thus verifying that the proposed cleavage reaction also occurs in the exchange reaction of **1d**. The similar peaks (+6.4 ppm) detected from substituent exchange reactions in **1a**−**1c** also originate from the same cleavage reactions. Scheme 3 provides a brief summary of the substituent exchange reaction of **1d** and the sequential cleavage reaction.

These results suggest that the first step in the side-group exchange reactions of the high-molecular-weight polymer may be at the end units, assuming that the end units are exposed and not buried in a convoluted conformation.

Reactions of Substituted Aryloxyphosphazene Oligomers (2a−2d, 3a−3d, and 4a−4d) with Sodium Trifluoroethoxide. All of these substituent exchange reactions followed a pattern similar to the one found for the phenoxyphosphazene oligomers (**1a**−**1d**) but with faster

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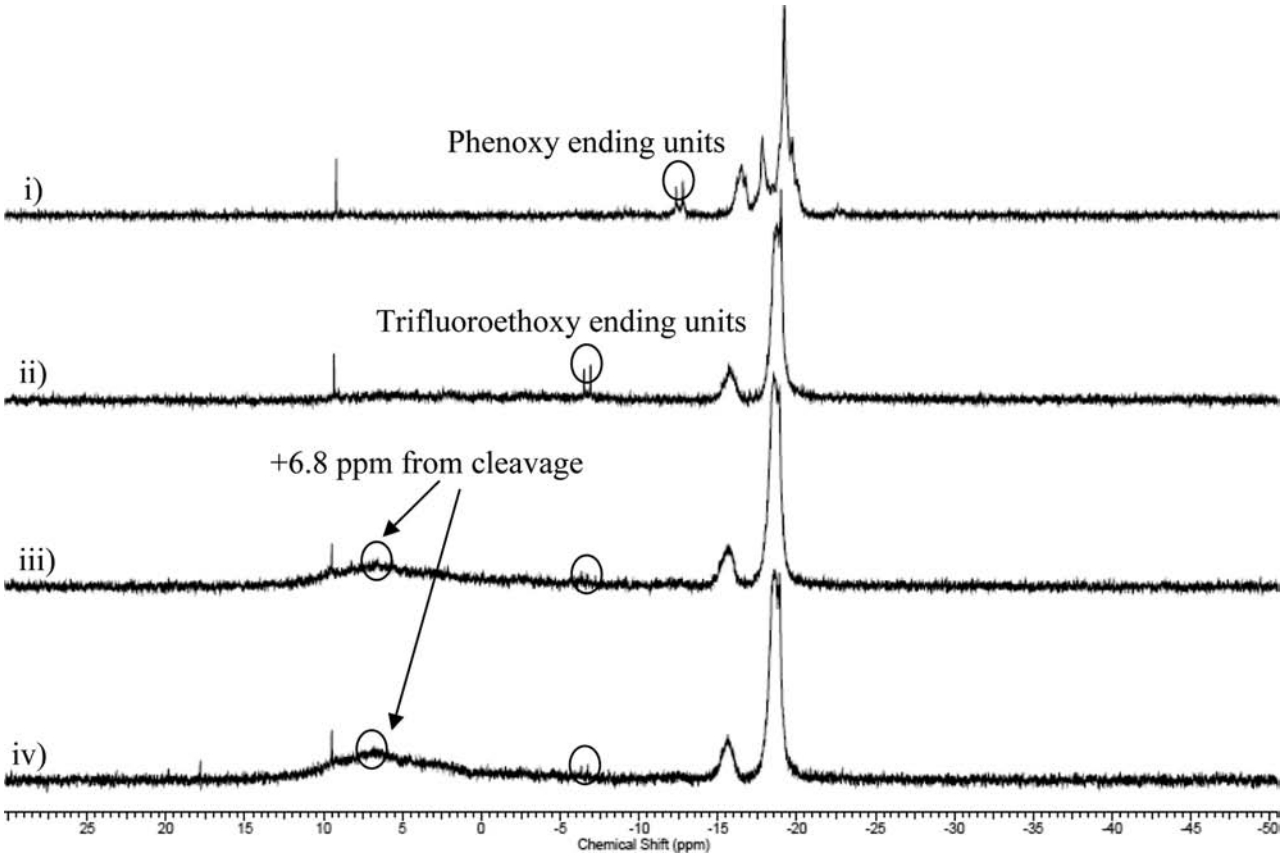
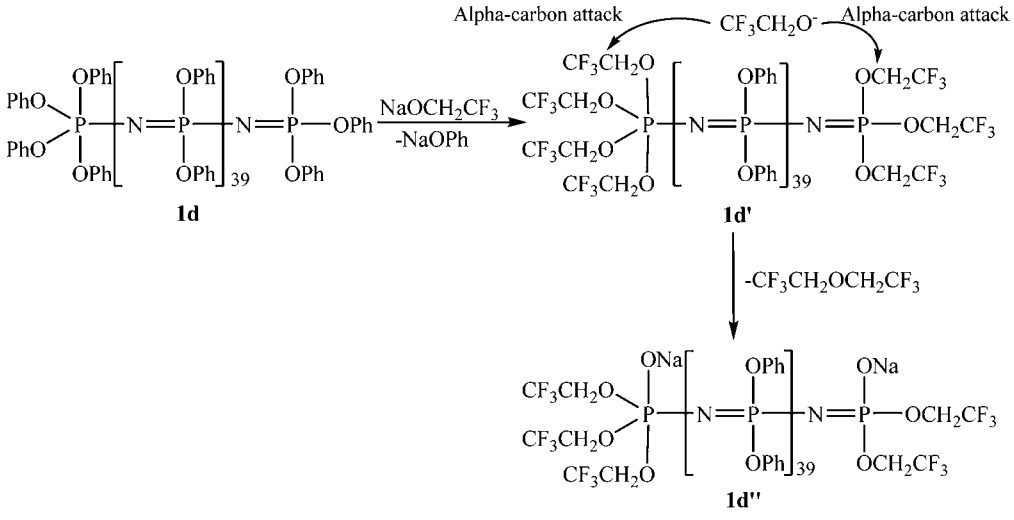


Figure 5. ^{31}P NMR spectra for the reaction between **1d** and sodium trifluoroethoxide (molar ratio 1:4): (i) 0 days; (ii) 5 days; (iii) 24 days; (iv) 32 days.

Scheme 3. Substituent Exchange Reaction Process of 1d



rates. Side-group replacement between sodium trifluoroethoxide and oligomers with 6 (**2a**, **3a**, and **4a**), 10 (**2b**, **3b**, and **4b**), and 20 (**2c**, **3c**, and **4c**) repeating units was complete within 1 day. For example, the reaction of **3c** with sodium trifluoroethoxide showed none of the original ^{31}P NMR signals after 1 day. Instead, only a major peak at −6.5 ppm from trifluoroethoxyphosphorus units was present. These replacement reactions presumably proceed much faster because of the electron-withdrawing substituent groups on the aryl rings. This renders the skeleton more electron-deficient and more liable to attack by nucleophiles. This phenomenon also occurs with the cyclic trimeric and tetrameric counterparts.[22] As with the phenoxy short-chain species, the introduced trifluoroethoxyphosphorus units on the oligomers were susceptible to nucleophilic attack by excess sodium trifluoroethoxide, leading to the formation of $-PO^{-}Na^{+}$ units, with the concurrent appearance of a new phosphrous signal near +6 ppm. However, unlike the phenoxyphosphazene oligomer **1d**, separate end-group replacement was not detected by ^{31}P NMR. However, the end-group replacement for **2d**, **3d**, and **4d** may occur, but

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because of the very low solubility of oligomers **2d**, **3d**, and **4d** in THF, it was hard to detect from the ^{31}P NMR spectra. Therefore, a general conclusion can be drawn that the ease of exchange reactions depends mainly on how well the backbone is protected by the side chains and not on physical factors such as solubility or crystallinity. For example, complete side-group replacement took place for oligomers **1a**−**1c**, **2a**−**2c**, **3a**−**3c**, and **4a**−**4c**, even though **2c**, **3c**, and **4c** are insoluble in THF and show a strong tendency for crystallinity. By contrast, **1d** shows excellent solubility in THF, but no middle unit exchange reactions were detected in the presence of sodium trifluoroethoxide. This is the same as the behavior of the high polymeric counterpart.[18] In addition, from the earlier study of small cyclic trimer and tetramer model reactions, 4-cyanophenoxy and 4-nitrophenoxy derivatives have a very limited solubility in THF, but the complete replacement of the aryloxy by trifluoroethoxy groups was still detected, with even faster rates,[22] probably because of their more open structure compared with the linear organophosphazenes, making the ring more liable to attack by nucleophiles. However, the most significant conclusion is that exchange reactions at the high polymer level appear to be modeled better by the behavior of short-chain linear counterparts than by small cyclic molecules, although these latter reactions are easier to perform.

■ CONCLUSIONS

A series of oligomeric aryloxyphosphazenes with phenoxy, 4-formylphenoxy, 4-cyanophenxy, and 4-nitrophenoxy side groups undergo substituent exchange reactions with sodium 2,2,2-trifluoroethoxide. Exchange reactions were detected for phosphazene chain lengths of 6, 10, and 20 repeating units. In this sense, the ease of displacement of OAr by CF_3CH_2O is similar to the situation for their cyclophosphazene counterparts. Fully substituted 2,2,2-trifluoroethoxyphosphazene linear oligomers were formed by side-group exchange, but these reactions are followed by an attack by trifluoroethoxide on the α-carbon of the 2,2,2-trifluoroethoxy groups linked to phosphorus to give a species in which one trifluoroethoxy group has been replaced by an ONa unit, and bis-(trifluoroethyl) ether is formed concurrently as a side product. However, when the number of repeating units exceeds 20, side-group exchange occurs only at the end groups because of the side-group steric hindrance in the middle units. Comparable reactions with phosphazene high polymers are currently underway.

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Notes

The authors declare no competing financial interest.

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