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Synthesis, Characterization, and Modification of Poly(organophosphazenes) with Both 2,2,2-Trifluoroethoxy and Phenoxy Side Groups

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ABSTRACT: High molecular weight polyphosphazenes that bear varying ratios of phenoxy and 2,2,2-trifluoroethoxy groups have been synthesized by the reactions of $(NPCl_2)_n$ with sodium phenoxide, PhO^-Na^+, and sodium 2,2,2-trifluoroethoxide, $CF_3CH_2O^-Na^+$, using either competitive or sequential exposure to the two nucleophiles. The relative amounts of $NP(OCH_2CF_3)_2$, $NP(OCH_2CF_3)(OPh)$, and $NP(OPh)_2$ units in the final polymer are dependent on both the synthesis method and the amounts of $CF_3CH_2O^-Na^+$ and PhO^-Na^+ used for the synthesis. The sequential reaction of poly(dichlorophosphazene), $(NPCl_2)_n$, with $CF_3CH_2O^-Na^+$ followed by PhO^-Na^+ yields mixtures of polymers that have different compositions depending on the presence or absence of tetra-*n*-butylammonium bromide or 15-crown-5 ether. The reactions are complicated by the fact that phenoxy groups in $NP(OCH_2CF_3)(OPh)$ units are replaced by 2,2,2-trifluoroethoxy groups at elevated temperatures or at 25 °C in the presence of either 15-crown-5 ether or tetra-*n*-butylammonium bromide. The sodium salt of 3-hydroxypropanol replaces both 2,2,2-trifluoroethoxy and phenoxy groups in these polymers at room temperature in the presence of either tetra-*n*-butylammonium bromide or 15-crown-5 ether. These side-group exchange reactions are affected by steric effects. The mechanisms of these reactions are interpreted from the perspective that the reaction of $CF_3CH_2O^-Na^+$ alone with the small-molecule model compound, $(NPCl_2)_3$, yields significant amounts of geminally substituted products in the presence of either tetra-*n*-butylammonium bromide or 15-crown-5 ether. The T_g of the mixed-substituent polymers increased as the fraction of phenoxy groups in the polymer increased. For the polymers containing equal amounts of 2,2,2-trifluoroethoxy and phenoxy groups, the polymers with the highest ratio of geminal $NP(OCH_2CF)_2$ units had the lowest T_g's.

Introduction

The widespread use of poly(dimethylsiloxane) (silicone) polymers as inert elastomers and biomedical polymers, and the recognition of their shortcomings, has stimulated a search for alternative elastomers with high solvent resistance, good energy-absorbing properties, and long-term biocompatibility. Polyphosphazenes offer some of the best alternatives to silicones,[1] mainly because the bulk and surface properties can be tuned over a very wide range by changes in the side-group structures. Moreover, surface reactions are possible that can markedly improve adhesion or biomedical interactions.

Two of the first stable polyphosphazenes synthesized and studied were poly[bis(2,2,2-trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$, and poly(diphenoxyphosphazene), $[NP(OPh)_2]_n$.[2,3] Both polymers are semicrystalline and have two first-order thermal transitions at $T(1)$ and $T(2)$.[4–9] The glass transition temperature, T_g, of $[NP(OCH_2CF_3)_2]_n$ is −66 °C, and that of $[NP(OPh)_2]_n$ is −6 °C. The $T(1)$'s of $[NP(OCH_2CF_3)_2]_n$ and $[NP(OPh)_2]_n$ are 80 and 130 °C, and the $T(2)$'s are 240 and 160 °C, respectively. Both polymers generate hydrophobic surface interactions, as determined by surface contact angles to water, and both are amenable to surface chemical reactions.[10–15] Although these two polymers are microcrystalline film- and fiber-forming species, similar polymers that bear two different types of either fluoroalkoxy or aryloxy side groups are noncrystalline elastomers.[16–20] These elastomers are used commercially both in general technology and in biomedicine.

With respect to the latter use, an early investigation of the biocompatibility and toxicity of several poly(organophosphazenes) showed that polymers with 2,2,2-trifluoroethoxy or aryloxy side groups are biocompatible and sufficiently nontoxic to be potentially useful for bioinert biomedical applications.[21]

$[NP(OCH_2CF_3)_2]_n$ and $[NP(OPh)_2]_n$ have different sets of properties and are immiscible with each other.[22] Nevertheless, materials that combine the attributes of each would be of considerable biomedical and general technological interest. Polymers cosubstituted with trifluoroethoxy and phenoxy groups may offer the combined advantages of both single-substituent macromolecules and may, in addition, provide elastomeric character due to the decreased degree of crystallinity.

The macromolecular substitution method used for the synthesis of these polymers allows mixed-substituent species to be formed by simultaneous or sequential cosubstitution reactions. In principle, this process can also lead to different arrangements of the two types of side groups along the polymer chain, depending on the reagents used and the reaction conditions employed.

In this study we have synthesized polyphosphazenes cosubstituted with 2,2,2-trifluoroethoxy and phenoxy groups using various synthesis sequences. The resulting polymers were studied to examine the effects of reaction conditions and the structure of the nucleophile on the polymer composition, preponderance of geminal versus nongeminal side-group arrangements, and physical properties. These polymers were then treated with $CF_3CH_2O^-Na^+$ or the sodium salts of diols to bring about *organic* side-group displacement reactions as a route to otherwise inaccessible polymers with additional new properties. These reactions led to the formation of products that could be examined reliably only by NMR spectroscopy, and this was the principal characterization method employed. Small-molecule model reactions were

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Scheme 1

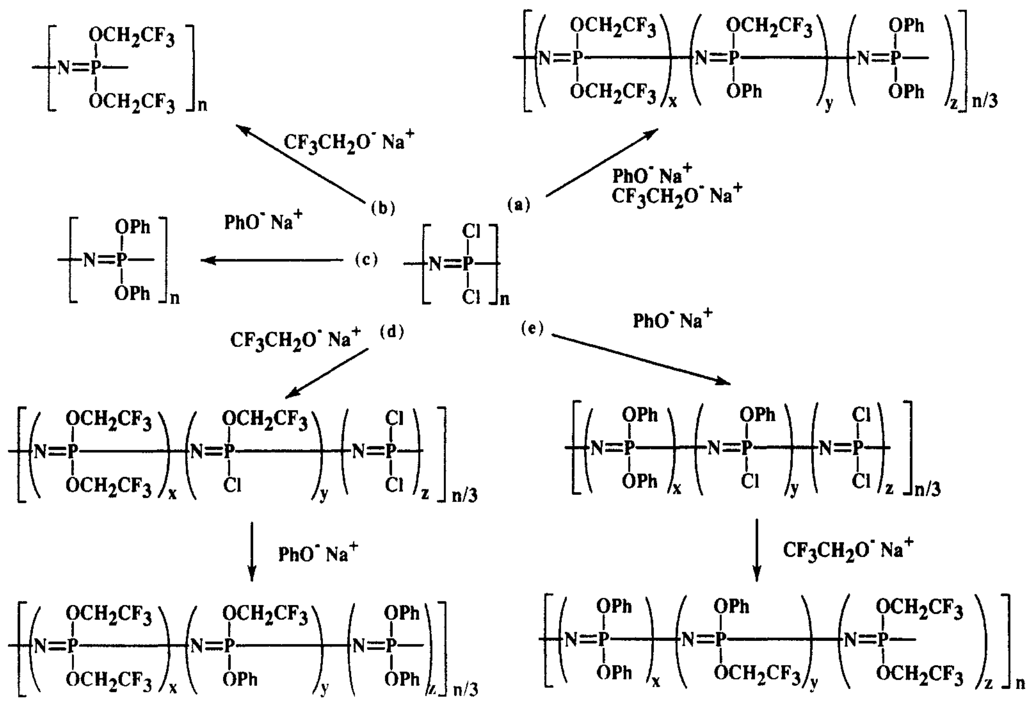


Table 1. Synthesis Methods To Prepare Polyphosphazenes Containing 2,2,2-Trifluoroethoxy and Phenoxy Groups in a Ratio of Roughly 1:1[a]

method	first nucleophile added A (equiv)	second nucleophile added B (equiv)	T(A),[b] °C	t(A),[c] h	T(B),[d] °C	t(B),[e] h
1	$CF_3CH_2O^-Na^+$ (1)	PhO^-Na^+ (1.5)	25	12	25–67	48 (25 °C) 24 (67 °C)
2	$CF_3CH_2O^-Na^+$ (1)	PhO^-Na^+ (1.5)	−78 to +25	5 (−78 °C) 12 (25 °C)	25–67	48 (25 °C) 24 (67 °C)
3	$CF_3CH_2O^-Na^+$ (1)	PhO^-Na^+ (1.5)	50	8	25–67	48 (25 °C) 24 (67 °C)
4	PhO^-Na^+ (1)	$CF_3CH_2O^-Na^+$ (1.3)	25	24	25	72
5	PhO^-Na^+ (1)	$CF_3CH_2O^-Na^+$ (1.3)	25	24	67	24
6	PhO^-Na^+ (1.2) $CF_3CH_2O^-Na^+$ (1.2)		25	72		

[a] The polymers were prepared by the sequential treatment of $(NPCl_2)_n$ first with one reagent and then with another. [b] T(A) is the temperature of reaction for the first nucleophile. [c] t(A) is the reaction time allowed for the reaction of $(NPCl_2)_n$ with the first reagent. [d] T(B) is the temperature of reaction for the second nucleophile. [e] t(B) is the reaction time following the addition of the second nucleophile.

also employed to probe the details of one of the substitution processes.

Results and Discussion

Synthesis and Composition of Polymers. (a) Competitive Reactions of Sodium 2,2,2-Trifluoroethoxide and Sodium Phenoxide with $(NPCl_2)_n$. $[NP(OCH_2CF_3)_2]_n$ and $[NP(OPh)_2]_n$ are synthesized individually either by the addition of a solution containing an excess amount of the sodium salt of the corresponding alcohol or phenol to a solution of poly(dichlorophosphazene), $(NPCl_2)_n$, or by the addition of a solution of $(NPCl_2)_n$ to the sodium salt solution (Scheme 1). The reaction of $(NPCl_2)_n$ with excess $CF_3CH_2O^-Na^+$ is rapid, with complete replacement of chlorine being achieved within 4 h at room temperature. However, the reaction of PhO^-Na^+ with $(NPCl_2)_n$ takes place more slowly, often requiring 72 h at 120 °C before total replacement of the chlorine can be achieved. The longer reaction time and the higher reaction temperature required for the complete reaction of $(NPCl_2)_n$ with PhO^-Na^+ can be explained by the more serious steric restrictions imposed by the phenoxy group.

The relative reactivities of $(NPCl_2)_n$ with $CF_3CH_2O^-Na^+$ and PhO^-Na^+ at room temperature were first estimated by the addition of a THF solution of $(NPCl_2)_n$ to a THF solution containing 4 equiv each of $CF_3CH_2O^-Na^+$ and PhO^-Na^+ (Scheme 1, reaction a). The recovered organophosphazene polymer contained 80 mol % of 2,2,2-trifluoroethoxy groups and 20 mol % of phenoxy groups as determined by ^{31}P NMR spectroscopy. This result confirms that the reaction rate of $CF_3CH_2O^-Na^+$ with $(NPCl_2)_n$ is faster than that of PhO^-Na^+, although the possibility also exists that these side-group ratios may to some degree reflect an ability by $CF_3CH_2^-$ to displace PhO^- groups introduced earlier in the reaction. In any case, it is difficult to prepare polymers with predictable compositions by the addition of $(NPCl_2)_n$ to mixtures that contain an excess of the two nucleophiles. The polymer contained 60 mol % of $NP(OCH_2CF_3)_2$ units and 40 mol % of $NP(OCH_2CF_3)(OPh)$ units based on ^{31}P NMR analysis. No $NP(OPh)_2$ units were detected.

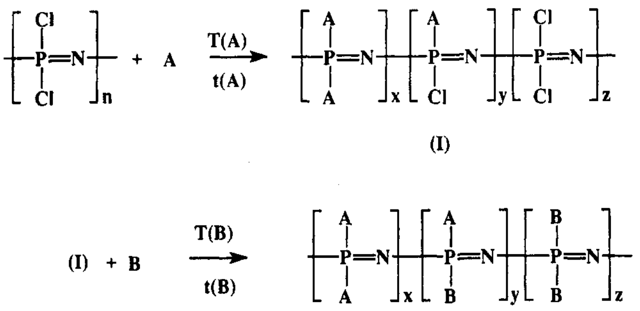
The addition of an equimolar mixture of the same two reagents to $(NPCl_2)_n$ (method 6 in Table 1 and 2) yielded a polymer with 51% trifluoroethoxy and 49% phenoxy groups. The side-group dispositions were 23% $NP(OCH_2CF_3)_2$ units, 56% $NP(OCH_2CF_3)(OPh)$ units, and 21% $NP(OPh)_2$ units, again as deduced from ^{31}P NMR spectra. Differences between the structure of this polymer and the one described above can be attributed to the much lower concentrations of the two competing reagents at the

Table 2. Compositions of Polymers Obtained by Various Methods[a]

polymer	2,2,2-trifluoroethoxy groups (mol %)	$NP(OCH_2CF_3)_2$ units (mol %)	$NP(OPh)_2$ units (mol %)	$NP(OCH_2CF_3)(OPh)$ units (mol %)	fraction of geminal substitution (%)
1	48	16	21	64	16[b]
2	49	16	18	66	17[b]
3	50	24	24	52	24[b]
4	52	15	12	73	12[c]
5	56	36	22	40	
6	51	23	21	56	19[c]

[a] Determined by ^{31}P NMR spectroscopy. [b] $([NP(OCH_2CF_3)_2]/2)/[Na^+ {}^-OCH_2CF_3] \times 100$. [c] $([NP(OPh)_2]/2)/[Na^+ {}^-OPh] \times 100$.

Scheme 2



A, B = Sodium 2,2,2-trifluoroethoxide or sodium phenoxide
T(A), T(B) = Temperature at which A or B is added
t(A), t(B) = Reaction times after A or B is added

reaction sites when the reagents are added to the solution of $(NPCl_2)_n$. This method 6 is the simplest route to synthesize polymers that have predictable compositions.

(b) Sequential Cosubstitution. An important objective was to understand the effect of reaction conditions on the formation of the three types of repeating units—$NP(OCH_2CF_3)_2$, $NP(OCH_2CF_3)(OPh)$, and $NP(OPh)_2$ units. The most probable factors that may affect the formation of these units are the reaction temperature, the inductive and steric effects of the nucleophiles, and the sequence of reagent addition to $(NPCl_2)_n$. To study these factors, polyphosphazenes that contain 2,2,2-trifluoroethoxy and phenoxy groups in an approximate ratio of 1:1 were synthesized by various reagent addition sequences (Scheme 1, reactions d and e). The reaction conditions and product polymer composition are shown in Scheme 2 and Tables 1 and 2, respectively. Polymers obtained by methods 1–6 listed in Table 1 are designated in the following text as polymers **1**–**6**, respectively.

To minimize any inhomogeneous condition that might be caused by a high local concentration of the first reagent added, reagent A was added dropwise to the $(NPCl_2)_n$ solution while the mixture was stirred vigorously. Polymers formed by the addition of 50% equivalents of A during either 2 or 60 min were identical provided the reaction mixture was stirred vigorously. The fraction of geminal substitution listed in Table 2 is defined by the fraction of A reagent molecules that reacted with preformed NP(A)(Cl) units even when unreacted $NPCl_2$ units remained. Therefore, the fraction of geminal substitution increases as more A molecules react with NP(A)(Cl).

The results listed in Tables 1 and 2 show that lowering the reaction temperature from +25 to −78 °C did not affect the geminal to nongeminal substitution ratio, since polymers **1** and **2** were essentially identical. However, an increase in the reaction temperature from 25 to 50 °C for an initial reaction with trifluoroethoxide increased the proportion of geminally $CF_3CH_2O^-$-substituted units (polymer **3**), a result that may reflect the effect of temperature increases in overcoming the small steric barriers to geminal substitution by this reagent.

On the other hand, when phenoxide ion was the initial reagent, the fraction of geminal phenoxy substitution was low (polymer **4**), a result that can be explained by the larger steric hindrance imposed by a phenoxy group in an NPCl(OPh) unit compared to that of a 2,2,2-trifluoroethoxy group in an $NPCl(OCH_2CF_3)$ unit.

Further variations in the reaction conditions for method 1 were explored by treating $(NPCl_2)_n$ with various amounts of $CF_3CH_2O^-Na^+$ and PhO^-Na^+ in sequence, and these data are listed in Table 3. The data show that the fraction of geminal substitution increases as the amount of reagent A is increased. This appears to reflect the higher probability that an NP(A)(Cl) unit will encounter another A molecule. The compositions of polymers synthesized by treating $(NPCl_2)_n$ with various amounts of PhO^-Na^+ and $CF_3CH_2O^-Na^+$ in sequence (method 4) are listed in Table 4. The results in Tables 3 and 4 show that PhO^- gives a lower fraction of geminal substitution compared to $CF_3CH_2O^-$.

Replacement of Phenoxy Groups by 2,2,2-Trifluoroethoxy Groups. In earlier work it was shown that side-group exchange is possible when $[NP(OCH_2CF_3)_2]_n$ is allowed to react with longer chain fluoroalkoxides.[23] Evidence was obtained here that the trifluoroethoxide ion can displace phenoxy groups from $NP(OCH_2CF_3)(OPh)$ units to yield $NP(OCH_2CF_3)_2$ units. For example, reactions 4 and 5 used virtually identical conditions except for the higher final temperature employed in reaction 5 (Table 1), but the reaction products were quite different. Polymer **5** contained a higher proportion of $NP(OCH_2CF_3)_2$ units and a lower proportion of $NP(OCH_2CF_3)(OPh)$ units than did **4**. Moreover, the $NP(OPh)_2$ content of **5** was much higher than in **4**. These results suggest that excess $CF_3CH_2O^-Na^+$ can replace the phenoxy groups in $NP(OCH_2CF_3)(OPh)$ units, but not in $NP(OPh)_2$ units. The following examples provide additional evidence for this phenomenon.

A reaction mixture prepared by method 4 (at 25 °C) was divided into two parts. One yielded a polymer identified by ^{31}P NMR analysis as **4**. The remaining reaction mixture was then heated at reflux (67 °C) overnight to obtain a polymer having an almost identical composition to that of polymer **5**. These results show that, at elevated temperatures, excess $CF_3CH_2O^-$ replaces phenoxy groups, but only in $NP(OCH_2CF_3)(OPh)$ units. In a separate experiment, a THF solution containing polymer **3** and 1 equiv of $CF_3CH_2O^-Na^+$ was heated to reflux. The composition change at different reaction times is shown in Figure 1 which indicates that $NP(OCH_2CF_3)_2$ units are produced at the expense of $NP(OCH_2CF_3)(OPh)$ units. Phosphorus NMR spectra of the reaction mixture showed a sharp peak at −8 ppm, attributed to $NP(OCH_2CF_3)_2$ units. This peak became larger as the replacement reaction

Table 3. Compositions of Polymers Synthesized by Method 1

polymer	$CF_3CH_2O^-Na^+$ used (mol %)[a]	trifluoroethoxy groups in the polymer (mol %)[b]	$NP(OCH_2CF_3)_2$ units (mol %)[b]	$NP(OCH_2CF_3)(OPh)$ units (mol %)[b]	$NP(OPh)_2$ units (mol %)[b]	fraction of geminal substitution
8	100	100	100	0	0	
9	90	89	77	23	0	0
10	77	79	58	42	0	0
11	68	69	42	53	5	4
12	60	57	34	46	21	17
13	57	57	28	58	14	12
1	48	48	16	64	21	17
14	46	46	17	58	25	19
15	38	41	18	42	39	22
16	25	27	9	36	54	19
17	15	18	3	30	68	8
18	0	0	0	0	100	

[a] Determined by ^1H NMR spectroscopy. [b] Determined by ^{31}P NMR spectroscopy.

Table 4. Compositions of Polymers Synthesized by Method 4[a]

polymer	phenoxy groups (mol %)	$NP(OCH_2CF_3)_2$ units (mol %)	$NP(OCH_2CF_3)(OPh)$ units (mol %)	$NP(OPh)_2$ units (mol %)	fraction of geminal substitution
19	87	0	29	72	0
20	78	0	45	55	0
21	73	0	54	46	0
22	58	6	73	21	5
23	49	15	73	12	12
24	15	70	30	0	0

[a] Determined by ^{31}P NMR spectroscopy.

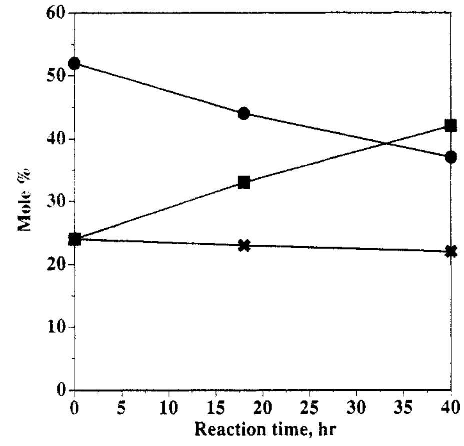


Figure 1. Mole percent of $NP(OCH_2CF_3)_2$, $NP(OCH_2CF_3)(OPh)$, and $NP(OPh)_2$ units in the polymer versus reaction time between polymer 3 and $CF_3CH_2O^-Na^+$: (●) $NP(OCH_2CF_3)(OPh)$ units; (■) $NP(OCH_2CF_3)_2$ units; (×) $NP(OPh)_2$ units.

proceeded. The ^{31}P NMR spectra of polymer 3 and the product are shown in parts a and b of Figure 2, respectively. The peak from the phosphorus in $NP(OCH_2CF_3)_2$ units in polymer 3 (Figure 2a) is broad (−7 to −13 ppm), while the newly produced peak is relatively narrow with a chemical shift around −8 ppm. the sharpness and value of the chemical shift suggest that phosphorus nuclei in the newly produced $NP(OCH_2CF_3)_2$ units are similar to those in $[NP(OCH_2CF_3)_2]_n$ which appears as a sharp singlet at −8 ppm. These results imply that the newly produced $NP(OCH_2CF_3)_2$ units form blocks, and this can happen when $CF_3CH_2O^-$ replaces phenoxy groups in $NP(OPh)(OCH_2CF_3)$ units in the vicinity of existing $NP(OCH_2CF_3)_2$ units, which is the least sterically hindered position.

Additional evidence was obtained when polymer 10, which contained 58% of $NP(OCH_2CF_3)_2$ and 42% of $NP(OCH_2CF_3)(OPh)$ units, was heated at reflux in THF (67 °C) in the presence of 3 equiv of $CF_3CH_2O^-Na^+$. No P–OPh groups were detected in the polymer after 4 days, as determined by ^{31}P NMR spectroscopy. The ^{31}P NMR spectra of polymer 10 and the product are shown in parts a and b of Figure 3, respectively. The ^{31}P NMR spectrum of the product showed a relatively narrow singlet at −8 ppm, similar to that of $[NP(OCH_2CF_3)_2]_n$. However, the physical character of this polymer was different from that

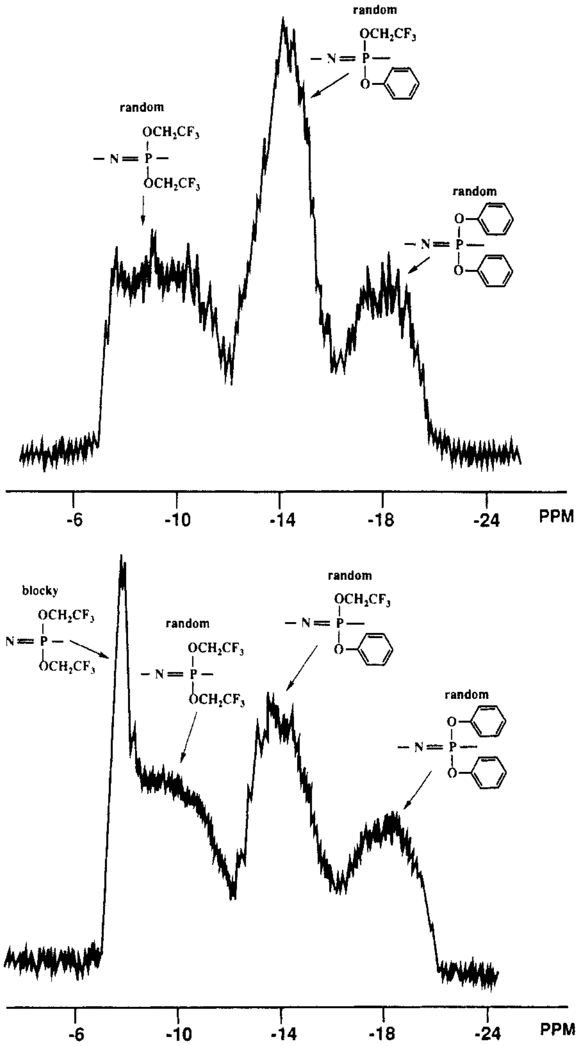


Figure 2. ^{31}P NMR spectra of (a) polymer 3 and (b) the product of the reaction of polymer 3 with $CF_3CH_2O^-Na^+$.

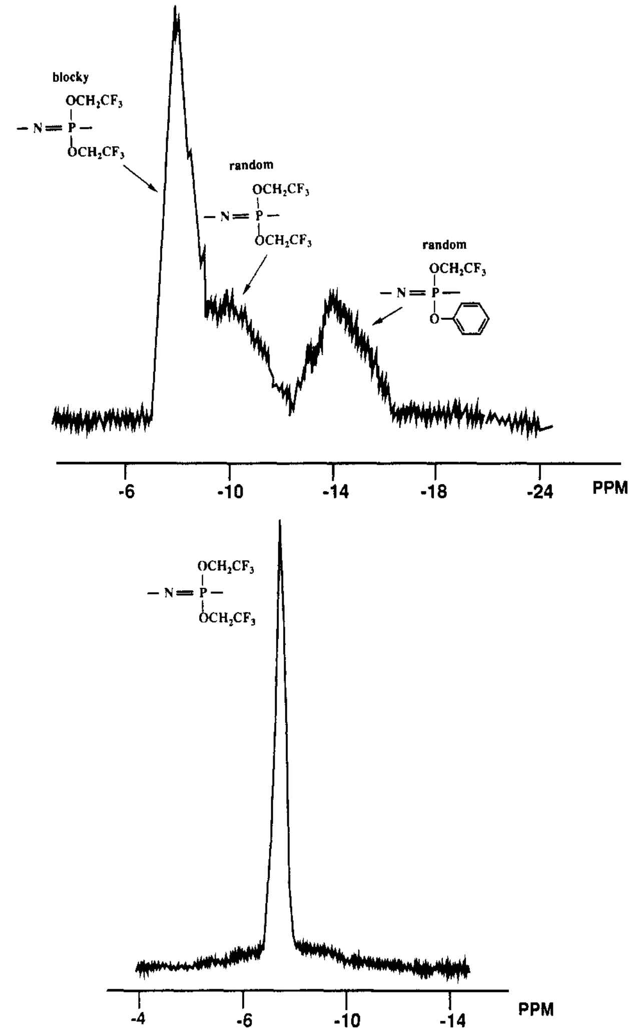


Figure 3. ^{31}P NMR spectra of (a) polymer **20** and (b) the product of the reaction of polymer **20** with $CF_3CH_2O^-Na^+$.

of samples of $[NP(OCH_2CF_3)_2]_n$ synthesized directly by the treatment of $(NPCl_2)_n$ with $CF_3CH_2O^-Na^+$. The ^{31}P NMR spectrum shown in Figure 3b is similar to that of a polymer obtained by Ferrar and co-workers by heating $[NP(OCH_2CF_3)_2]_n$ with $CF_3CH_2O^-Na^+$.[24] The change in the ^{31}P NMR spectrum was explained in that earlier work by the supposition that some of the OCH_2CF_3 groups were replaced by OH groups. Whatever the explanation, it appears that organic side-group exchange affects the polymer structure in ways other than would be expected from simple ligand exchange. Polymers isolated after organic side-group exchange reactions are generally more brittle than their counterparts that have been prepared by a more direct route. This raises general questions about the relationship of the polyphosphazene structure and properties to synthesis reaction conditions such as reagent concentrations and reaction times.

There are limits to the number of phenoxy groups that can be replaced by trifluoroethoxy groups. For example, a polymer that contained approximately 30 mol % of $NP(OCH_2CF_3)_2$, 20 mol % of $NP(OPh)_2$, and 50 mol % of $NP(OCH_2CF_3)(OPh)$ units was exposed to $CF_3CH_2O^-$. The fraction of $NP(OCH_2CF_3)_2$ units increased as the reaction with $CF_3CH_2O^-$ proceeded, while the fraction of $NP(OPh)_2$ units did not change. However, replacement of phenoxy groups by 2,2,2-trifluoroethoxy groups ceased after 72 h, but a broad ^{31}P NMR peak, centered at 4 ppm, appeared and became larger as the system was exposed to $CF_3CH_2O^-$ beyond that point. The nature of this long-term reaction is not known, but it could involve dehydroflourination from trifluoroethoxy groups, or perhaps chain cleavage.

The fact that the replacement reactions slows down markedly after a certain number of phenoxy groups in $NP(OCH_2CF_3)(OPh)$ units have been replaced suggests that $CF_3CH_2O^-Na^+$ cannot replace phenoxy groups in polymers that contain more than a certain proportion of phenoxy groups. This may reflect the steric hindrance in regions that contain high concentrations of phenoxy groups. Thus, polymers **16**, **19**, and **18**, bearing 73, 87, and 100 mol % of phenoxy groups, were heated at reflux in THF or dioxane in the presence of excess amounts of $CF_3CH_2O^-Na^+$. No change in polymer composition was detected by ^{31}P NMR spectroscopy after 4 days. This reinforces the view that steric effects control the limits of the organic side-group replacement reaction.

Effect of Tetra-*n*-butylammonium Bromide and 15-Crown-5 Ether on the Reaction between $NPCl_2$ Units and $CF_3CH_2O^-Na^+$ or PhO^-Na^+. (i) Rationale. Tetra-*n*-butylammonium bromide has been used to accelerate the synthesis of poly(organophosphazenes) that contain bulky side groups or for reactions of $(NPCl_2)_n$ with poor nucleophiles.[25] For example, sodium *p*-nitrophenoxide does not react with P–Cl bonds in the absence of tetra-*n*-butylammonium bromide, but reaction occurs in the presence of this reagent. $[NP(OPh)_2]_n$ can be synthesized at lower temperatures and with shorter reaction times in the presence of tetra-*n*-butylammonium bromide than in the absence of this reagent. These results were explained by assuming that the tetra-*n*-butylammonium counterion increases the lyophilicity and nucleophilicity of the oxyanions.

The addition of tetra-*n*-butylammonium bromide or 15-crown-5 ether to reactions of the type discussed here also provides opportunites to control the polymer molecular structure. The rationale behind this approach is as follows. When $CF_3CH_2O^-Na^+$ (sufficient to react with every chlorine atom) is added to $(NPCl_2)_n$, the replacement of chlorine is probably not completely random but is affected by the inductive and steric effects of the side groups already present. Assuming that the electron-withdrawing effect of the CF_3CH_2O group predominates, a phosphorus atom in an $NPCl(OCH_2CF_3)$ unit should be more electrophilic than in an $NPCl_2$ unit, and the regions along the polymer chain that bear the most 2,2,2-trifluorophenoxy groups should be the most electrophilic. If steric effects predominated, the substitution would proceed via a trans-nongeminal pathway. In our previous investigation of the reaction between small molecule hexachlorocyclotriphosphazene and $CF_3CH_2O^-Na^+$, it was found that 2,2,2-trifluoroethoxy groups replace chlorine atoms in a trans-nongeminal pattern.[26] This result suggests that the stereochemistry, at least at the small-molecule level, may be controlled by steric effects. However, the reaction patterns may also be influenced by the nucleophilicity of the organic anion, and this can be controlled by the use of alkylammonium halides or crown ethers. The following experiments indicate that such additives can indeed influence the structure of the final product.

(ii) Reaction with $CF_3CH_2O^-$ Only. The ^{31}P NMR spectrum of a product mixture obtained by adding 1 equiv of $CF_3CH_2O^-Na^+$ to $(NPCl_2)_n$ in THF is shown in Figure 4a. The peaks in Figure 4a are relatively broad and not well resolved, perhaps because the replacement follows a trans-nongeminal random pathway. When the same reaction was carried out in the presence of either tetra-*n*-butylammonium bromide or 15-crown-5 ether, the ^{31}P NMR spectrum of the reaction mixture contained two sharp peaks, as shown in Figure 4b. The narrow peaks in

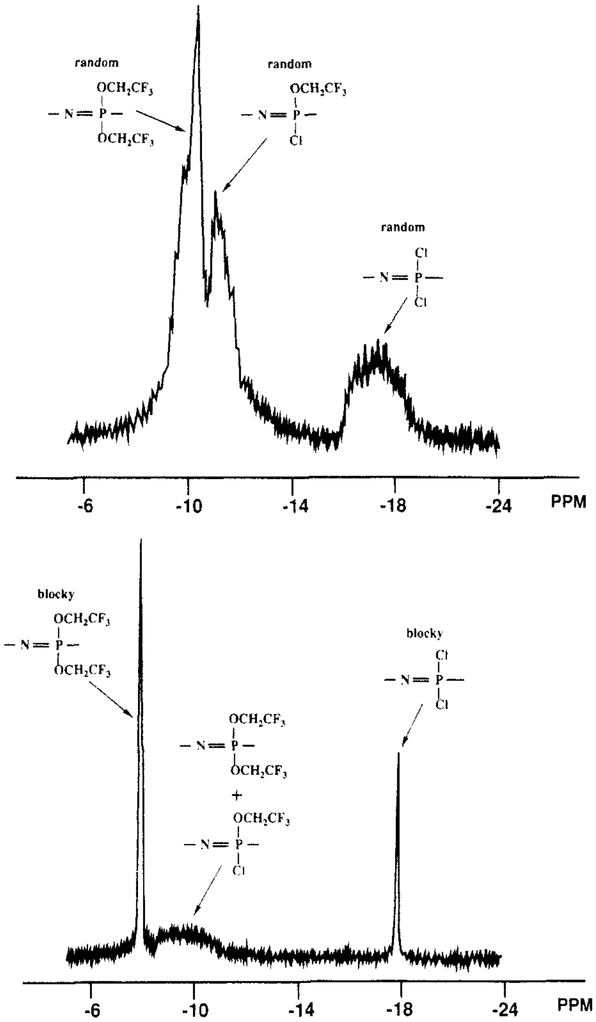


Figure 4. ^{31}P NMR spectra of polymers synthesized by the sequential treatment of poly(dichlorophosphazene) with equimolar amounts of $CF_3CH_2O^-Na^+$ and PhO^-Na^+ (a) in the absence of 15-crown-5 ether and (b) in the presence of 15-crown-5 ether.

Figure 4b can be interpreted in two different ways, (a) that the product is a homogeneous polymer containing mostly blocks of $NPCl_2$ and $NP(OCH_2CF_3)_2$ units or (b) that it is a mixture of two types of polymers that bear mainly $NP(OCH_2CF_3)_2$ or $NPCl_2$ units. The weaker broad peak at −10 ppm indicates the formation of $NP(OCH_2CF_3)Cl$ units as well. However, the spectrum is consistent with the interpretation that $NP(OCH_2CF_3)_2$ and $NPCl_2$ units are the main repeating units in one product polymer and that, in the presence of the additives, the system has discriminated against the formation of $NPCl(OCH_2CF_3)$ units.

(iii) Competitive Cosubstitution. A polymer synthesized by adding a *mixture* containing 1.2 equiv of both $CF_3CH_2O^-Na^+$ and PhO^-Na^+ to an $(NPCl_2)_n$ solution in the presence of 15-crown-5 ether contained 60 mol % of 2,2,2-trifluoroethoxy and 40 mol % of phenoxy groups. At an early stage in the reaction, the ^{31}P NMR spectrum of the reaction mixture did not show any unusual peaks, but the ^{31}P NMR spectrum of the product mixture taken after 14 h showed a small additional sharp peak at −8 ppm which indicates the formation of blocks of $NP(OCH_2CF_3)_2$ units. These results suggest that the higher fraction of 2,2,2-trifluoroethoxy groups may be the result of both the faster reaction rate of $CF_3CH_2O^-Na^+$ and the replacement of phenoxy groups by 2,2,2-trifluoroethoxy groups. These results also suggest that phenoxy groups may be replaced by trifluoroethoxy groups at room temperature in the presence of either 15-crown-5 ether or tetra-*n*-butylammonium bromide.

(iv) Sequential Cosubstitution. A polymer synthesized by the sequential reaction of $(NPCl_2)_n$ with equimolar amounts of $CF_3CH_2O^-Na^+$ and excess PhO^-Na^+ in the presence of 15-crown-5 ether was fractionated. One fraction, obtained by precipitation from methanol, contained 22 mol % of 2,2,2-trifluoroethoxy groups and 78 mol % of phenoxy groups. The unprecipitated polymer was recovered by evaporating the methanol. The recovered polymer contained 65 mol % of 2,2,2-trifluoroethoxy groups and 35 mol % of phenoxy groups. Similar results were obtained for a polymer synthesized in the presence of tetra-*n*-butylammonium bromide. These results show that 15-crown-5 ether or tetra-*n*-butylammonium bromide induces the formation of polymers that contain ratios of phenoxy and 2,2,2-trifluoroethoxy groups that are very different from those produced in the absence of these compounds. The polymers synthesized by sequential addition of PhO^-Na^+ followed by $CF_3CH_2O^-Na^+$ at 25 °C in the presence of tetra-*n*-butylammonium bromide or 15-crown-15 ether were identical to those synthesized without these additives.

(v) Small-Molecule Model Reactions. The effect of tetra-*n*-butyl ammonium bromide or 15-crown-5-ether was further investigated by comparing the reactions of the small-molecule model compound, hexachlorocyclotriphosphazene, $(NPCl_2)_3$, with various amounts of $CF_3CH_2O^-Na^+$ in the presence or in the absence of these additives. The reaction mixtures were analyzed by GC/MS, and the relative amounts of each 2,2,2-trifluoroethoxy-substituted product were determined by the peak areas. In Figures 5–8 the relative amounts of 2,2,2-trifluoroethoxy-substituted cyclotriphosphazenes obtained under various reaction conditions are shown. Figure 5 shows that the reaction of hexachlorocyclotriphosphazene with only 1 mol equiv of $CF_3CH_2O^-Na^+$, in the presence of 60 mol % of tetra-*n*-butylammonium bromide or 15-crown-5 ether, yields an unexpectedly large amount of $[NP(OCH_2CF_3)_2]_3$. Several unidentified products were also detected by GC/MS. The unknown products had molecular weights lower than that of $(NPCl_2)_3$, and some of them contained bromine or chlorine. These results correspond to those shown in Figure 5 in that no hexachlorocyclotriphos-

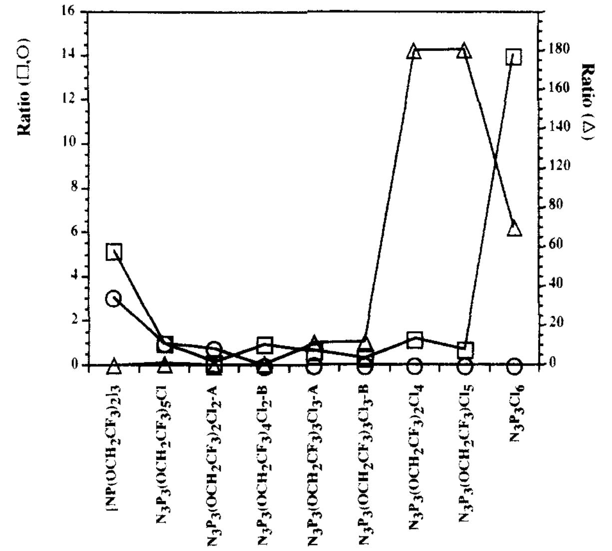


Figure 5. Ratio of cyclic trimeric products from reactions of hexachlorophosphazene with 1 equiv of $CF_3CH_2O^-Na^+$: (□) without tetra-*n*-butylammonium bromide or 15-crown-5 ether; (○) in the presence of 60 mol % of tetra-*n*-butylammonium bromide; (△) in the presence of 60 mol % of 15-crown-5 ether.

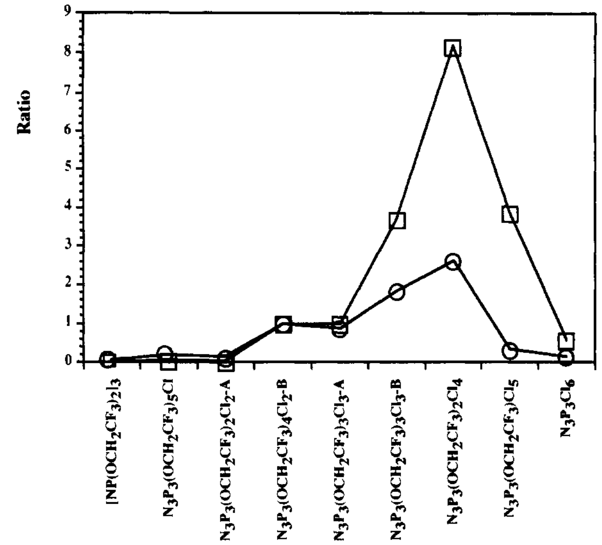


Figure 6. Ratio of cyclic trimeric products from reactions of hexachlorophosphazene with 2 equiv of $CF_3CH_2O^-Na^+$: (□) without tetra-*n*-butylammonium bromide or 15-crown-5 ether; (○) 4.9 mol % of tetra-*n*-butylammonium bromide.

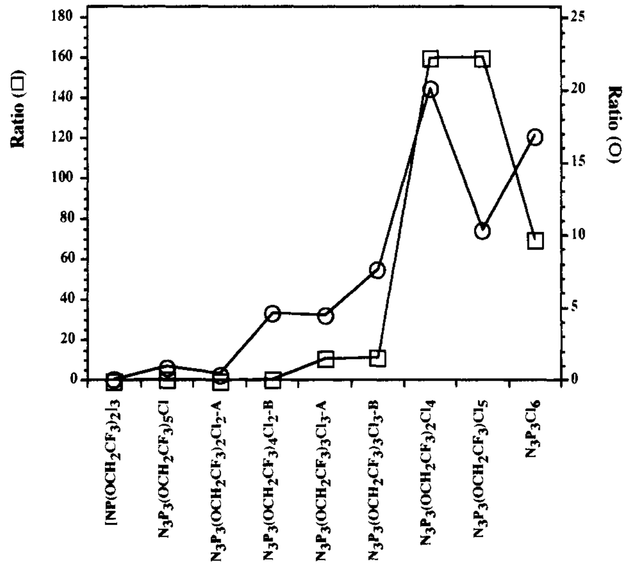


Figure 7. Ratio of cyclic trimeric products from reactions of hexachlorophosphazene with 1 equiv of $CF_3CH_2O^-Na^+$: (□) without tetra-*n*-butylammonium bromide or 15-crown-5 ether; (○) in the presence of 3.5 mol % of tetra-*n*-butylammonium bromide.

phazene remained in the reaction mixture. No such side reaction was detected when 15-crown-5 ether was used in a similar ratio. The results shown in Figures 5–8 illustrated two trends for the model reactions in the presence of tetra-*n*-butylammonium bromide or 15-crown-5 ether: (1) Products are formed that contain more 2,2,2-trifluoroethoxy groups than expected, and (2) the production of some isomers is enhanced. These isomers are probably geminally substituted products.

The role of 15-crown-5 ether or tetra-*n*-butylammonium bromide may be to increase the reactivity of the incoming nucleophiles to such a degree that the minor steric restrictions imposed by trifluoroethoxy groups already present are overpowered. This would result in larger ratio of geminal substitution. However, the ^{31}P NMR spectra of product mixtures formed in the presence of tetra-*n*-butylammonium bromide or 15-crown-5 ether were always more complicated than those obtained without these compounds. Also, the ^{31}P NMR spectra of product mixtures obtained in the presence of tetra-*n*-butylammonium bromide always showed extra peaks which were not present in mixtures obtained in the presence of 15-crown-5 ether or in the absence of additives. These results correspond to the results of GC/MS analysis.

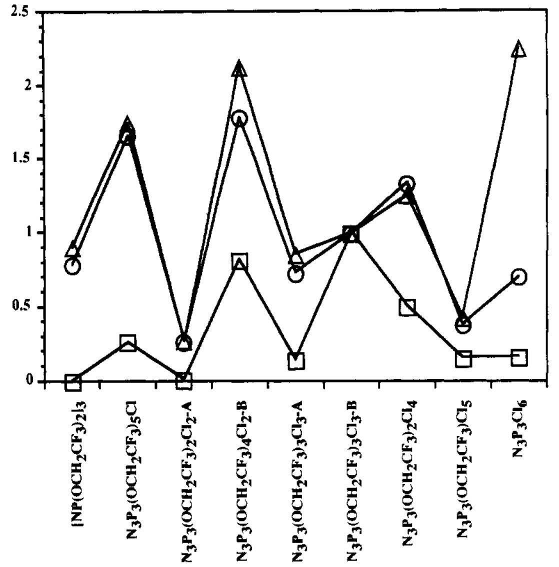


Figure 8. Ratio of cyclic trimeric products from reactions of hexachlorophosphazene with 3 equiv of $CF_3CH_2O^-Na^+$: (□) without tetra-*n*-butylammonium bromide or 15-crown-5 ether; (○) in the presence of 1.2 mol % of tetra-*n*-butylammonium bromide; (△) in the presence of 1.1 mol % of 15-crown-5 ether.

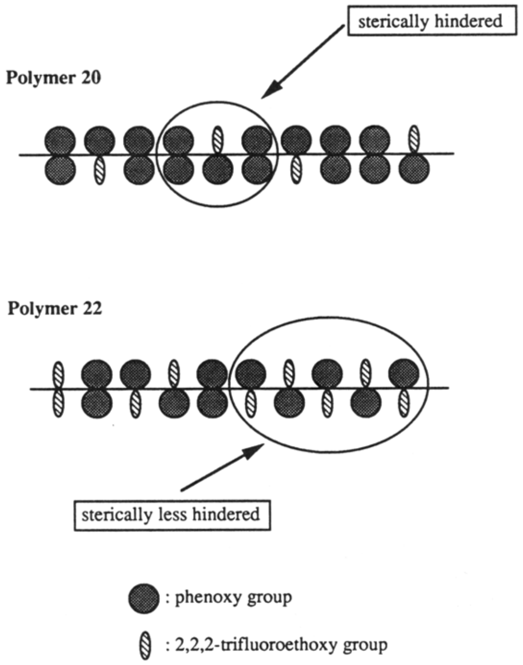
Effect of Tetra-*n*-butylammonium Bromide and 15-Crown-5 Ether on the Replacement of Phenoxy Groups by 2,2,2-Trifluoroethoxy Groups. As a control, no reaction was detected when a solution containing 15-crown-5 ether and polymer **20**, which contained 22% trifluoroethoxy and 78% phenoxy groups, was heated in boiling THF for 4 days. No reaction occurred even after tetra-*n*-butylammonium bromide was added to the same solution.

However, when polymer **22** (with 42% trifluoroethoxy and 58% phenoxy groups) was dissolved in THF in the presence of 2 equiv of $CF_3CH_2O^-Na^+$ and 0.2 equiv of 15-crown-5 ether, a sharp peak in the ^{31}P NMR spectrum at −7 ppm appeared after 10 min and no further reaction was detected after 18 h by ^{31}P NMR spectroscopy. The resulting polymer contained only 2 mol % of phenoxy groups. These results show that phenoxy groups in both $NP(OPh)_2$ and $NP(OCH_2CF_3)(OPh)$ units were replaced by trifluoroethoxy groups. The important point is that phenoxy groups in $NP(OPh)_2$ units were replaced under these conditions, but not in the absence of 15-crown-5 ether or tetra-*n*-butylammonium bromide. This is probably related to the higher reactivity of $CF_3CH_2O^-$ in the presence of 15-crown-5 ether. An explanation for the different reactivity of $NP(OPh)_2$ in polymers **22** and **20** is shown schematically in Chart 1.

Reaction of Poly[(2,2,2-trifluoroethoxy)phenoxyphosphazenes] with the Sodium Salt of 1,3-Propanediol in the Presence of 15-Crown-5 Ether. As discussed, the high reactivity of the organophosphazene polymers synthesized in this study with alkoxides in the presence of 15-crown-5 ether can be used for the synthesis of new polymers that have hitherto been inaccessible. It also opens possibilities for the linkage of other organic groups to a phosphazene chain. For example, the reaction of polymers of the types discussed above with the sodium salts of diols may cause cross-linking or yield polymers with pendent hydroxyl functional groups.

Thus, a polyphosphazene containing approximately 39 mol % of phenoxy groups and 61 mol % 2,2,2-trifluoro-

Chart 1



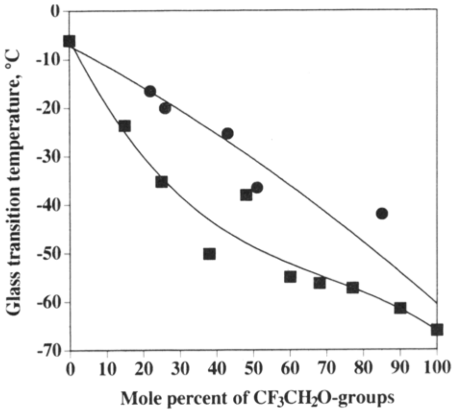


Figure 9. Glass transition temperature versus mole percent of 2,2,2-trifluoroethoxy groups in the polymer. (●) Polymers synthesized by method 4. (■) Polymers synthesized by method 1.

Table 5. First-Order Transition Data of Some Polymers

polymer	temp[a] (°C)	ΔH (J/g)	polymer	temp[a] (°C)	ΔH (J/g)
18	50	4.7	**11**	40	6.1
	78	0.7	**10**	36	4.8
16	42	0.2	**15**	21	2.8

[a] The temperature range for the DSC scan was −100 to +150 °C with a temperature of 40 °C/min. All results are from the first heating cycle.

ethoxy groups (polymer **25**) was treated for 2 h at room temperature in the presence of 0.5 equiv of 15-crown-5 ether with a suspension prepared from a reaction of 8 equiv of sodium hydride and 4 equiv of 1,3-propanediol. The resultant polymer was elastomeric and was not soluble in THF but was soluble in hot DMSO and pyridine. Thus, it was not cross-linked. A ^{31}P NMR spectrum showed that the polymer now contained approximately 33 mol % of phenoxy groups, and the ^{1}H NMR spectrum suggested the presence of approximately 16 mol % of 3-hydroxypropoxy groups. The $NP(OPh)_2$ groups were not affected by the reaction. When polymer **25** was treated for an hour with a suspension prepared from a reaction between 4 equiv of sodium, 2 equiv of 1,3-propanediol, and 0.1 equiv of 15-crown-5 ether, the fraction of phenoxy groups remaining in the polymer did not change. The recovered polymer was elastomeric and was soluble in THF. ^{1}H NMR spectra of the product indicated that the polymer contained approximately 7 mol % of 3-hydroxypropoxy groups. These results suggest that only the 2,2,2-trifluoroethoxy groups are replaced by 3-hydroxypropoxy groups under mild conditions but that phenoxy groups are also replaced under more vigorous conditions.

The greater toughness and elasticity of the product may be due to hydrogen bonding by hydroxy groups.

Physical Properties. Glass transition temperatures of the synthesized polymers are shown in Figure 9. The glass transition temperature increases as the fraction of phenoxy groups in the polymer increases. Figure 9 also shows that the T_g's of polymers synthesized by method 4 are higher than those of polymers synthesized by method 1 (which contain more geminal $NP(OCH_2CF_3)_2$ units than polymers synthesized by method 4). The lower T_g's of these polymers are most likely due to the higher fraction of $NP(OCH_2CF_3)_2$ units.

Most of the mixed-substituent polymers synthesized in this study showed negligible birefringence when observed through a polarizing optical microscope. The glass transitions of most of these polymers could not be detected by DSC analysis if the heating rate was less than 40 °C/min. This high a heating rate may lead to artificially high values of T_g, but the results are reproducible. Most of the polymers had first-order endothermic transitions between 30 and 50 °C as detected by DSC analysis. Some of the polymers showed more than one transition. The first-order transitions of some polymers within the temperature range of −100 and +150 °C are listed in Table 5.

The contact angles of water droplets on the surface of solvent-cast films of the polymers were in the range between 95° and 107°, the values for $[NP(OPh)_2]_n$ and $[NP(OCH_2CF_3)_2]_n$ respectively, with most samples having values between 98° and 104°.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was purified by recrystallization from heptane and by sublimation. The recrystallization and sublimation were repeated twice. Poly(dichlorophosphazene) was synthesized by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C.[2] Phenol was dried azeotropically with benzene and was then sublimed. Poly(dichlorophosphazene) and sodium were stored and handled in a glovebox. 2,2,2-Trifluoroethanol was treated with sodium carbonate and was then distilled and stored over molecular sieves. Tetrahydrofuran and dioxane were freshly distilled from sodium benzophenone ketyl. All the reactions were carried out under a stream of dry argon.

Synthesis of Poly[(2,2,2-trifluoroethoxy)phenoxyphosphazenes]. The relative reactivities of $CF_3CH_2O^-Na^+$ and PhO^-Na^+ were examined by adding a solution of $(NPCl_2)_n$ (1 g, 3.6 mmol, in 200 mL of THF) to a solution containing 14.4 mmol each of $CF_3CH_2O^-Na^+$ and PhO^-Na^+. Sodium 2,2,2-trifluoroethoxide and PhO^-Na^+ were synthesized by reacting 2,2,2-trifluoroethanol and phenol separately with excess amounts of sodium in THF for approximately 20 h. The polymeric reaction mixtures were stirred at room temperature for approximately 72 h. THF was removed by evaporation under reduced pressure. When the mixture became very viscous, it was added dropwise to 1 L of vigorously stirred deionized water. The precipitated polymer was recovered by filtration and was then redissolved in a minimum amount of THF. The polymer solution was reprecipitated into water to remove sodium salts until the THF solution of the recovered polymer became clear. Usually two to four reprecipitations were necessary. The polymer was finally purified by precipitation into hexane or heptane.

Polyphosphazenes cosubstituted with an equimolar amount of trifluoroethoxy and phenoxy units were synthesized as follows.

In a 1-L three-neck, round-bottomed flask, $(NPCl_2)_n$ (2 g, 17.2 mmol) was dissolved in 300 mL of dry THF. A solution of $CF_3CH_2O^-Na^+$ was prepared by adding trifluoroethanol (1.7 g, 17.2 mmol) to a 500-mL three-neck, round-bottomed flask containing sodium metal (0.5 g, 21.7 mmol) and 200 mL of dry THF. The reaction mixture was warmed gently overnight. The $CF_3CH_2O^-Na^+$ solution was transferred into a 250-mL dropping funnel using a cannular technique. The $CF_3CH_2O^-Na^+$ solution was then added dropwise to the $(NPCl_2)_n$ solution at room temperature (method 1), −78 °C (method 2), and 50 °C (method 3) during approximately 30 min. In practice, the amount of the first added nucleophile (A) was usually slightly less than the amount required to replace 50% of the chlorine atoms due to the unavoidable experimental losses of the reagent during product transfer. The reaction mixtures prepared by methods 1 and 2 were stirred for approximately 20 h before the PhO^-Na^+ solution was added. The reaction mixtures prepared by method 2 were stirred at −78 °C for 4 h and then warmed to room temperature slowly. The mixtures were stirred for an additional 18 h at room temperature. To the reaction mixtures described above were added PhO^-Na^+ solutions, prepared for phenol (2.5 g, 25.9 mmol) and sodium (0.7 g, 30 mmol) in 100 mL of dry THF, at room temperature. The reaction mixtures were then refluxed for at least for 48 h.

The synthesis of polymers by methods 4 and 5 was carried out in a similar way. In this method, 1 equiv of PhO^-Na^+ was added to $(NPCl_2)_n$ first and the reaction mixture was stirred at room temperature for approximately 36 h and then warmed for approximately 4 h to ensure maximum substitution. To this mixture was added 1.5 equiv of $CF_3CH_2O^-Na^+$, and the reaction mixture was stirred at room temperature for 18 h (method 4) or for 6 h and was then refluxed for 18 h (method 5). The product was recovered by the same procedure described above.

Polymer 6 was synthesized by the addition of a mixture of 1.2 equiv of $CF_3CH_2O^-Na^+$ and PhO^-Na^+ to a THF solution containing 1 equiv of $(NPCl_2)_n$. Polymer 7 was synthesized by adding 1 equiv of a $CF_3CH_2O^-Na^+$ solution in THF to a solution containing 1 equiv of $(NPCl_2)_n$ and 0.1 equiv of tetra-*n*-butylammonium bromide. A total of 2 equiv of PhO^-Na^+ were added to the mixture after approximately 20 h, and then the reaction mixture was refluxed for approximately 24 h.

Polymers having other compositions were prepared by following similar procedures. Polymers with more than 50 mol % of phenoxy groups were synthesized using dioxane as a solvent.

Replacement of Phenoxy Groups in $NP(OCH_2CF_3)(OPh)$ Units. A reaction mixture prepared by method 1 was divided into two fractions. One fraction was concentrated, and the polymer was isolated as described above. The other fraction was heated at reflux overnight. The reaction mixture was treated in the same manner as described above to obtain the polymeric product.

Fractionation of Polymers Synthesized in the Presence of 15-Crown-5 Ether. A total of 300 mg of a polymer synthesized by the sequential reaction of $(NPCl_2)_n$ with equimolar amounts of $CF_3CH_2O^-Na^+$ and PhO^-Na^+ was dissolved in THF and was then added dropwise to methanol. The precipitated polymer was recovered by centrifugation (89.1 mg), and the polymer still dissolved in methanol was recovered by evaporation of the methanol under reduced pressure (206.6 mg).

Reaction of Polymer 12 with Sodium Salts of 1,3-Propanediol. 1,3-Propanediol (0.7 g, 9.2 mmol) was added to a sodium hydride suspension [0.8 g (60%), 20 mmol] in 30 mL of THF. The mixture was refluxed for 36 h and was then cooled to room temperature. The remaining sodium hydride was allowed to settle out, and the upper layer of sodium salts of 1,3-propanediol was transferred by a syringe technique into a THF solution containing polymer 12 (0.5 g, 2.33 mmol) and 15-crown-5 ether (0.9 g, 4.1 mmol). The reaction mixture was agitated for 2 h, and then the mixture was concentrated by evaporation of THF under reduced pressure. The polymer was recovered by precipitation into water and hexane. A similar reaction was carried out using sodium (0.5 g, 21.7 mmol), 1,3-propanediol (1 g, 13.2 mmol), polymer 12 (1.1 g, 5.13 mmol), and 15-crown-5 ether (0.1 g, 0.45 mmol). The reaction was carried out for 1 h.

Characterization. (a) Composition and Side-Group Disposition. ^{31}P NMR analysis was used almost exclusively to determine the degree of chlorine replacement, the organic side-group ratios, and (tentatively) the presence of block structures. The fractions of $NP(OCH_2CF_3)_2$, $NP(OCH_2CF_3)(OPh)$, and $NP(OPh)_2$ units were estimated from the integration values of the corresponding phosphorus signals in ^{31}P NMR spectra. The total fractions of trifluoroethoxy and phenoxy groups were determined from ^{31}P and ^1H NMR spectra. The total fractions of trifluoroethoxy and phenoxy groups determined using these two spectra corresponded to each other within 2 mol %. Both types of NMR spectra were recorded using a Bruker WP 300 NMR spectrometer equipped with a multinuclear probe. The pulse delay was set to 5 s. Elemental analyses were obtained in a few cases to supplement the NMR data, but these provided only limited information.

(b) Molecular Weight Determination. Molecular weights of the polyphosphazenes were estimated using a gel permeation chromatography system equipped with a Hewlett-Packard 1090 HPLC system, PL gel 10^5–, 10^6-, and 10^4-Å columns, a Hewlett-Packard 1037A refractive index detector, and a Hewlett-Packard 85B data station. The eluent was THF containing 0.875 g of tetra-*n*-butylammonium bromide/1 L. A universal calibration curve was established using polystyrene standards. The GPC average molecular weights of polymers synthesized in this study were in the region of 1 000 000, and the polydispersity index was approximately 2.5.

(c) Thermal Analysis. Glass transition temperatures and melting temperatures were determined using a Perkin-Elmer DSC 7 system. In a typical run, the temperature was scanned from −120 to +90 °C with a temperature increase of 40 °C/min. The temperature was then lowered at a rate of 200 °C/min to −120 °C for the second heating cycle. Glass transition temperatures were determined from the second heating cycle. Glass transitions of some of the polymers were not detectable at lower rates of temperature increase.

Contact Angle Measurements. A contact angle goniometer (Ramé-Hart, Inc., Model 100-00) was used. The polymer films were placed in a chamber saturated with water vapor. Onto each film was placed 1 μL of deionized distilled water. The water droplets were allowed to stand for 3 min before estimation of the contact angle.

GC/MS. A Carlo Erba GC connected to Kratos MS-25 mass spectrometer and a J&W Scientific OB5 capillary column (60 m × 0.25 mm i.d.) was used. The temperature of the oven was raised from 60 to 300 °C at a rate of 20 °C/min. The temperature of the injector was 280 °C. The concentrations of the samples were 0.5–10 mg/mL, and approximately 4 μL was injected in a splitless mode.

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