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The effect of steric hindrance on the synthesis of poly(aryloxyphosphazenes) that bear bulky aryloxy substituents is discussed. The syntheses of poly(aryloxyphosphazenes) with the general formula, $[NP(OAr')_x(OAr'')_y]_n$, where OAr' and OAr'' are phenoxy, 2-methylphenoxy, 4-methylphenoxy, 2-phenylphenoxy, 3-phenylphenoxy, 4-phenylphenoxy, 4-benzylphenoxy, 4-cumylphenoxy, and 4-tert-butylphenoxy, and x+y=2, is described. These polymers were prepared by the interaction of the corresponding sodium aryloxide with poly(dichlorophosphazene) in dioxane at 150°C in an autoclave. This procedure allows the synthesis of poly(aryloxyphosphazenes) with bulky side groups while avoiding equilibration-depolymerization. The influence of side group structural parameters on the thermal transition behavior of the polymers is dicussed. The refractive indices of the polymers were measured using a modified critical angle method at λ=632 nm, and were found to vary between 1.561 and 1.686.

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POLY(ARYLOXYPHOSPHAZENE) WITH PHENYLPHENOXY AND RELATED SIDE GROUPS.

SYNTHESIS, THERMAL TRANSITION BEHAVIOR, AND OPTICAL PROPERTIES

by

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June 9, 1989

Poly(aryloxyphosphazenes) with Phenylphenoxy and Related Bulky Side Groups. Synthesis, Thermal Transition Behavior, and Optical Properties.

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Abstract: The effect of steric hindrance on the synthesis of

poly(aryloxyphosphazenes) that bear bulky aryloxy substituents is discussed.

The syntheses of poly(aryloxyphosphazenes) with the general formula

$[NP(OAr')_x(OAr'')_y]_n$, where OAr' and OAr'' are phenoxy, 2-methylphenoxy,

4-methylphenoxy, 2-phenylphenoxy, 3-phenylphenoxy, 4-phenylphenoxy,

4-benzylphenoxy, 4-cumylphenoxy, and 4-tert-butylphenoxy, and $x + y = 2$, is

described. These polymers were prepared by the interaction of the corre-

sponding sodium aryloxide with poly(dichlorophosphazene) in dioxane at 150°C

in an autoclave. This procedure allows the synthesis of

poly(aryloxyphosphazenes) with bulky side groups while avoiding

equilibration-depolymerization. The influence of side group structural

parameters on the thermal transition behavior of the polymers is discussed.

The refractive indices of the polymers were measured using a modified criti-
cal angle method at $\lambda=632$ nm, and were found to vary between 1.561 and
1.686.

A wide variety of poly(organophosphazenes) has been prepared by the replacement of the chlorine atoms in soluble poly(dichlorophosphazene) by organic nucleophiles[1] such as amines, alkoxides, or aryloxides.[2] The properties of these polymers vary widely depending on the structure of the organic substituents attached to the skeletal phosphorus atoms.[3-5] For example, different organic substituents yield low temperature elastomers,[6,7] microcrystalline materials,[2] or brittle glasses.[1] The properties of the polyphosphazene may be modified further by the incorporation of two or more different substituents (Figure 1).[8,9] Because of the large number of polymer structures available in this system, an opportunity exists to develop molecular structure-property correlations that may eventually allow the prediction of properties.

Figure 1 near here.

One objective of this work was to examine the variation in thermal transition and optical properties of poly(aryloxyphosphazenes) as a function of changes in side group structure. For example, aromatic side groups might be expected to generate high refractive indices. The use of different side groups would provide absorption or transmission in different regions of the spectrum. In addition, the types of side groups should influence the amorphous or microcrystalline character, and hence determine the transparency. Materials for linear or non-linear optical experiments should also possess a high glass transition temperature, a feature that should also depend on side group structure.

Results and Discussion.

General Factors Involved in Synthesis. In general, the glass transition temperature of a polyphosphazene increases with increasing substituent size

and rigidity.[10-12] Thus, rigid, glass-like polyphosphazenes should be accessible by the incorporation of large, rigid, sterically hindered side groups, such as aryloxy units, into the polymer. However, the complete replacement of the chlorine atoms in poly(dichlorophosphazene) by aryloxy groups is a difficult process because of steric retardation effects.[2] Thus, it was necessary to use a synthetic approach that would overcome the steric inhibition to full substitution while, at the same time, preventing thermally-induced depolymerization. In the following sections we describe a method that accomplishes this objective, and allows the preparation of highly hindered single-substituent or mixed-substituent poly(aryloxyphosphazenes).

Conventional Synthetic Procedure. Although some nucleophiles react with poly(dichlorophosphazene) at low temperatures,[13] the steric size of aryloxide ions requires more forcing reaction conditions. The traditional synthesis method[2] allows poly(dichlorophosphazene) to react with a large excess of a sodium aryloxide in a high boiling solvent, such as toluene or xylene, for 3 days or longer. At longer reaction times and elevated temperatures, the kinetically favored linear macromolecules often equilibrate to more thermodynamically stable oligomers.

Modified Synthetic Procedure. For the present studies we have used a modified synthetic procedure, originally described by Futumura, Valaitis, Lucas, Fieldhouse, Cheng, and Tate.[14] In this procedure, the halogen replacement reaction is carried out in a solvent such as dioxane with a boiling point in the 100°C/ 1 atm range, in a sealed reaction vessel at temperatures up to 150°C. For example, poly(dichlorophosphazene) in dioxane was allowed to react with four equivalents of sodium aryloxide in the presence of tetra-n-butylammonium bromide at 150°C in a stirred autoclave for 24 h to yield polymers 1-6 (Scheme I). The rate of the substitution reaction is

increased by virtue of the higher reaction temperature, and complete re-placement of chlorine by aryloxy units can be effected.

Scheme I near here

Reaction Conditions and Polymer Stability. It was first necessary to determine the stability of the phosphazene skeleton under these forcing reaction conditions. Some poly(aryloxyphosphazenes) are known to undergo molecular weight decline at temperatures as low as 100°C.[15] It was also important to ascertain if the substituted polymer undergoes molecular weight decreases <u>after</u> the halogen replacement reaction is complete but before the reaction mixture is cooled to room temperature. If this occurred, the advantages of the method would be lost.

Thus, the following experiments were performed. Two samples of $[NP(OC_6H_5)_2]_n$ were synthesized from the same batch of poly(dichlorophosphazene). The first was prepared at 100°C in refluxing dioxane (1a), and the second was synthesized with the use of an autoclave at 150°C (1b). After isolation, <u>both</u> polymers had weight average molecular weights of 1.2×10^6 (as determined by gel permeation chromatography). Thus, if depolymerization occurred in the autoclave at 150°C, it occurred at the same rate as in the reaction carried out at 100°C. This is unlikely. Polymers 1a and 1b were then dissolved in dioxane and were placed in an autoclave vessel at 150°C for 24 hours. The molecular weight of polymer 1a declined from 2×10^6 to 7×10^5, while the molecular weight of 1b remained unchanged. Thus, the polymer prepared in the autoclave appeared to have a higher thermal stability than the polymer prepared by conventional methods.

We speculate that this is a consequence of a lower concentration of unreacted chlorine remaining in **1b**.

Limits of Substituent Steric Size: Ortho-Substituted Aryloxy Groups. One goal of this investigation was to assess the steric size limit for substituents attached to a polyphosphazene chain. Aryloxy groups with substituents in the meta and para position have been attached to polyphosphazenes previously, but no fully derivatized, ortho-substituted poly(aryloxyphosphazenes) have been reported. The synthesis of $[NP(OC_6H_4CH_3-o)_2]_n$ (7) and $[NP(OC_6H_4C_6H_5-o)_2]_n$ (8) was, therefore, attempted to determine whether a high loading of o-methylphenoxy or o-phenylphenoxy groups could be introduced using the synthetic method described above.

First, several small-molecule, model compound reactions[16] were carried out in which the cyclic trimer, $(NPCl_2)_3$, and the cyclic tetramer, $(NPCl_2)_4$, were allowed to react with sodium o-methylphenoxide or with sodium o-phenylphenoxide. In all four cases, total replacement of chlorine atoms by aryloxy units occurred in the presence of tetra-n-butylammonium bromide within 48 h at 100°C.

The corresponding reactions at 150°C were then attempted at the high polymeric level with $(NPCl_2)_n$ using two equivalents of sodium o-methylphenoxide or sodium o-phenylphenoxide for each chlorine atom. Complete chlorine replacement did not occur. The concentration of the nucleophile was then increased and longer reaction times were used. Even under these forcing conditions, only 85% of the chlorine atoms in **7** and 76% of the chlorine atoms in **8** could be replaced. Remarkably, these polymers remained soluble in organic media, and did not crosslink even after repeated precipitations into water and exposure to atmospheric moisture. Less shielded P-Cl bonds would have hydrolyzed to P-OH units and formed crosslinks
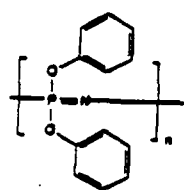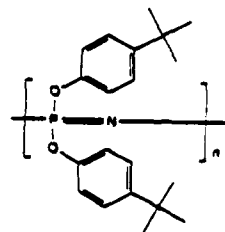
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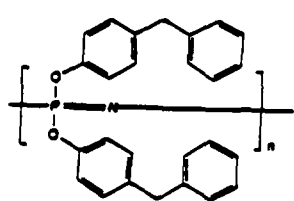
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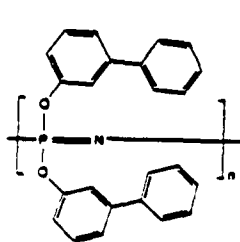**2**
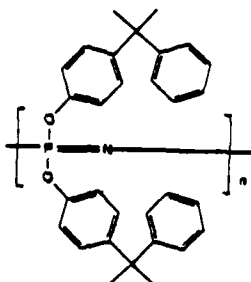
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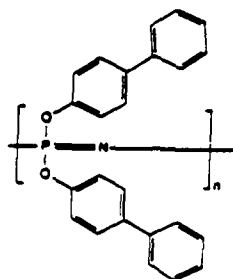**3**

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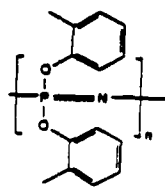
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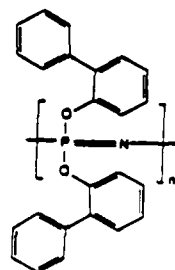
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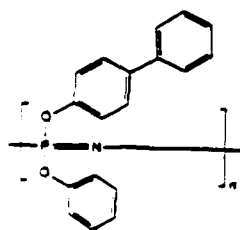
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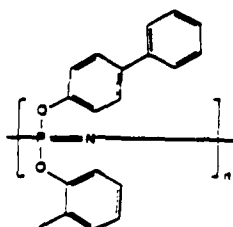
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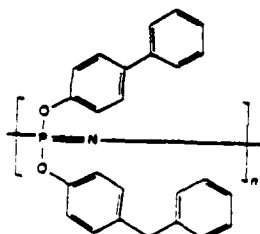
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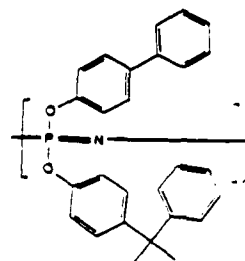
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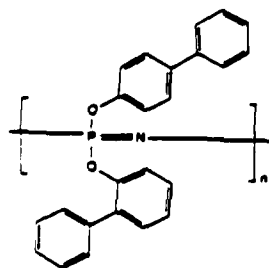
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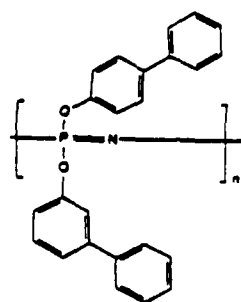
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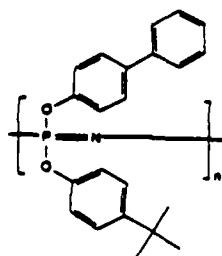
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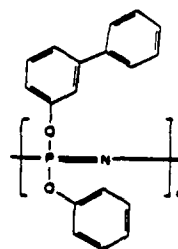
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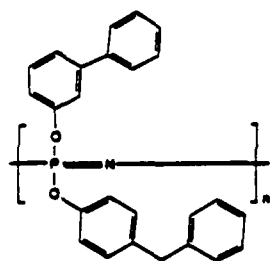
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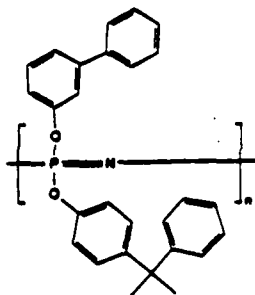
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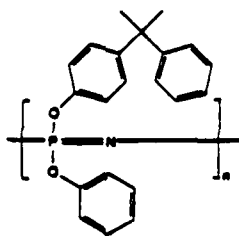
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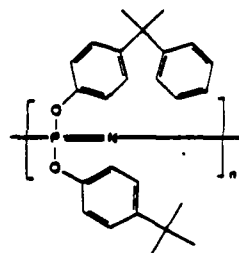
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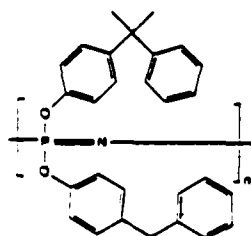
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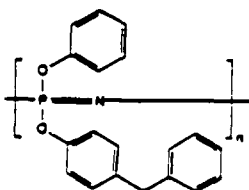
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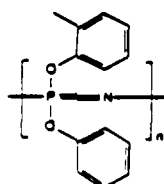
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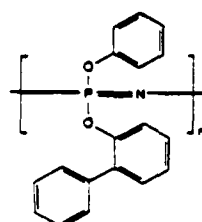
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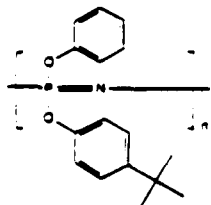
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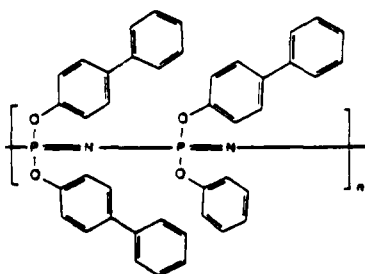
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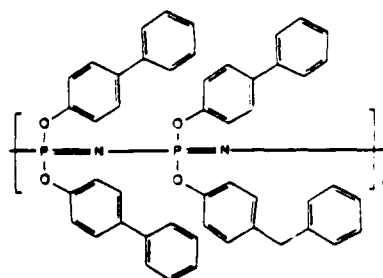
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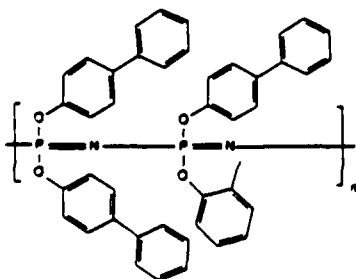
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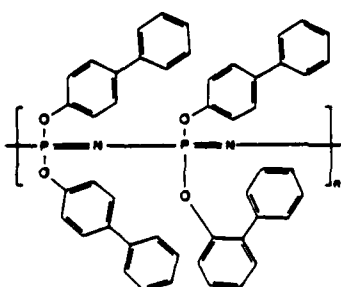
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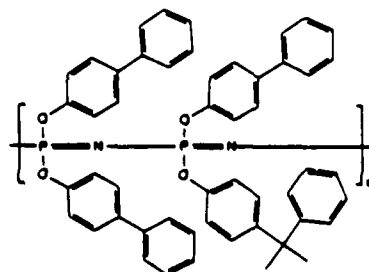
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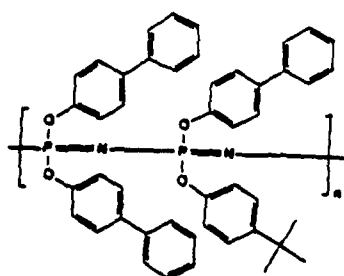
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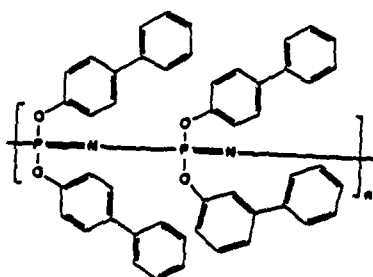
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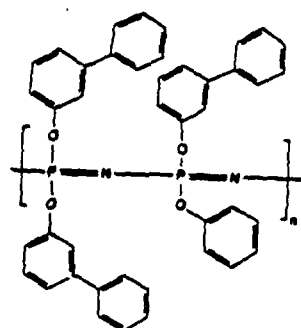
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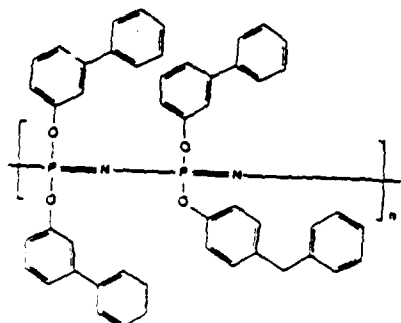
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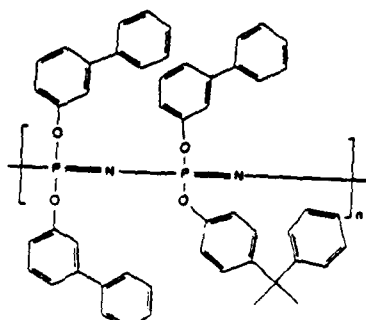
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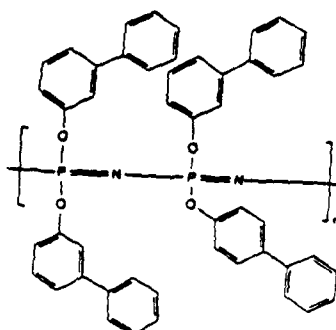
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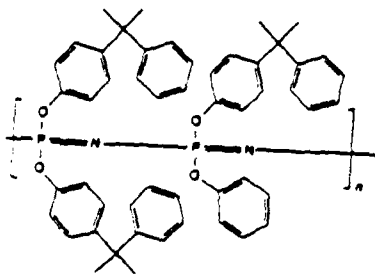
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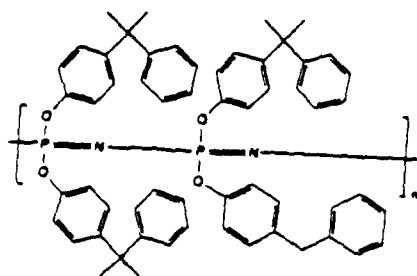
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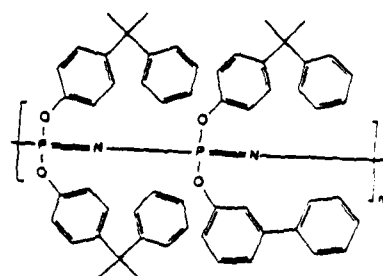
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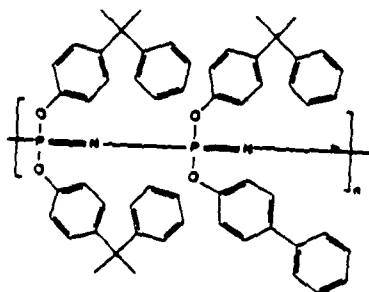
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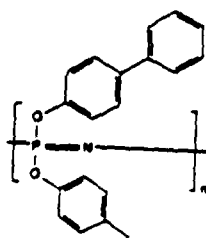
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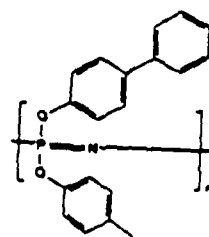
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under the same conditions. This result emphasizes the difficulty associated with replacement of a chlorine atom geminal to a bulky ortho-substituted aryloxy group even by an unhindered nucleophile such as water. For these systems, a degree of halogen replacement of 75%-85% is apparently the maximum that can be achieved using this procedure.

Reduction of Polymer Crystallinity by Preparation of Mixed-Substituent Poly(aryloxyphosphazenes). The absence of microcrystallinity is an important requirement for a polymer that is to be considered for uses in optical fibers, lenses, or non-linear optical devices. Most known single-substituent poly(aryloxyphosphazenes) are microcrystalline solids. However, it is known that the incorporation of two different substituents randomly along the phosphazene chain can disrupt and lower the symmetry of the system and the crystallinity. Some mixed-substituent poly(organophosphazenes) are elastomeric materials with low glass transition temperatures.[6,9] In this work, the challenge was to prepare polymers that would be amorphous but have high glass transition temperatures.

Two different classes of mixed-substituent poly(aryloxyphosphazenes) were prepared during the course of this investigation, with the differences being based on the ratios of the side groups (Table I). In the first series, the different side groups were present in equimolar amounts (9-25). In the second series, the side groups were present in the ratio of one to three (26-40).

Mixed-substituent polymers 9-25, which contained equal numbers of both types of side groups, were prepared in the following manner. Poly(dichlorophosphazene) was allowed to react with sufficient of the first nucleophile to replace only one half of the available chlorine atoms. The product was then treated with an excess of the second nucleophile (Scheme

I). It is probable that the initial replacement of chlorine would follow a mainly non-geminal pattern. Replacement of the remaining chlorine atoms by the second nucleophile would give a polymer with a final distribution of repeating units close to that of a non-geminal (all (OR)(OR')) distribution (See Figure 1).

In the second series, only one third of the chlorine atoms was replaced by the first nucleophile, and the remaining halogen was then replaced by an excess of the second aryloxide. The process yielded polymers **26-40**, in which the different side groups are present in a 1:3 ratio. In the ideal case, a random distribution of equal numbers of (OR)(OR) and (OR)(OR') side group pairs would be present (See Figure 1).

The mixed-substituent polymers described here were amorphous solids. Polymers **14, 21, 27, 31,** and **37** all showed one weak endothermic transition in addition to the glass transition, as revealed by differential scanning calorimetry. However, films of these polymers were not birefringent when viewed between crossed polarizers. Reports have appeared of mixed-substituent poly(aryloxyphosphazenes) that are either crystalline[8] or show evidence of crystal-crystal type phase transitions.[9]

Differences Between Sequential and Simultaneous Addition of Nucleophiles. Sequential addition of the nucleophiles is necessary in order to achieve precise control over the ultimate composition of the derivative polymer. If the halogen replacement reaction is carried out with a mixture of nucleophiles, each in excess of the amount needed for replacement of the corresponding P-Cl units, slight differences in the rates of reaction would yield polymers with a side group stoichiometry different from that of the original reagent mixture. Sequential addition of the different nucleophiles

avoids this complication, and allows the composition of the product to be inferred from the stoichiometry of the first reagent.

Polymers 41 and 42 were synthesized to compare the physical properties of species prepared using sequential or simultaneous addition of two nucleophiles. Polymer 41 was prepared by allowing poly(dichlorophosphazene) to react with one equivalent of sodium p-phenylphenoxide at 150°C for 8 h. Three equivalents of sodium p-methylphenoxide were then added and the mixture was heated to 150°C for 16 h. Polymer 42 was prepared by allowing an equimolar mixture of sodium p-phenylphenoxide and sodium p-methylphenoxide to react with poly(dichlorophosphazene) for 24 h at 150°C.

The ^{1}H NMR spectrum of 41 showed unresolved peaks for the aromatic and aliphatic protons in the ratio of 1:0.25, compared with the theoretical ratio of 1:0.23. Polymer 42 had an integrated aromatic:aliphatic ratio of 1:0.23. These data, and the results of the elemental microanalyses, suggest that the compositional differences between the two polymers are very small. However, the two polymers do show different thermal transition behavior. Polymer 41, prepared by sequential nucleophile addition, had a glass transition temperature of 42°C and an additional endothermic transition at 108°C. The T_g of polymer 42 was 46°C, with a second endothermic transition occurring at 131°C.

Differences in the pattern of substitution, or randomness of substitution, may account for the small differences in the thermal transition behavior of these polymers. For example, the pattern of substitution in polymer 42 should be more random than that of 41. In 41, the first nucleophile would be expected to react in a non-geminal pattern to give a polymer with a more regular structure.

Sequential addition of the nucleophiles was necessary when ortho-substituted aryloxy groups were incorporated into mixed-substituent poly(aryloxyphosphazenes). As discussed earlier, complete replacement of the chlorine atoms in poly(dichlorophosphazene) by ortho-substituted aryloxy groups is not possible even under forcing reaction conditions. However, polymers could be prepared in which 25% of the chlorine atoms were first replaced by o-methylphenoxy groups (28) or o-phenylphenoxy groups (29), and the remaining chlorine atoms were then replaced by p-phenylphenoxy groups. In addition, related polymers in which 50% of the chlorine atoms were replaced by o-methylphenoxy groups (10, 23) or o-phenylphenoxy groups (13, 24) have also been prepared.

Possibility of Side Group Exchange in the Substitution Reaction.
Organophosphazenes are known to undergo side group exchange reactions.[17,18]
These processes could affect the physical properties of the final polymers. The available evidence suggests that, under the conditions used here, aryloxy groups attached to the phosphazene skeleton were not displaced by different aryloxide ions during the sequential preparation of mixed-substituent polyphosphazenes. The microanalytical data for polymers 9-42, and the integrated ^{1}H NMR spectra of polymers 41 and 42 showed that the products had the composition expected based on the ratios of the reactants used in the substitution reaction.

Spectroscopic Characterization. The polymers were studied by a combination of ^{31}P and ^{1}H NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, and elemental microanalysis. The characterization data are listed in Table I. The structural examination of polymers 5, 9, and 34 will be discussed as representative examples of each class of polymer prepared.

The ^{31}P NMR spectrum of polymer 5 in THF/CDCl$_3$ consisted of a singlet centered at -20.7 ppm, and this was indicative of a high degree of chlorine replacement. Gel permeation chromatography suggested that the polymer had a high molecular weight, with a weight average molecular weight of 1.5 x 10^6 and the broad, bimodal molecular weight distribution typical of polyphosphazenes (M_w/M_n = 15). The glass transition temperature of this polymer is 37°C.

The mixed-substituent polymer 9 yielded a singlet ^{31}P NMR spectrum at -19.6 ppm, which is typical of aryloxy-substituted polyphosphazenes. Even though three different phosphorus environments are probably present, the chemical shift differences are insignificant, making line broadening negligible. The ^{1}H NMR spectrum of 9 showed only aromatic protons, and integration of the peaks did not provide information about the level of incorporation of the different side groups. However, the microanalytical data are consistent with the structure shown in Table I. Polymer 9 had a GPC weight average molecular weight of 1.5 x 10^6. This polymer had a glass transition temperature of 43°C.

The ^{31}P NMR spectrum of polymer 34 consisted of a singlet at -20.2 ppm, and the integrated ^{1}H NMR spectrum suggested that the side groups are present in the ratio of one-to-three. The elemental microanalysis was also consistent with that structure. Gel permeation chromatography suggested that the weight average molecular weight was 1.4 x 10^6, with a broad molecular weight distribution (M_w/M_n = 12). Polymer 34 had a glass transition temperature of 25°C.

Relationship Between Side Group Structure and Thermal Transition Behavior. In polyphosphazenes, as in other polymer systems, the flexibility of the skeleton defines the maximum materials flexibility that can be expected.

For example, skeletal systems that are comprised of bonds that have a high torsional barrier cannot be expected to generate materials flexibility or low temperature elasticity. The polyphosphazene skeleton (together with the polysiloxane backbone) has one of the most flexible backbones known. This undoubtedly explains why $[NPCl_2]_n$ has a T_g at -65°C,[19] and $[NPF_2]_n$ has a T_g at -96°C.[20] The low inherent barrier to backbone torsional motions, coupled with the small size of fluorine or chlorine as side groups, is presumably responsible for this behavior.[21]

However, superimposed on the character of the backbone is the influence by side groups.[22] This influence is minimal if the side group itself is highly flexible, for example, the T_g of $[NP(O(CH_2)_3CH_3)_2]_n$ is -105°C. However, rigid, bulky side groups raise the glass transition temperature markedly.[22] $[NP(OC_6H_5)_2]_n$ (1) has a T_g of -6°C, a value that is 90°C higher than that of $[NPF_2]_n$. In this work and in earlier studies,[8,9] it was found that larger aromatic side groups cause the T_g of the polymer to increase further, although not in a completely predictable manner. Moreover, the simple relationships that often hold for organic copolymers[23] seem not to apply to mixed substituent polyphosphazenes.

Any attempt to provide even a qualitative explanation of the way in which T_g values vary with side group structure must take into account a complex group of interconnected influences. We prefer to view these phenomena in terms of three types of contributions. First, side groups can restrict the torsional motions of the skeletal bonds by intramolecular interactions usually with other side groups but sometimes with skeletal atoms. The interactions may involve van der Waals- or polar-type forces. Second, intermolecular steric or polar interactions between the side groups on neighboring polymer molecules may "anchor" side chains to each other and

limit the conformational freedom of both participating molecules. An ex-
treme consequence would be the stacking of side groups from neighboring
chains,[24,25] side chain liquid crystallinity, or the generation of conven-
tional microcrystallinity. Finally, molecular asymmetry in the disposition
of side groups along the chain, especially when side groups are present with
markedly different dimensions, or when highly flexible side groups are
present, will generate free volume in the solid. This would facilitate
molecular reorientation and lead to materials flexibility. The first effect
is a purely molecular phenomenon. The second two are solid state effects.

The compounds synthesized in this present work allow an insight into
the relative importance of these three factors in aryloxy-substituted
phosphazenes. Some conclusions will be drawn first from the behavior of the
single-substituent polymers 1-8. The effect of introducing a second
substituent will then be considered.

For the single-substituent polymers 1-6 and two related polymers de-
scribed in the literature,[10] the glass transition temperature rises with
side group changes in the order: $-OC_6H_4C_2H_5$-p (44) (-18°C)[10] $< -OC_6H_5$ (1)
(-6°C) $< -OC_6H_4CH_3$-p (43) (0°C)[10] $< -OC_6H_4CH_2C_6H_5$ (2) (6°C)[26] $< -OC_6H_4C_6H_5$-m
(5) (37°C)$\approx -OC_6H_4C(CH_3)_2C_6H_5$ (3) (39°C) $< -OC_6H_4C(CH_3)_3$ (4) (50°C)[9] $<$
$-OC_6H_4C_6H_5$-p (6) (93°C). As a general trend, side groups that contained
only one aryl ring (1, 43, 44) generated lower T_g values than those that
contained two aryl units (2, 3, 5, 6). This is not surprising since
two of the influences mentioned above would be greater for the bulkier side
groups in 2, 3, 5, and 6 than for the side groups that contain only one aryl
ring.

However, the presence of an angular structure within each double-ring
side group has a distinct influence on the properties. (See, for example,

Figure 2.) The T_g value of 93°C measured for $[NP(OC_6H_4C_6H_5-p)_2]_n$ (**6**) is the highest yet found for an aryloxyphosphazene polymer.[27] Yet the meta-orientation of the two rings in **5** lowers the T_g by 56°C. Similarly, the presence of an intervening methylene unit in **2** lowers the T_g by 87°C compared to **6**, and a connecting $C(CH_3)_2$ unit in **3** lowers the transition by 54°C. We interpret these effects in terms of a high efficiency of intra- and inter-molecular packing for the linear, rigid aryl units in **6**, contrasted with the ability of the angular side groups in **2**, **3**, and perhaps **5** to undergo side chain "avoidance" motions as skeletal conformational changes occur.[28] The shape of the side groups in **2**, **3**, and **5** would also be expected to generate more free volume and hence permit more extensive molecular movement than would be possible in the case of **6**. It should be noted also that all the polymers mentioned above, except **5**, showed T_1 or T_m transitions, and this is a further indication of strong intermolecular interactions.

Figure 2 near here.

The seemingly anomolous high T_g's of polymers such as **4** that contain p-tert-butylphenoxy side groups can be understood in terms of the bulk, symmetry, and rigidity of the tert-butyl unit. The T_g of **4** is 50°C higher than the value reported for its p-methylphenoxy counterpart.

The mixed substituent polymers provide a further insight into the influence of side group structure on physical properties. First, consider the series of polymers 9-15 in which each skeletal phosphorus bears one p-phenylphenoxy side group and one other aryloxy unit. All the T_g values in this series fall within a fairly narrow range of 34°C - 57°C in spite of the broad variations in cosubstituent dimensions. In fact, if species 11 is

excluded (with its bulky but flexible cosubstituent group) the range is only from 43°C to 57°C. We intepret this to mean that the rigidity of the polymer and the intermolecular interactions are dominated by the one p-phenylphenoxy group per repeating unit. This side group is so bulky, rigid, and symmetrical that it overwhelms all other influences. Of these polymers, only 14 showed detectable crystallinity.

As the ratio of p-phenylphenoxy side groups increases from 50% to 75% of the total, the effects mentioned above become even more obvious. The overwhelming influence of the p-phenylphenoxy unit becomes manifest in the very narrow range of T_g values from 59°C to 68°C found for polymers 26-27 and 29-32. Within this series, changes in the minor cosubstituent from $-OC_6H_4C(CH_3)_2C_6H_5$ (30), through $-OC_6H_4C_6H_5$-o (29), $-OC_6H_4CH_2C_6H_5$ (27), and $-OC_6H_5$ (26), to $-OC_6H_4C_6H_5$-m (32) raises the T_g by only 5°C, a value that is close to the experimental error of the measurement. Only the t-butylphenoxy group (in 31) appears to have a significant influence as a cosubstituent. Thus, it appears that small or more flexible side groups buried within a matrix of p-phenylphenoxy units have little influence on the glass transition temperature. However, the second substituent, even in 25% concentration, may be sufficient to eliminate crystallinity.

Polymers in which 75% of the side groups are m-phenylphenoxy units (33-36) are influenced hardly at all by the shape and dimensions of the minor cosubstituent. Polymer 33-36 were all non-crystalline, and had T_g values within the range of 27°C to 38°C. The single-substituent polymer (5) (T_g = 37°C) also falls within the same range. The lower T_g values within this series are associated with the presence of minor cosubstituents such as $-OC_6H_5$ or $-OC_6H_4CH_2C_6H_5$ which probably generate free volume within the solid state matrix.

Similarly, the series of polymers **37-40** in which 75% of the side groups are $-OC_6H_4C(CH_3)_2C_6H_5$ units have T_g values that mainly reflect the size and shape characteristics of the majority side group. The crystalline single-substituent polymer (**3**) has a T_g of 39°C. Replacement of 25% of these side groups by $-OC_6H_4C_6H_5$-m units (**39**) lowers the T_g by only 6°C. The $-OC_6H_4C_6H_5$-p group lowers the T_g by 10°C, the $-OC_6H_4CH_2C_6H_5$ unit by 17°C, and the $-OC_6H_5$ group by 21°C. This last polymer is crystalline.

In earlier papers we discussed the steric influence of small side groups in terms of their influence on the torsional freedom of a polyphosphazene backbone.[21,22] However, it is clear from these present results that this simple intramolecular interpretation is no longer suffi-cient when the side groups are bulky aryloxy units. Yeung, Frank, and Singler, using excimer fluoroscence spectroscopy, found that the aryl rings of **1** and **43** were stacked at temperatures between -80°C and 150°C.[29] The formation of liquid-crystalline-type stacks of side groups,[30,31] will drastically affect the reorientational freedom of the polymer chain. Under these circumstances the solid state properties appear to be dominated by strong side group interactions and by free volume effects. In this sense, the rotational freedom of a side group becomes as important as or more important than the conformational freedom of the backbone.

Optical Properties. (a) UV/Visible and Infrared Spectroscopy of Mixed-Substituent Poly(arlyoxyphosphazenes). The optical absorption charac-teristics of polymers **1-40** were examined by UV/visible spectroscopy in solution, and by infrared spectroscopy in the solid state. No absorbances were detected in the near UV to visible region between 280 nm and 800 nm. The absorbances between 245 nm and 280 nm showed little fine structure and

are characteristic of the aromatic side groups. The phosphazene P-N skeleton

absorbs at wavelengths shorter than 180 nm[1]. No evidence was found for

extended conjugation in any of the aromatic side groups.

The infrared spectra of **1-40** showed absorbances expected for

poly(aryloxyphosphazenes). No strong absorptions were found between the C-H

stretch region (3100-2800 cm^{-1}) and the C=C stretch region (1600 cm^{-1}).

Absorbances for the P=N skeleton (1250-1200 cm^{-1}) were detected.

(b) Refractive Index Measurements. The refractive indices of polymers

1-40 were measured at λ=632nm using a modified critical angle method[32]

(Figure 3). Films of the polymers were cast on one surface of a heavy flint

glass equilateral prism, which was mounted on a calibrated rotational stage.

The films were illuminated by a HeNe laser, and the prism was rotated so

that the angle the incident beam made with the polymer-glass interface

passed through the critical angle. The apparatus was calibrated with

Figure 3 near here

poly(methylmethacrylate) and polycarbonate. Good agreement with literature

values for these polymers was obtained. However, no readily available sam-

ples of polymers with refractive indices in the range found for these

polyphosphazenes could be obtained for comparison. The refractive indices

are shown in Table I. The values vary from 1.561 (4) to 1.686 (32). In

general, the polymers with phenylphenoxy substituents only had the highest

refractive indices, values that are among the highest measured for synthetic

high polymers. This suggests that the polymers described here may be partic-

ularly useful as lenses or waveguides.

Experimental Section.

Equipment and Materials. Hexachlorocyclotriphosphazene was provided by
Ethyl Corporation. Poly(dichlorophosphazene) was prepared according to a
previously published procedure.[1] Dioxane was distilled from sodium
benzophenone ketyl under an atmosphere of dry argon before use. Tetra-n-
butylammonium bromide was dried by azeotropic removal of water from a
benzene solution, followed by recrystallization from benzene and drying
under high vacuum. Phenols were purified by distillation under reduced
pressure or sublimation, as appropriate. Manipulation of reagents before the
substitution reaction was carried out using standard Schlenk and drybox
techniques. Substitution reactions were performed with the use of a Buchi
BEP280 stirred autoclave equipped with an inert gas manifold and a Lauda
KS-6 circulator. All transfers of reagents into the autoclave were performed
under an atmosphere of dry argon using modified Schlenk techniques. ^{31}P and
^{1}H NMR spectra were recorded on a JEOL FX90Q spectrometer operated at 36.23
MHz and 89.55 MHz respectively. Molecular weights were determined using a
Hewlett-Packard HP1090 gel permeation chromatograph equipped with a refrac-
tive index detector. The samples were eluted with a 0.1% by weight solution
of tetra-n-butylammonium bromide in tetrahydrofuran, through Polymer Labora-
tories PL Gel columns. Approximate molecular weight calibrations were per-
formed using narrow molecular weight distribution polystyrene standards.
Poly[bis(trifluoroethoxy)phosphazene] samples, provided by Drs R. Singler
and G. Hagnauer of the U.S. Army Materials Technology Laboratories were used
as controls for the GPC work. These fractionated samples were of known
molecular weights as determined by GPC measurements and light scattering.
Good agreement between our GPC data and the standards was obtained.
UV/visible spectra of the polymers as solutions in tetrahydrofuran were
obtained using a Hewlett-Packard 8450A spectrometer. Infrared spectra were

recorded on a Perkin-Elmer 1710 FTIR instrument. Thin films of the polymers
were cast on NaCl plates. The refractive indices were measured using the
apparatus described in the text. The poly(methylmethacrylate) and
polycarbonate calibration standards were obtained from Aldrich. Prisms
(Spindler & Hoyer) were 30mm x 30mm equilateral heavy flint glass, with n_{632}
= 1.72309. Elemental microanalyses were obtained by Galbraith Laboratories,
Knoxville, Tennessee.

Synthesis of Poly(aryloxyphosphazenes). Poly(aryloxyphosphazenes) 1-40
were synthesized in a similar manner, but were purified differently depend-
ing on the solubility of the product polymer in various solvents at room
temperature. The reactant stoichiometries, reaction times, and method of
purification for each sample are listed in Table I.

General Preparation of Soluble Polymers (Purification Method A).
Poly(dichlorophosphazene) (5.00 g, 43.2 mmol) was dissolved in dioxane (250
ml). Solutions of the nucleophiles were prepared by the slow addition of a
dioxane solution (50 ml) of the phenol (10% mol excess) to a stirred suspen-
sion of sodium metal and tetra-n-butylammonium bromide (0.50 g, 1.5 mmol) in
dioxane (100 ml). The mixtures were heated to reflux until the sodium had
dissolved. The poly(dichlorophosphazene) solution was then transferred to
the autoclave by syringe; the solution containing nucleophile A was trans-
ferred to the autoclave and the mixture was stirred at 150°C for the time
indicated in Table 1. The mixture was then cooled to room temperature and
the solution of nucleophile B was transferred to the autoclave by syringe.
The mixture was reheated to 150°C for the times listed in Table I, and was
allowed to cool to room temperature. The contents were then removed using a
cannula. The reaction mixture was concentrated to a volume of approximately
150 ml by rotary evaporation. The product was then isolated by precipitation

from the concentrated reaction solution into distilled water. The polymer was purified further by successive precipitations from tetrahydrofuran into distilled water, until no precipitate of silver chloride was detected after the addition of several drops of aqueous silver nitrate to the precipitant solution. The product was further purified by Soxhlet extraction with methanol for 72 h, followed by Soxhlet extraction with hexanes for 72 h. The polymer was dried under high vacuum for 48 h before characterization.

General Preparation of Insoluble Polymers (Purification Method B). Those polymers that were insoluble in the reaction solvents at room temperature were prepared following the procedure outlined above, with the following modifications. After completion of the substitution reaction at 150°C, the reaction mixture was cooled to room temperature. The product precipitated from the cooled mixture and was then collected by filtration. The product was washed with large quantities of distilled water to remove occluded salts, and was purified by Soxhlet extraction with methanol for 96 h and hexanes for 96 h. The product was dried under high vacuum for 48 h before characterization.

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28. Side group rotamers have been identified from the crystal structure of $[NP(OC_6H_4-CH_3-o)_2]_4$. Allcock, H.R.; Birdsall, W.J.; Al-Shali, S.; Dembek, A.A.; Parvez, M.; Mang, M.N.; manuscript in preparation.

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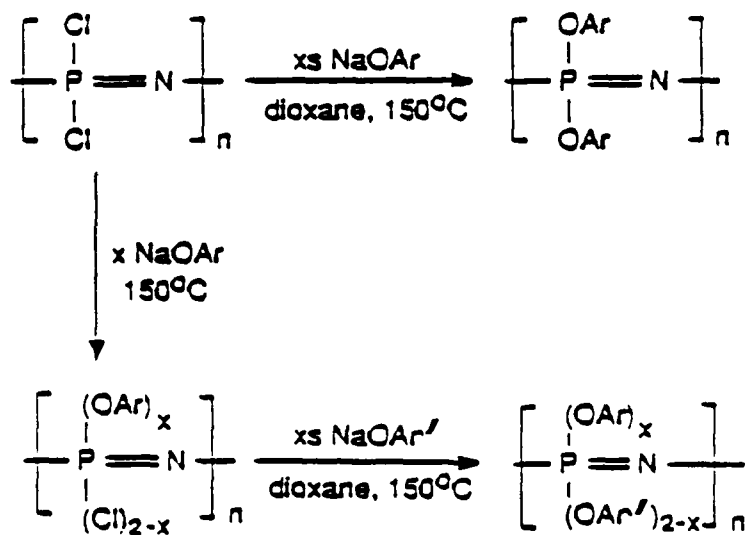32. Meeten, G.H., Ed., "Optical Properties of Polymers"; Elsevier, New York, **1986**.

Scheme I

Figure Captions

Figure 1. Possible side group distributions in mixed-substituent
polyphosphazenes. (a) Statistical distribution with equal
numbers of different side groups (OR and OR'). (b) "Ideal"
distribution with equal numbers of different side groups. (c)
"Ideal" distribution when different side groups are present in
one-to-three proportions.

Figure 2. Projection down axis of P-N bond illustrating possible side group
rotational isomers for a $[NP(OC_6H_4C_6H_5-m)_2]$ repeat unit.

Figure 3. Apparatus used for refractive index measurements.[36] HeNe laser
(A) illuminates polymer film (C) - prism (B) interface. Rotation
of prism until total internal reflection occurred allowed
calculation of critical angle θ_c.
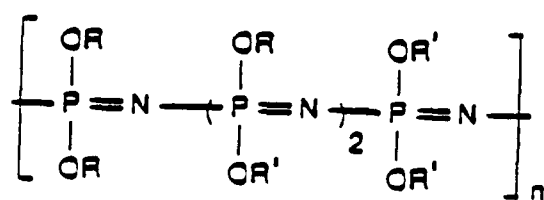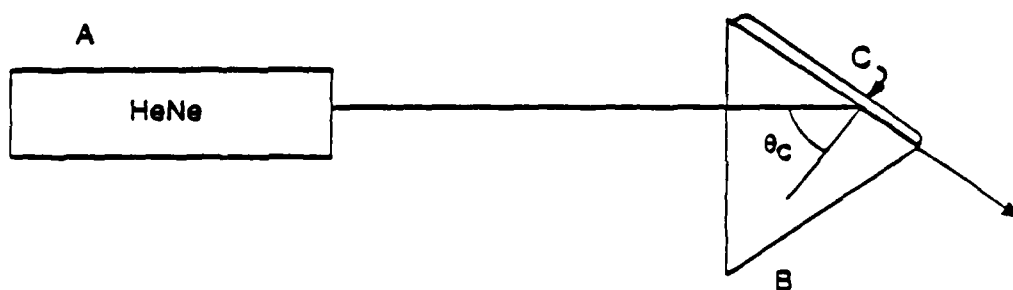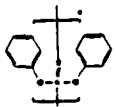
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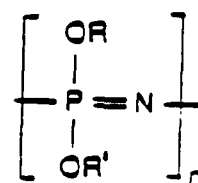
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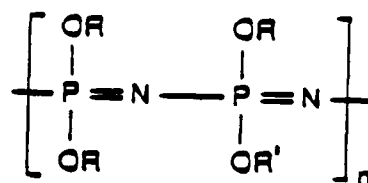
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Figure 2.
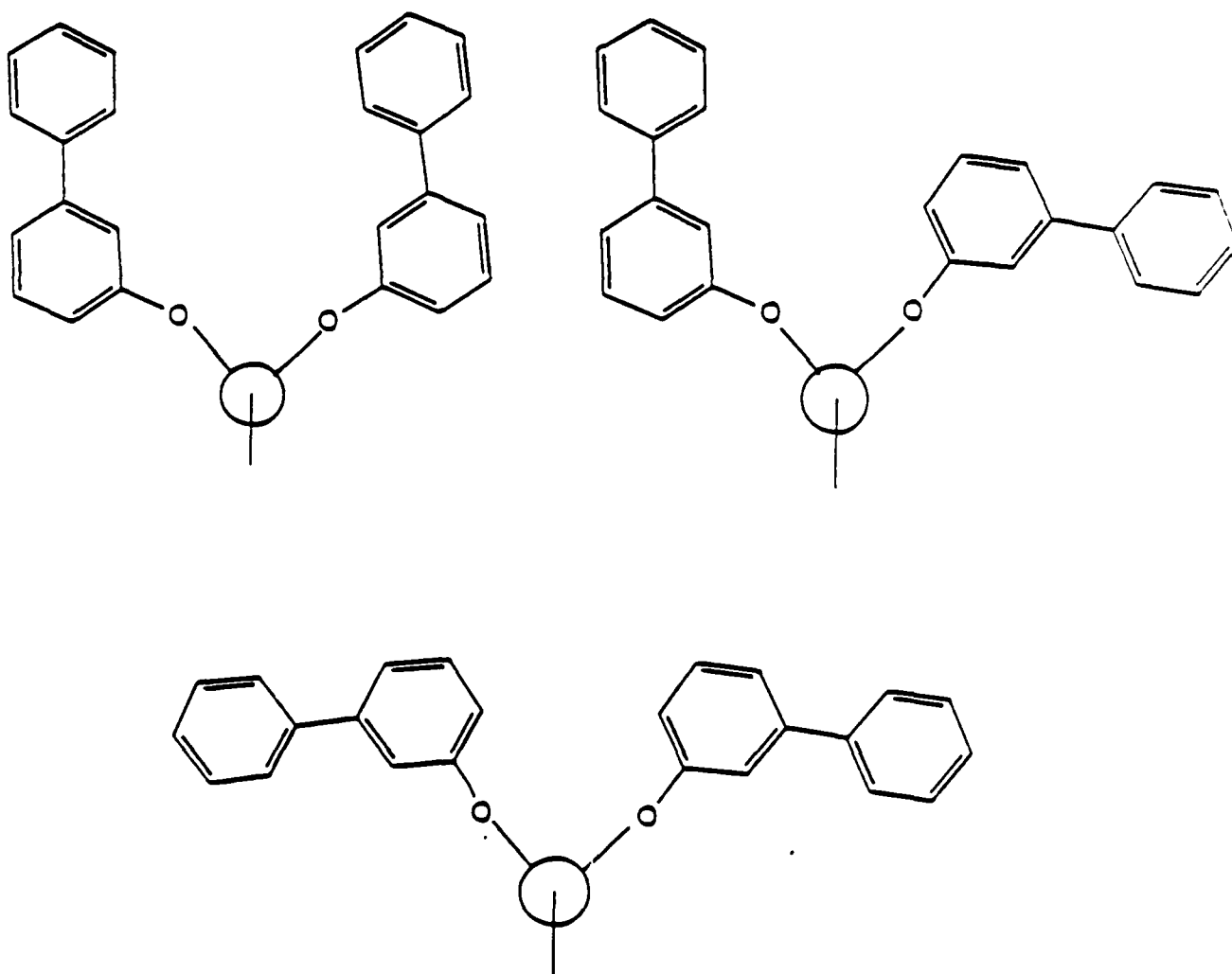
Figure 3.
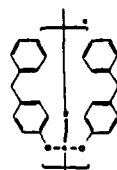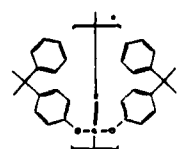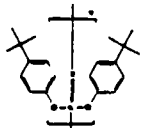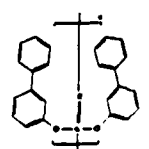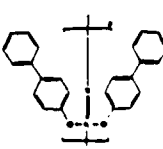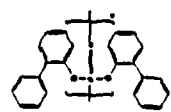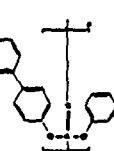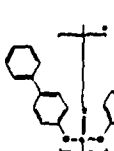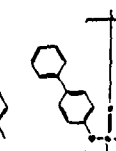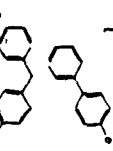
Table Captions

Table I. [a]Compounds 43-45 have been prepared previously. See reference 10.
[b]See Experimental Section. [c]THF/CDCL$_3$. [d]Complete chlorine
replacement was not achieved. Characterization data suggest that
the composition of 7 is $[NP(OC_6H_4CH_3-o)_{1.70}Cl_{0.30}]_n$, and that of 8
is $[NP(OC_6H_4C_6H_5-o)_{1.52}Cl_{0.48}]_n$. [e]Gel permeation chromatography
was not attempted on this polymer because of the large number of
residual P-Cl units.

Table I. Reaction Stoichiometries and Characterization Data for 1-42.[a]

	Reactant Stoichiometry (equiv/P=N) Nucleophile 1	Time(h)	Nucleophile 2	Time(h)	Purif Meth[b]	^{31}P shift (ppm)[c]	M_w	M_n	Elemental Analysis	Calcd	Found	T(1)	$\gamma(632\omega)$
1	4.0 NaOC$_6$H$_5$	24	-	-	A	-20.0	1.1×10^6	4.6×10^4	C H N Cl	62.36 4.33 6.06 0	61.88 4.64 5.86 0.03	147	1.619
2	4.0 NaOC$_6$H$_4$CH$_2$C$_6$H$_5$	24	-	-	A	-19.7	1.9×10^6	9.5×10^4	C H N Cl	75.93 5.35 3.41 0	75.61 5.34 3.30 0.16	11	1.639
3	4.0 NaOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_5$	24	-	-	B	-	-	-	C H N Cl	77.11 6.42 3.00 0	76.12 5.84 3.01 0.90	119	1.614
4	4.0 NaOC$_6$H$_4$C(CH$_3$)$_3$	24	-	-	A	-19.0	2.5×10^6	1.5×10^5	C H N Cl	69.95 7.63 4.08 0	69.80 7.28 4.04 <0.50	135	1.561
5	4.0 NaOC$_6$H$_4$C$_6$H$_5$-m	24	-	-	A	-20.7	1.5×10^6	1.0×10^5	C H N Cl	75.22 4.70 3.66 0	75.26 4.98 3.55 0.03	-	1.657
6	4.0 NaOC$_6$H$_4$C$_6$H$_5$-p	24	-	-	B	-	-	-	C H N Cl	75.22 4.70 3.60 0	74.77 4.55 3.68 0.01	-	-

Reactant Stoichiometry (equiv/P=N)

	Nucleophile 1	Time(h)	Nucleophile 2	Time(h)	Purif Meth[b]	^{31}P shift (ppm)[c]	M_w	M_n		Elemental Analysis Calcd	Found	(T(1))	n(632n)
7[d]	20.0 $NaOC_6H_4CH_3$-o	67	-	-	B	-22.0, br	1.7×10^6	7.0×10^4	C H N Cl	64.86 5.41 5.40 0	59.62 5.30 5.62 4.10	—	1.594
8[d]	16.0 $NaOC_6H_4C_6H_5$-o	84	-	-	A	-24.0, br	°	-	C H N Cl	75.22 4.70 3.66 0	63.89 4.52 5.02 5.02	—	1.646
9	1.0 $NaOC_6H_4C_6H_5$-p	8	3.0 $NaOC_6H_5$	16	A	-19.6	1.5×10^6	4.7×10^4	C H N Cl	70.13 4.90 4.54 0	69.61 4.78 4.52 0.13	—	1.646
10	1.0 $NaOC_6H_4CH_3$-o	24	3.0 $NaOC_6H_4C_6H_5$-p	24	A	-19.9	1.1×10^6	1.2×10^5	C H N Cl	70.02 5.02 4.36 0	69.98 4.85 4.37 0.65	—	1.627
11	1.0 $NaOC_6H_4CH_2C_6H_5$	8	3.0 $NaOC_6H_4C_6H_5$-p	16	A	-19.1	1.5×10^6	1.1×10^5	C H N Cl	75.57 5.04 3.51 0	71.40 5.36 3.26 0.04	—	1.649
12	1.0 $NaOC_6H_4C(CH_3)_2C_6H_5$	8	3.0 $NaOC_6H_4C_6H_5$-p	16	A	-18.9	1.1×10^6	5.5×10^4	C H N Cl	76.25 5.64 3.29 0	75.39 5.61 3.34 0.30	—	1.635

Reactant Stoichiometry (equiv/P-N)

#	Nucleophile 1	Time(h)	Nucleophile 2	Time(h)	Purif Meth[b]	^{31}P shift (ppm)[c]	M_w	M_n		Elemental Analysis Calcd	Found	T(t)	n(632)
13	1.0 NaOC$_6$H$_4$C$_6$H$_5$-p	18	12.0 NaOC$_6$H$_4$C$_6$H$_5$-o	72	A	-22.0,br	1.2x10^6	2.5x10^5	C H N Cl	75.19 4.73 3.65 0	74.80 5.25 3.29 0.82	—	1.617
14	1.0 NaOC$_6$H$_4$C$_6$H$_5$-m	18	3.0 NaOC$_6$H$_4$C$_6$H$_5$-p	24	A	-19.2	8.9x10^5	5.1x10^4	C H N Cl	75.22 4.70 3.66 0	74.38 4.83 3.25 0.14	121	1.66?
15	1.0 NaOC$_6$H$_4$C(CH$_3$)$_3$	8	3.0 NaOC$_6$H$_4$C$_6$H$_5$-p	16	A	-18.4	2.5x10^6	1.5x10^5	C H N Cl	72.75 6.06 3.86 0	72.91 5.58 3.44 0.06	—	1.613
16	1.0 NaOC$_6$H$_4$C$_6$H$_5$-m	8	3.0 NaOC$_6$H$_5$	16	A	-20.5	1.0x10^6	4.8x10^4	C H N Cl	70.13 4.90 4.54 0	70.83 4.64 4.31 0.10	—	1.619
17	1.0 NaOC$_6$H$_4$C$_6$H$_5$-m	8	3.0 NaOC$_6$H$_4$CH$_2$C$_6$H$_5$	16	A	-19.9	9.2x10^5	1.2X10^5	C H N Cl	75.59 5.03 3.53 0	75.45 4.90 3.48 0.15	—	1.644
18	1.0 NaOC$_6$H$_4$C$_6$H$_5$-m	8	3.0 NaOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_5$	16	A	-19.9	2.0x10^6	1.5x10^5	C H N Cl	76.25 5.64 3.29 0	76.17 5.79 3.12 0.09	—	1.629
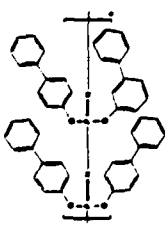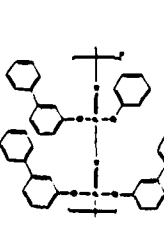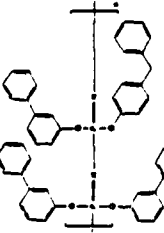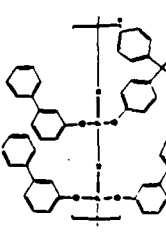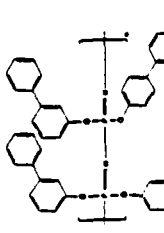
Reactant Stoichiometry (equiv/P=N)

#	Nucleophile 1	Time(h)	Nucleophile 2	Time(h)	Purif Meth[b]	^{31}P shift (ppm)[c]	M_w	M_n		Elemental Analysis Calcd	Found	T(1)	n(632.)
19	1.0 NaOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_5$	8	3.0 NaOC$_6$H$_5$	16	A	-20.0	1.2x10^6	4.6x10^4	C H N Cl	72.23 / 5.73 / 4.01 / 0	71.80 / 5.06 / 3.87 / 0.31	—	1.613
20	1.0 NaOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_5$	8	3.0 NaOC$_6$H$_4$C(CH$_3$)$_3$	16	A	-19.5	1.4x10^6	9.5x10^4	C H N Cl	74.05 / 6.96 / 3.46 / 0	73.98 / 6.52 / 3.35 / 0.05	—	1.588
21	1.0 NaOC$_6$H$_4$C(CH$_3$)$_2$C$_6$H$_5$	8	3.0 NaOC$_6$H$_4$CH$_2$C$_6$H$_5$	16	A	-19.7	1.6x10^6	9.5x10^4	C H N Cl	76.56 / 5.92 / 3.19 / 0	76.69 / 6.05 / 2.94 / 0.11	140	1.619
22	1.0 NaOC$_6$H$_4$CH$_2$C$_6$H$_5$	8	3.0 NaOC$_6$H$_5$	16	A	-20.0	1.5x10^6	9.7x10^4	C H N Cl	71.02 / 4.98 / 4.36 / 0	70.25 / 5.13 / 4.21 / 0.18	—	1.621
23	1.0 NaOC$_6$H$_4$CH$_3$-o	18	3.0 NaOC$_6$H$_5$	24	A	-20.9	8.5x10^5	4.1x10^5	C H N Cl	63.67 / 4.93 / 5.71 / 0	62.73 / 4.88 / 5.87 / 0.86	—	1.609
24	1.0 NaOC$_6$H$_4$C$_6$H$_5$-o	18	3.0 NaOC$_6$H$_5$	24	A	-24.2,br	9.6x10^5	1.2x10^5	C H N Cl	70.35 / 4.59 / 4.56 / 0	69.14 / 5.26 / 4.44 / 2.34	—	1.631
25	1.0 NaOC$_6$H$_4$C(CH$_3$)$_3$	8	3.0 NaOC$_6$H$_5$	16	A	-19.8	7.7x10^5	9.0x10^4	C H N Cl	66.89 / 6.32 / 4.88	66.52 / 6.51 / 4.57 / 0.33	—	1.571

Reactant Stoichiometry (equiv/P=N)

#		Nucleophile 1	Time(h)	Nucleophile 2	Time(h)	Purif Meth[b]	^{31}P shift (ppm)[c]	M_w	M_n	Elemental Analysis	Calcd	Found	T(1)	n(63..)
26		0.5 $NaOC_6H_5$	8	5.5 $NaOC_6H_4C_6H_5$-p	16	B	-	-	-	C H N Cl	73.06 4.64 4.06 0	70.67 4.28 3.92 0.01	—	1.65
27		0.5 $NaOC_6H_4CH_2C_6H_5$	8	3.5 $NaOC_6H_4C_6H_5$-p	18	B	-	-	-	C H N Cl	75.40 4.87 3.59 0	75.28 4.91 3.53 0.17	152	1.661
28		0.5 $NaOC_6H_4CH_3$-o	24	3.5 $NaOC_6H_4C_6H_5$-p	96	A	-18.8	3.8×10^5	1.0×10^5	C H N Cl	73.29 4.86 3.98 0	72.06 5.13 3.86 0.17	—	1.654
29		0.5 $NaOC_6H_4N=C_6H_5$-o	8	3.5 $NaOC_6H_4C_6H_5$-p	16	A	-20.0	9.1×10^5	2.0×10^5	C H N Cl	75.20 4.70 3.66 0	71.15 4.70 3.38 0.11	—	1.661
30		0.5 $NaOC_6H_4C(CH_3)_2C_6H_5$	8	4.0 $NaOC_6H_4C_6H_5$-p	16	A	-18.3	9.9×10^5	3.7×10^4	C H N Cl	75.73 5.23 4.46 0	74.32 4.99 3.35 0.12	—	1.650
31		1.5 $NaOC_6H_4C_6H_5$	12	2.5 $NaOC_6H_4C(CH_3)_3$	16	B	-	-	-	C H N Cl	73.98 5.40 3.75 0	72.03 5.25 3.54 0.08	140	1.654

Reactant Stoichiometry (equiv/P=N)

	Nucleophile 1	Time(h)	Nucleophile 2	Time(h)	Purif Meth[b]	^{31}P shift (ppm)[c]	M_w	M_n	Elemental Analysis			T(1)	n(632m)
										Calcd	Found		
32	1.5 NaOC$_6$H$_4$C$_6$H$_5$-m	8	0.5 NaOC$_6$H$_4$C$_6$H$_5$-P	16	B	-	-	-	C H N Cl	75.22 4.70 3.66 0	74.86 4.70 3.59 0.11	—	1.680
33	1.5 NaOC$_6$H$_4$C$_6$H$_5$-m	8	2.5 NaOC$_6$H$_5$	16	A	-20.5	5.6x10^5	1.3x10^4	C H N Cl	73.06 4.64 4.06 0	72.26 4.98 3.74 0.16	—	1.644
34	1.5 NaOC$_6$H$_4$C$_6$H$_5$-m	8	2.5 NaOC$_6$H$_4$CH$_2$C$_6$H$_5$	16	A	-20.2	1.4x10^6	1.2x10^5	C H N Cl	76.48 4.94 3.64 0	75.29 4.60 3.50 0.25	—	1.648
35	1.5 NaOC$_6$H$_4$C$_6$H$_5$-m	8	2.5 NaOC$_6$H$_4$C(CH$_3$)$_3$C$_6$H$_5$	16	A	-20.1	7.8x10^5	1.1x10^5	C H N Cl	75.74 5.20 3.46 0	75.66 4.98 3.35 0.03	—	1.640
36	1.5 NaOC$_6$H$_4$C$_6$H$_5$-m	8	2.5 NaOC$_6$H$_4$C$_6$H$_5$-p	16	A	-20.1	5.5x10^5	1.0x10^5	C H N Cl	75.22 4.70 3.66 0	75.65 5.19 3.26 0.03	—	1.675

Reactant Stoichiometry (equiv/P=N)

	Nucleophile 1	Time(h)	Nucleophile 2	Time(h)	Purif Meth[b]	^{31}P shift (ppm)[c]	M_w	M_n		Elemental Analysis Calcd	Found	T(°C)	$n(\delta \pm 2)$
37	0.5 $NaOC_6H_5$	8	1.5 $NaOC_6H_4C(CH_3)_2C_6H_5$	16	A	-19.9	1.1×10^6	1.0×10^5	C H N Cl	75.02 6.12 3.43 0	74.79 6.27 3.21 0.23	155	1.610
38	0.5 $NaOC_6H_4CH_2C_6H_5$-m	8	3.5 $NaOC_6H_4C(CH_3)_2C_6H_5$	16	A	-19.8	2.1×10^6	9.8×10^4	C H N Cl	76.84 6.18 3.09 0	76.84 6.36 2.96 0.14	—	1.619
39	0.5 $NaOC_6H_4C_6H_5$-m	8	3.5 $NaOC_6H_4C(CH_3)_2C_6H_5$	16	A	-19.8	3.0×10^6	1.7×10^5	C H N Cl	76.68 6.05 3.14 0	77.72 6.50 3.17 0.14	—	1.627
40	1.5 $NaOC_6H_4CH_2C_6H_5$	8	2.5 $NaOC_6H_4C_6H_5$-p	16	A	-19.4	9.8×10^5	9.9×10^4	C H N Cl	76.68 6.05 3.14 0	76.71 6.24 2.94 0.08	—	1.630
41	1.0 $NaOC_6H_4C_6H_5$-p	8	3.0 $NaOC_6H_4CH_3$-p	16	A	-18.9	1.9×10^6	9.9×10^4	C H N Cl	71.02 4.98 4.36 0	70.31 4.97 4.65 0.26	108	
42	2.0 $NaOC_6H_4C_6H_5$-p	24[a]	2.0 $NaOC_6H_4CH_3$-p	24	A	-18.8	2.1×10^6	9.3×10^4	C H N Cl	71.02 4.98 4.36 0	71.28 4.91 4.15 0.12	131	

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