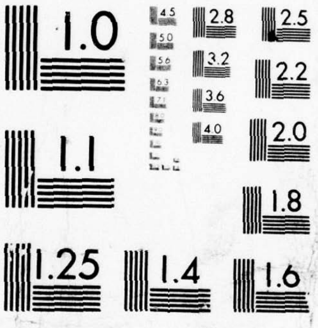
AD-A066 183 PENNSYLVANIA STATE UNIV UNIVERSITY PARK DEPT OF CHEMISTRY F/G 7/3
THE REACTION OF PHENYLLITHIUM WITH POLY-(DICHLOROPHOSPHAZENE).(U)
MAR 79 H R ALLCOCK, C T CHU N00014-75-C-0685
UNCLASSIFIED TR-7 NL

1 OF 1
AD
A066 183

END
DATE
FILMED
5--79
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A0 66183

DDC FILE COPY

LEVEL II

⑫

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 7 ✓
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER: B S

4. TITLE (and Subtitle): ⑥ THE REACTION OF PHENYLLITHIUM WITH POLY-(DICHLOROPHOSPHAZENE).
5. TYPE OF REPORT & PERIOD COVERED: ⑨ Interim Technical Report,
6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): (10) H. R./Allcock ~~and~~ C. Ting-Wah/Chu
8. CONTRACT OR GRANT NUMBER(s): (15) N00014-75-C-0685 ✓

9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 356-577

11. CONTROLLING OFFICE NAME AND ADDRESS:
Department of the Navy
Office of Naval Research, Arlington, Va. 22217
12. REPORT DATE: March 8, 1979
13. NUMBER OF PAGES: 25

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): (11) 8 Mar 79 (12) 28p.
15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution unlimited; approved for publication (14) TR-7

DDC
RECEIVED
MAR 22 1979
D

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Submitted for publication in the Journal - Macromolecules

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Polymers, polyphosphazenes, organometallic reagents, chain-cleavage, phenylphosphazenes, trifluoroethoxyphosphazenes, butylaminophosphazenes.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The reaction between polydichlorophosphazene, $(NPCl_2)_n$, leads to both halogen substitution and chain cleavage. A new series of polymers was prepared when 10% of the chlorine atoms were replaced by phenyl groups and the remaining halogen in then replaced by trifluoroethoxy or butyl-amino groups.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

JOB

400 343

79 03 19 078

Office of Naval Research

Contract No. N00014-75-C-0685

Project No. NR 356-577

Technical Report No. 7

THE REACTION OF PHENYLLITHIUM WITH POLY(DICHLOROPHOSPHAZENE)

by

H. R. Allcock* and C. Ting-Wah Chu

Prepared for publication in the Journal
Macromolecules

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

March 8, 1979

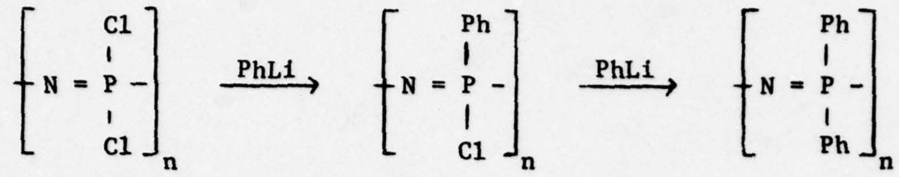
The Reaction of Phenyllithium with Poly(dichlorophosphazene)[1]

H. R. Allcock* and C. Ting-Wah Chu

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

ABSTRACT: The reaction between poly(dichlorophosphazene), $(NPCl_2)_n$, and phenyllithium has been studied with changes in temperature, reaction time, media, mole ratio of reactants, and in the presence of chelate complexes. The results showed that the chlorine substitution reaction is a slow process, while chain cleavage is much faster and dominates the overall reaction pattern. The nucleophilic replacement of halogen atoms yields polymers of formula $N_nP_nCl_xPh_y$ that contain a low percentage of phenyl groups. The remaining chlorine atoms can be replaced by treatment with sodium trifluoroethoxide or n-butylamine. The properties and molecular structure of the products are discussed.

This work on the synthesis of aryl-substituted polyphosphazenes is an outgrowth of our earlier synthesis of the first high polymeric phosphazenes that contained amino,[2,3] alkoxy, or aryloxy[4] groups. These were formed by the nucleophilic displacement of chlorine in poly(dichlorophosphazene), $(NPCl_2)_n$ (I), by amines, alkoxides, or aryloxides. We now report the reactions of $(NPCl_2)_n$ with phenyllithium with a view to the replacement of chlorine by phenyl to yield phenyl-substituted polyphosphazenes, such as II or III.



$$\left[-N=\overset{Cl}{\underset{Cl}{P}}-\right]_n \xrightarrow{PhLi} \left[-N=\overset{Ph}{\underset{Cl}{P}}-\right]_n \xrightarrow{PhLi} \left[-N=\overset{Ph}{\underset{Ph}{P}}-\right]_n$$

I II III

The phenyl substituent was chosen for this study for three reasons. First, phosphorus-phenyl bonds are known to have a high stability. Second, in contrast to the use of alkyllithium reagents, no complications were expected from α-metallation reactions when phenyllithium was used as a nucleophile. Third, phenyllithium has a higher nucleophilicity and lower electrophilicity than phenylmagnesium bromide or diphenylmagnesium and, hence, would be expected to offer the best prospects for halogen replacement rather than nucleophilic chain cleavage. As will be shown, this latter factor of the ease of substitution versus chain cleavage is the most critical feature of the reactions of poly(dihalophosphazenes) with organometallic reagents.

Attempts have been made in the past by other investigators to synthesize polymers of this type. For example, the reaction of sodium azide with phenyldichlorophosphine was reported to yield low polymeric phenyl-chlorophosphazenes[5] with an average molecular weight of about 5,000. Other attempts have been made to use Grignard or organolithium reagents to replace the halogen in $(NPCl_2)_n$.[6-8] One report described the heterophase interaction of phenylmagnesium bromide or phenyllithium with crosslinked $(NPCl_2)_n$ to form a resin of unspecified composition.[6] It has also been reported that $(NPCl_2)_n$ reacts with phenyllithium to yield phenylated products of low molecular weight and uncertain structure.[7]

Of particular interest are a series of papers by Biddlestone and Shaw[8-10] on the reactions of the cyclic chlorophosphazenes, $(NPCl_2)_{3 \text{ and } 4}$, with phenylmagnesium halides, diphenylmagnesium, or phenyllithium in which it was shown that the skeletal cleavage reactions actually preceded substitution. These cleavages have also been observed in our laboratory.[11] However, it was reported[8-10] that the initial ring cleavage yielded a linear oligomer which subsequently reacted rapidly with the organometallic reagent in a halogen substitution sequence. Such interactions can be viewed as model systems for the reactions of $(NPCl_2)_n$ with organometallic reagents. Hence, based on these reports, the prospect existed that the reaction of phenyllithium with open-chain $(NPCl_2)_n$ might proceed in a manner which favored substitution of halogen rather than skeletal cleavage. This would be similar to the remarkably clean interactions of $(NPCl_2)_n$ with alkoxides, aryloxides, or amines.[2-4] As will be demonstrated, the reactions of $(NPCl_2)_n$ with phenyllithium are much more complex than those with the simple oxygen- or nitrogen-containing nucleophiles.

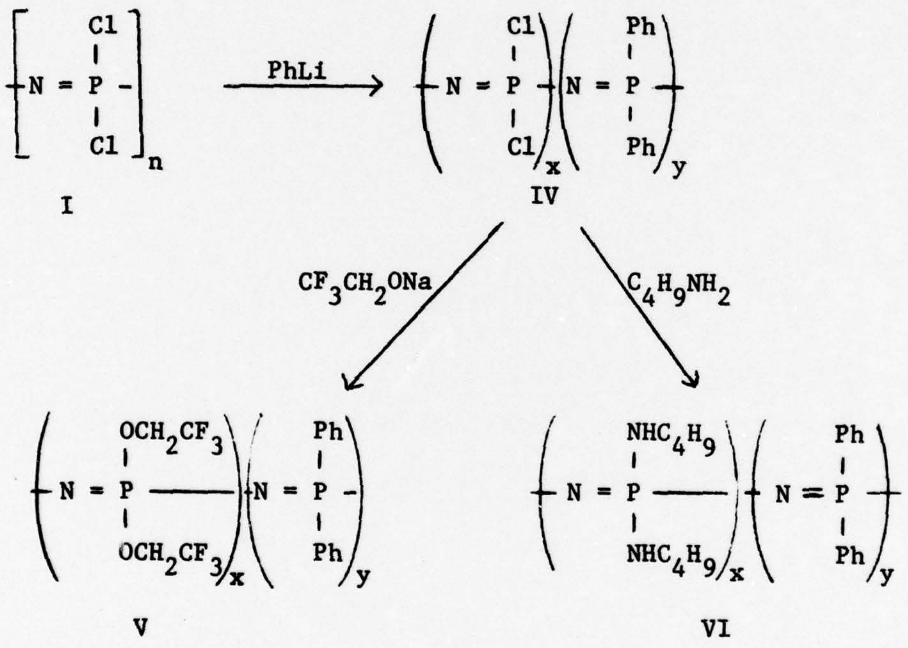
Earlier work in our laboratory was directed toward reducing the skeletal cleavage reaction by the use of poly(difluorophosphazene) as a substrate for organometallic reactions.[12] However, poly(difluorophosphazene) is a more difficult polymeric intermediate to work with than is poly(dichlorophosphazene). Hence, our objectives in this present study were to establish an alternative route to the synthesis of aryl-substituted polyphosphazenes, to investigate the reaction mechanism for the interaction of $(NPCl_2)_n$ with phenyllithium, and to examine the properties of aryl-substituted polyphosphazenes in order to assess the prospects for structure-property variations in polyphosphazenes that contain phosphorus-carbon bonds in the side group structure.

Results and Discussion

The reactions of $(NPCl_2)_n$ with phenyllithium were investigated with the use of different reaction temperatures, reaction times, solvents, and coordinative additives. The following discussion will be divided into: (1) The reactions of $(NPCl_2)_n$ with less than stoichiometric amounts of phenyllithium to permit a study of the relationship between the reactant molar ratio and the molecular weight of the products; (2) Reactions of $(NPCl_2)_n$ in the presence of an excess of phenyllithium and the effect of different experimental conditions; (3) The effect of coordinative additives; (4) The structure of the polymers; (5) The properties of the polymers, and (6) Mechanistic conclusions.

Relationship between the degree of phenyl substitution and the polymer chain length. Both phenylation and chain cleavage occurred when $(NPCl_2)_n$ was allowed to react with phenyllithium. The cleavage process took place even when a molar deficiency of phenyllithium existed in the reaction mixture. Thus, it was of considerable interest to determine if a relationship exists between the degree of phenylation and the extent of chain cleavage. The objective was to find a set of reaction conditions that would lead to the maximum degree of phenylation coupled with an acceptable minimum amount of chain cleavage.

Therefore, a number of reactions were performed in which the reactant ratio of $NPCl_2$ units to phenyllithium was varied from 1 : 0.3 to 1 : 1. Experimental problems did not permit the isolation of the partially substituted phenyl-chlorophosphazene polymers formed in the reaction mixture. These species were found to be hydrolytically unstable and prone to crosslinkage[13] (via hydrolysis of P-Cl to P-OH groups and condensation to P-O-P crosslinks) during purification. Hence, before isolation and purification, the reaction products were treated with a second nucleophile (sodium trifluoroethoxide or butylamine) in order to replace the residual chlorine atoms and form hydrolytically stable derivatives. The overall substitution pathway is illustrated in the conversion of I to IV, V, and VI.



Scheme 1

The use of this reaction sequence made it necessary to first establish that the chain length was not altered by the subsequent treatment with the alkoxide or the amine. Thus, a control reaction was carried out in which a sample of IV was separated into two portions. One portion was treated with sodium trifluoroethoxide, and the other with n-butylamine. Gel permeation chromatography showed that the molecular weights of both polymeric products were similar.

Hence, based on the widely differing nucleophilicities of these two reagents, it seems unlikely that chain cleavage takes place with the second nucleophile.

The chain length of the polymers decreased rapidly as the ratio of phenyllithium to $NPCl_2$ units in the reaction mixture was increased and as the phenyl group content of the polymers increased. The results are summarized in Table I and Figure 1. Thus, the question must be raised of whether phenylation is coincident with or in some way directly connected with chain cleavage. This prospect is discussed in a later section.

From a practical point of view it appears that the introduction of more than about 10% phenyl substituents by this technique reduces the molecular weight to an unacceptably low value (<50,000). However, even 10% of a phosphorus-carbon bonded side group could, in principle, have a marked effect on molecular properties such as chain packing or conformational mobility, and polymers of this type could,therefore, possess advantages over the alkoxy- or amino-substituted homopolymers. This topic is discussed in a later section.

Role of Temperature, Solvent, and Additives. Because the chain cleavage reaction exerts such a powerful influence on this process, an attempt was made to investigate the way in which this process was affected by changes in reaction conditions. In these experiments an excess of phenyllithium over $NPCl_2$ units was maintained throughout each reaction in order to provide unrestricted opportunities for both cleavage and substitution to take place.[14]

The reaction temperature was varied from -50°C to -20°C to 0°C, with reaction times of 1 hr.[15] Reactions at temperatures below -20°C were very slow.

However, the rates of both substitution and chain cleavage increased noticeably at 0°C, and the rates of both substitution and cleavage appeared to be affected similarly by the temperature variations. Moreover, it was not possible to favor substitution at the expense of cleavage by changes in reaction time at low temperatures. For example, reactions at -20°C were allowed to proceed for 5 min, 1 hr, and 5 hr. No reaction could be detected after 5 min. After 1 hr of reaction, the product had a high molecular weight but possessed a low percentage of phenyl substituent groups (10%). After 5 hr reaction, the product contained a high percentage (30%) of phenyl groups, but had suffered severe chain cleavage. Thus, in each case the two processes appear to be coupled either by a mechanistic interaction or by similar activation energies.

Because the reactivity of organometallic reagents (and their preferred reaction pathways) are known to be sensitive to the reaction medium, the effects of solvent changes on the reaction were examined. However, the ratio of phenylation to chain cleavage was unaffected when the solvent system was changed from toluene/diethyl ether to glyme/diethyl ether. This also ruled out the possibility that the process was affected by a reaction of phenyllithium with the etheric solvent[16] since such reactions would be slower in hydrocarbon-ether mixtures.[17]

The reaction pathways followed by organometallic reagents are also influenced by the presence of coordinative additives. Tetramethylethylenediamine normally increases the nucleophilicity of phenyllithium by the formation of a chelate complex with a more polar carbon-lithium bond.[18] This additive did not alter the relative amounts of substitution versus cleavage at -20°C. After 30 min reaction, a high molecular weight product with a low phenyl content (10%)

was obtained. After 2 hr, extensive chain cleavage had taken place.

Reactions of phenyllithium with trifluoroethoxy-chloro-phosphazenes. The possibility existed that the substitution and chain cleavage processes might be influenced in a different manner by the presence of organic substituent groups already present. Thus, an investigation of the reaction of phenyllithium with a polymer that contained 50% chlorine and 50% trifluoroethoxy groups was carried out. The main reaction product was a crosslinked polymer. The minor product (20%) was a soluble phenyl-trifluoroethoxy-phosphazene polymer with 20% phenyl groups present and a molecular weight of 1.0×10^5. This suggested that chain cleavage decreased when trifluoroethoxy groups were present. However, metallation at the α-hydrogen of the trifluoroethoxy groups almost certainly was responsible for the crosslinking process.

Structure of the polymers. All the polymers that contained phenyl and trifluoroethoxy or butylamino substituent groups, synthesized by the method shown in Scheme 1, were soluble in organic media. Hence, they did not possess a crosslinked structure. The general structure is believed to be derived directly from that of poly(dichlorophosphazene)[20,21] and to be analogous to the structures of the alkoxy-, aryloxy-, or amino-substituted homopolymers.[2-4] This general structure was confirmed by the similarities between the infrared spectra of the polymers produced in this study and those of $[NP(OCH_2CF_3)_2]_n$ and $[NP(NHC_4H_9)_2]_n$, together with the presence of characteristic infrared bands for phenyl groups at 1440 (P-Ph), 3020 (C-H), and 1580, 737, 712, and 688 (aryl) cm^{-1}.

However, a critical question is the disposition of the phenyl groups along the chain. In theory, they could be visualized as being disposed geminally (two phenyl groups per phosphorus), non-geminally (no more than one phenyl group on each phosphorus), or restricted to the chain ends.

The ^{31}P and ^{1}H nmr data provided tentative evidence that the phenyl groups were arrayed geminally. The polymers of structure VI showed two ^{31}P peaks at 3.65 and 10.7 ppm. Moreover, the peak areas varied according to the degree of phenylation. For example, for the following degrees of phenylation, the ratios of these two peaks are given in parentheses: 8% (11.2 : 1); 13% (6.8 : 1); 23% (3.4 : 1), and 33% (1.9 : 1). The peak at 3.65 ppm was assigned to the $P(NHC_4H_9)_2$ unit because of the identical chemical shift shown by the homopolymer $[NP(NHC_4H_9)_2]_n$.[3] The 10.07 ppm peak could, therefore, be attributed to either a PPh_2 or a $P(Ph)NHC_4H_9$ structure. However, the ^{1}H nmr spectra showed phenyl and NHC_4H_9 proton peaks in the same area ratios as the two ^{31}P peaks mentioned above, and this provides marginal evidence that the ^{31}P nmr peak at 10.07 ppm can be attributed to the PPh_2 structure. Geminal phenylation occurs with cyclic oligomeric chlorophosphazenes.[8-10]

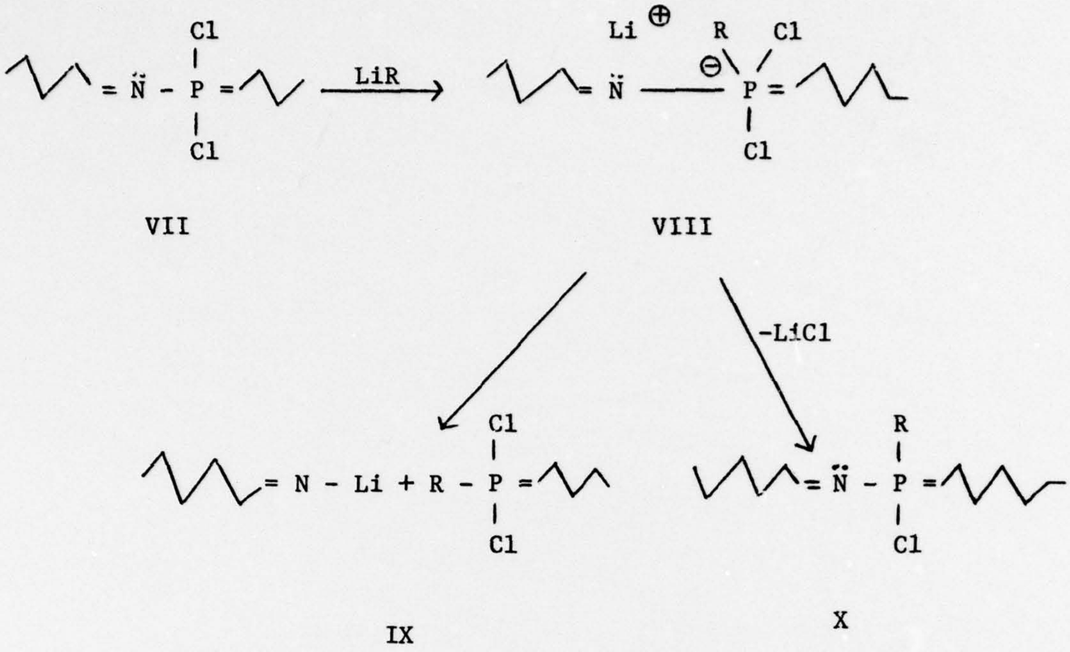
However, the question still remains of whether the phenyl groups occupy sites at the chain ends, ie. at points adjacent to the sites of chain cleavage. First, a comparison of the phenyl content of a number of polymers with their (GPC) average molecular weights led to the conclusion that the number of phenyl groups was, on the average, higher than could be accounted for by the presence of two (or three) phenyl groups at one end of each chain. For example, a polymer of average molecular weight, 1.5×10^5 had an average of 37 phenyl groups per 617 repeating unit chain. Even when the chain length had declined to 200 repeating units, an average of 20 phenyl groups were attached to each molecule. Moreover, the change in glass transition temperatures as the phenyl content of each polymer increases could not be accounted for entirely by the shorter chain length (Table I).

Properties of the polymers. In appearance, polymers of structure V and VI resemble the homopolymers $[NP(OCH_2CF_3)_2]_n$ or $[NP(NHC_4H_9)_2]_n$. Polymers of type V are colorless, transparent, or opalescent, film-forming, flexible materials that show a tendency toward low strength only when the molecular weight falls below ~50,000. The polymers of structure VI are glasses at room temperature. However, the polymers are adhesive when the phenyl content is higher than 10%.

The solubilities also resemble those of the homopolymers. For example, V dissolves in tetrahydrofuran, trifluoroethanol, or piperidine. They are insoluble in aqueous media.

An increased phenyl content brings about an increase in the glass transition temperature. For example, for polymers of structure V, an increase in the phenyl side group percentage in the sequence 0%, 5%, 9%, 15%, resulted in an increase in the Tg from -66°C to -58°C, -42°C, and -30°C respectively. Of course, the sequence also represents a decrease in average molecular weight from 3×10^6 to 1.5×10^5, 5×10^4, and 3×10^4, and it is not yet possible to predict the molecular weight for polyphosphazenes below which the physical properties become dependent on chain length. However, it seems reasonable to assume that the Tg changes in the molecular weight range above 1×10^5 are a consequence of the different ratios of phenyl groups to trifluoroethoxy groups. Further evidence for this viewpoint is provided by the fact that a high polymer with 60% phenyl groups and 40% trifluoroethoxy groups, prepared by another synthetic route,[12] had a Tg value of +60°C. The glass transition temperature is believed to provide a measure of the torsional mobility of the backbone bonds and, hence, these changes can be ascribed to the effect by phenyl groups in sterically restricting the torsional motions of the skeletal bonds. It has already been shown that trifluoroethoxy groups, because of their inherent conformational mobility, permit an unusual degree of skeletal torsional flexibility in $[NP(OCH_2CF_3)_2]_n$.[22,23] Aryl groups bound directly to phosphorus would be expected to raise the barriers to backbone motions and, indeed, to restrict those motions to minor perturbations from very specific conformations. In fact, it is almost impossible to construct space-filling models of $(NPPh_2)_n$ because of the steric hindrance.

Reaction mechanism. It is generally assumed that the nucleophilic replacement of chlorine in chlorophosphazenes takes place via the formation of a pentacoordinate transition state at phosphorus.[24] With substitutions that involve organometallic reagents, a serious mechanistic complication can be envisaged in which the metal of the organometallic species becomes coordinatively bound to the lone pair electrons of a skeletal nitrogen atom (VIII). Thus, either halogen replacement (X) or chain cleavage (IX) are possible. Which one of these processes predominates will depend on the electron-withdrawing capabilities of those side groups that are already present. If the side group already present is sufficiently electron-withdrawing that a significant decrease occurs in the electron density in the lone-pair at nitrogen, then metallation may be unimportant, and halogen replacement (X) will predominate. On the other hand, if the electron-withdrawing power of the side group is insufficient to reduce the electron density on nitrogen, then cleavage of the chain will be the principal reaction.



Poly(dichlorophosphazene) appears to lie on the borderline between these two extremes. Although chlorine is an electronegative element, it is not sufficiently electron-withdrawing to prevent metal coordination and cleavage. Thus, both substitution and cleavage occur. However, in these terms, it is curious that the phenylation process appears to proceed by a geminal pathway. A phenyl group already attached to phosphorus, being less electronegative than chlorine, would be expected to favor chain cleavage rather than geminal substitution. It is possible that the presence of one phenyl group at phosphorus sterically shields the nearby nitrogen atoms to retard metallation. Alternatively, the high polarizability[25] of the Ph-P-Cl grouping may assist the separation of Cl^- (ie. cause "metallation" to take place at chlorine rather than at nitrogen).

Chlorine is clearly not sufficiently electronegative to allow the synthesis of highly phenylated high polymers by this route. On the other hand, fluorine is more electronegative than chlorine and, hence, poly(difluorophosphazene) provides a reaction substrate that is less susceptible to skeletal cleavage. This prospect will be discussed in a future paper.

Experimental Section

Materials. Diethyl ether (Fisher, Anhydrous Reagent), N,N,N',N'-tetramethylethylenediamine (TMED) (Eastman), ethylene glycol dimethyl ether (glyme) (Aldrich, Reagent Grade) and tetrahydrofuran (Fisher, Reagent Grade) were dried by distillation from calcium hydride. Toluene (Fisher, Reagent Grade) was dried by azeotropic distillation. Bromobenzene (Fisher, Reagent Grade) was filtered from P_2O_5 and distilled. *n*-Butylamine and triethylamine (Fisher) were dried over potassium hydroxide and distilled immediately before use. Trifluoroethanol (Halocarbon Products, Reagent Grade) was filtered from magnesium sulfate and was stored over molecular sieves. A lithium dispersion in mineral oil (Ventron) was washed with diethyl ether. Dimethylamine (Matheson, anhydrous) and monomethylamine (Matheson, anhydrous) were used without further purification.

Poly(dichlorophosphazene) was prepared by the polymerization of $(NPCl_2)_3$ (kindly supplied by The Firestone Tire and Rubber Company) at 250°C.[13,15] An average of 20-30% conversion to polymer was obtained. Sodium trifluoroethoxide was obtained by the reaction of sodium with trifluoroethanol in THF solution.[4] Phenyllithium in diethyl ether was prepared in the usual manner from bromobenzene and a lithium dispersion. The solution was filtered and standardized by acid-base titration.[26] All manipulations of poly(dichlorophosphazene) and phenyllithium were performed under a nitrogen atmosphere by the use of a glove bag or Schlenk glassware.

Analytical Equipment. Infrared spectra were recorded on a Perkin-Elmer 267 grating spectrometer. ^{31}P, ^{13}C, and ^{1}H Nmr spectra were recorded on a JEOL PS-100 FT nmr spectrometer. Gel permeation chromatography was carried out on Waters Associates instruments (ALC/GPC 50) with 10^5 and 10^6 styragel columns and (Model-6000A unit) with 500, 10^3, 10^4, 10^5, and 10^6 styragel columns for THF solutions. Intrinsic viscosity measurements were made with a Canon Ubbelohde 75-E-157 dilution viscometer, held in a constant temperature water bath at 30°C. The glass transition temperatures (Tg) were measured with the use of a Chemical Instruments Corp. torsional braid analyzer kindly provided by N.A.S.A., Langley Field. Microanalyses were performed by Galbraith Laboratories, Inc. Knoxville, Tenn..

Synthesis of phenyl-trifluoroethoxy-phosphazene polymers. The following procedure is typical: Phenyllithium was prepared from lithium (0.45 g, 0.65 mole) and bromobenzene (3.05 ml, 0.029 mole) in ether solution. The freshly prepared solution of phenyllithium was added dropwise to a solution of poly(dichlorophosphazene) (11.3 g, 0.097 unit mole) in toluene at -20°C. The reaction mixture was stirred at -20°C for 1 hr. Trifluoroethanol (5 ml, 0.069 mole) was then added to quench the unreacted phenyllithium reagent. Sodium trifluoroethoxide, prepared from sodium (20 g, 0.87 mole) and trifluoroethanol (56.45 ml, 0.78 mole) in tetrahydrofuran (300 ml) was added over 15 min to the reaction mixture. The reaction mixture was then boiled at reflux overnight. Dilute hydrochloric acid was then added to precipitate the product. Further precipitation was carried out by precipitation from THF into water twice, and from THF into benzene twice. The polymer was soluble in THF and acetone. The infrared spectrum showed characteristic absorption bands for trifluoroethoxy and phenyl phosphazene groups as follows (in cm^{-1}): 3020 w (C-H); 1420 (P-O-C); 1280 s (P-N); 965, 880 (P-O-C); 750 vw (P-N); 737 w, 712 w, and 688 w (aryl). A ^{1}H nmr spectrum (in d^{6} acetone) showed the unresolved peaks at 4.32 ppm for the trifluoroethoxide group and at 7.42 ppm for the phenyl group. The microanalysis was compatible with the presence of 5% phenyl side groups.

The preparation of the 15% phenyl-substituted product was carried out with the use of the same procedure as described above. The mole ratio of $NPCl_2$ units to phenyllithium was 1 : 0.7. This reaction was also performed in toluene/diethyl ether solutions. The molecular weights of these polymers were estimated by gel permeation chromatographic analysis in THF. The results are listed in Table I.

Synthesis of phenyl-n-butylaminophosphazene polymers. The following procedure is typical of the method used. A freshly prepared solution of phenyllithium (0.028 mole) in diethyl ether was added dropwise to a stirred solution of poly(dichlorophosphazene) (8.2 g, 0.071 unit mole) in toluene at -20°C. The reaction mixture was stirred at -20°C for 1 hr. Triethylamine (29.8 ml, 0.21 mole) and n-butylamine (28 ml, 0.28 mole) were added. The reaction mixture was then stirred for another 24 hr. The product was obtained by precipitation of the concentrated reaction mixture into water. It was then reprecipitated from trifluoroethanol into acetone to remove oligomers. Salts were removed by centrifugation of the polymer solution in THF and by precipitation into water twice. The polymer was dried in vacuum for several days. The solubility properties were similar to those of poly(bis-n-butylamino)phosphazene, ie. the polymer was soluble in trifluoroethanol and chloroform. It was also soluble in THF, whereas the homopolymer is not. The infrared spectrum showed absorption bands similar to those of poly(bis-n-butylamino)phosphazene, ie. at 1250 s (P-N), 910 w (P-N, C-N), and 1190 s (C-N) cm^{-1}, in addition to the characteristic absorption bands of phenyl groups at 1440 m (P-Ph), 3020 w (C-H), and 1580 w, 737 s, 712 m, 688 m (aryl) cm^{-1}. ^{31}P NMR spectra (in $CDCl_3$) showed two broad singlets at 10.52 and 3.54 ppm relative to H_3PO_4. ^{13}C NMR spectra (in $CDCl_3$) showed peaks at 13.93, 20.36, 34.02 and 41.04 ppm (NHC_4H_9), and a broad singlet at 127.5 ppm (C_6H_5). ^1H NMR spectra (in $CDCl_3$) showed peaks at 0.84, 1.33, 2.78, and 3.88 ppm (NHC_4H_9), and a broad peak at 8.33 ppm (phenyl). The percentage of phenyl substituents on the polymer, as suggested by both ^1H and ^{31}P nmr spectra, was about 8%.

Other reactions were carried out with the same procedure described above. The reactant mole ratios of $NPCl_2$ units to phenyllithium for the generation of the different phenyl contents were: 1 :1 (13%), 1 : 1.5 (23%), 1 : 2 (33%). Considerable difficulty was encountered with the reproducibility of the microanalyses of these products. Aminophosphazenes in general suffer from this problem.

Reactions of $(NPCl_2)_n$ with large quantities of phenyllithium. The procedures for these reactions were the same as described above, except that this set of reactions was performed by the addition of a solution of $(NPCl_2)_n$ to a phenyllithium solution. Thus, an excess of phenyllithium was always present.

A solution of poly(dichlorophosphazene) (9.1 g, 0.078 unit mole) in glyme was added to a freshly prepared solution of phenyllithium (0.157 mole) in diethyl ether. Following treatment with sodium trifluoroethoxide and trifluoroethanol, and purification as described above, a ^1H nmr spectrum (d^6 acetone) showed peaks at 4.30 and 7.45 ppm with an area ratio of 3.5 : 1. ^{31}Nmr spectra showed peaks at -8.48 and

3.33 ppm. (The peak at 3.33 ppm was too broad to integrate). Microanalysis showed the presence of 9% of phenyl substituent groups. The results are listed in Table I.

The following variations to the reaction conditions were explored. (a) Effect of temperature variations. Reactions were performed at -50°C, -20°C, and 0°C in glyme solution for 1 hr.(including the addition time of 5 min). The product obtained from the reaction at -50°C was identical to the product obtained at -20°C, ie. with a low percentage of phenyl substituents ($\sim$10%) and a high molecular weight (MW $\sim 10^5$). The product obtained from the 0°C reaction was a low molecular weight product (MW $<10^4$). (b) Variation of reaction time. Reactions were carried out at -20°C in glyme solution for 5 min, 1 hr, and 5 hr. The product obtained from the 5 min reaction was identified as $[NP(NHC_4H_9)_2]_n$. The product obtained after 5 hr showed a high percentage of phenyl substituents (30%) but had a low molecular weight (MW $<10^4$). ^{13}C Nmr spectra gave phenyl resonances at 127.9, 128.6 and 130.9 ppm. (c) Effect of reaction media. Reactions were performed at -20°C for 1 hr in glyme/diethyl ether and toluene/diethyl ether. No solvent effect was observed.

Reaction of phenyllithium with trifluoroethoxy-chlorophosphazenes. A freshly prepared solution of sodium trifluoroethoxide (0.057 mole) in THF was added to a solution of $(NPCl_2)_n$ (6.6 g, 0.057 mole) in toluene. The reaction mixture was boiled at reflux overnight. An ethereal solution of phenyllithium (0.046 mole) was added dropwise to the reaction mixture at 25°C. The mixture was allowed to stir for 2 hr. A freshly prepared solution of sodium trifluoroethoxide in THF was added, and the mixture was stirred overnight. The isolation and purification was identical to that used for phenyl-trifluoroethoxyphosphazenes. GPC measurements showed a molecular weight of 1.0×10^5. Anal. Calcd. for $NP(C_6H_5)_{0.4}(OCH_2CF_3)_{1.6}$: C, 28.72; H, 2.22; N, 5.82; P, 13.23; F, 38.93. Found: C, 28.06; H, 2.90; N, 5.80; P, 13.42; F, 32.49.

Other attempted substitution reactions. A freshly distilled tetramethylenediamine solution (27.6 ml, 0.18 mole) was added to a freshly prepared etheric solution of phenyllithium (0.18 mole). The mixture was stirred for 1 hr and was then added to a solution of poly(dichlorophosphazene) (10.6 g, 0.09 unit mole) in glyme at -20°C during 0.5 hr. Triethylamine (38.4 ml, 0.27 mole) and *n*-butylamine (36.1 ml, 0.37 mole) were added and the reaction mixture was stirred at room temperature for 2 days. The work-up procedure was the same as described for the synthesis of phenyl-*n*-butylaminophosphazene polymers.

Another reaction was performed with the same conditions as above except that the time for the phenyllithium/TMED reaction with $(NPCl_2)_n$ was extended to 2 hr. The product isolated from the 0.5 hr reaction was high molecular weight polymer with a phenyl substituent content of less than 10%. From the 2 hr reaction, the product was a low molecular weight polymer with a phenyl substituent content of about 30%.

1. For the previous paper related to this topic see, H. R. Allcock, P. P. Greigger, J. E. Gardner, and J. L. Schmutz, *J. Am. Chem. Soc*., in press.
2. H. R. Allcock, W. J. Cook, and D. P. Mack, *Inorg. Chem*., *11*, 2584 (1972).
3. H. R. Allcock and R. L. Kugel, *Inorg. Chem*., *5*, 1716 (1966).
4. H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem*., *5*, 1709 (1966).
5. D. L. Herring, *Chem. Ind*., 717 (1960).
6. C. F. Liu and R. L. Evans, U.S. Pat. 3,169,933 (1965).
7. J. R. MacCallum and J. Tanner, *J. Polymer Sci*., Part A-1, *6*, 3163 (1968).
8. M. Biddlestone and R. A. Shaw, *J. Chem. Soc*., (A), 178 (1969).
9. M. Biddlestone and R. A. Shaw, *J. Chem. Soc.*, (A), 1750 (1970).
10. M. Biddlestone and R. A. Shaw, *Phosphorus*, *3*, 95 (1973).
11. J. E. Brown, M.S. Thesis, The Pennsylvania State University (1969).
12. H. R. Allcock, D. B. Patterson, and T. L. Evans, *J. Am. Chem. Soc*., *99*, 6095 (1977).
13. H. R. Allcock, J. E. Gardner, and K. M. Smeltz, *Macromolecules*,*8*, 36 (1975).
14. In these reactions the solution of $(NPCl_2)_n$ was added to an excess of phenyllithium solution in order to ensure that an excess of the latter reagent existed at all stages of the reaction.
15. This reaction time included the 5 min time for reagent addition.
16. H. Gilman, A. H. Haubein, and H. Hartzfeld, *J. Org. Chem*., *19*, 1034 (1954).
17. D. L. Esmay and C. W. Kamiensky, U.S. Patent 1,346, 692 (1963) (to Lithium Corp. of America, Inc.)
18. G. G. Eberhardt and W. A. Butte, *J. Org. Chem*., *29*, 2928 (1964).
19. G. Tesi and P. J. Slotta, *Proc. Chem. Soc.*, London, 404 (1960).
20. H. R. Allcock, "*Phosphorus-Nitrogen Compounds*," Academic Press, New York (1972).
21. E. Giglio, F. Pompa, and A. Ripamonti, *J. Polymer Sci*., *59*, 222 (1962).

22. H. R. Allcock, R. W. Allen, and J. J. Meister, Macromolecules, 9, 950 (1976).

23. R. W. Allen and H. R. Allcock, Macromolecules, 9, 956 (1976).

24. H. R. Allcock and L. A. Smeltz, J. Am. Chem. Soc., 98, 4143 (1976).

25. A. P. Carroll and R. A. Shaw, J. Chem. Soc., (A), 914 (1966).

26. H. Gilman and F. K. Cartledge, J. Organomet. Chem., 2, 447 (1964).

Acknowledgments. This work was supported by the Office of Naval Research through project number NR 356-577. We also thank T. L. Evans and D. B. Patterson for conducting some preliminary experiments.

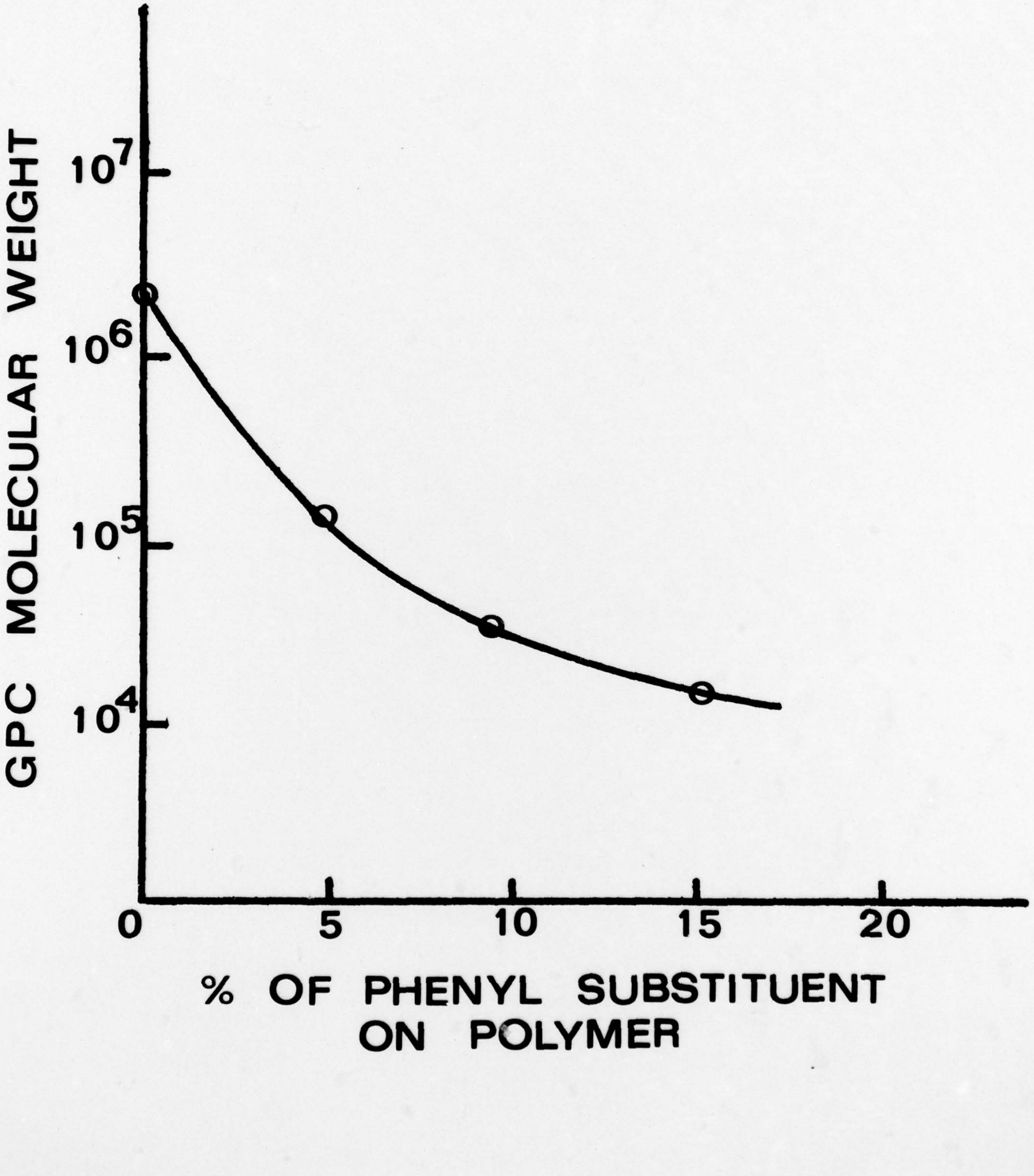
Table I. Analytical Data for $[NP(C_6H_5)_x(OCH_2CF_3)_y]_n$

% Phenyl	% C		% H		% N		% P		% F		Tg	Mol wt[b]
Substituent	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	(°C)	
0	19.78	19.80	1.65	1.74	5.76	5.84	12.75	12.83	46.90	47.10	-66	3.0×10^6
5	21.95	21.60	1.79	1.85	5.83	5.88	12.86	12.85	44.96	43.03	-58	1.5×10^5
9	23.72	23.04	1.90	2.07	5.86	6.26	12.96	13.62	43.39	39.62	-42	5.0×10^4
15	26.42	25.69	2.07	2.16	5.92	6.14	13.10	13.60	40.98	35.17	-30	3.0×10^4

[a] All polymers contained no residual chlorine (Beilstein test).

[b] By gel permeation chromatography in tetrahydrofuran.

Figure 1. Changes in the GPC molecular weight as a function of the percentage of phenyl substituents in the polymer. The cosubstituent is trifluoroethoxy.


GPC MOLECULAR WEIGHT
10^7
10^6
10^5
10^4
0
5
10
15
20
% OF PHENYL SUBSTITUENT ON POLYMER

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 Attn: Code 472	2
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1
ONR Area Office One Hallidie Plaza, Suite 601 San Francisco, California 94102 Attn: Dr. P. A. Miller	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1

	No. Copie
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U.S. Army Research Office P.O. Box 1211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
Naval Weapons Center China Lake, California 93555 Attn: Dr. A. B. Amster Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93401 Attn: Dr. R. W. Drisko	1
Professor K. E. Woehler Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Naval Ship Research and Development Center Annapolis, Maryland 21401 Attn: Dr. G. Bosmajian Applied Chemistry Division	1
Naval Ocean Systems Center San Diego, California 91232 Attn: Dr. S. Yamamoto, Marine Sciences Division	1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

No. Copies

Dr. T. C. Williams
Union Carbide Corporation
Chemical and Plastics
Tarrytown Technical Center
Tarrytown, New York 1

Dr. R. Soulen
Contract Research Department
Pennwalt Corportion
900 First Avenue
King of Prussia, Pennsylvania 19406 1

Dr. A. G. MacDiarmid
University of Pennsylvania
Department of Chemistry
Philadelphia, Pennsylvania 19174 1

Dr. C. Pittman
University of Alabama
Department of Chemistry
University, Alabama 35486 1

~~Dr. H. Allcock~~
~~Pennsylvania State University~~
~~Department of Chemistry~~
~~University Park, Pennsylvania 16802~~ ~~1~~

Dr. M. Kenney
Case-Western University
Department of Chemistry
Cleveland, Ohio 44106 1

Dr. R. Lenz
University of Massachusetts
Department of Chemistry
Amherst, Massachusetts 01002 1

Dr. M. David Curtis
University of Michigan
Department of Chemistry
Ann Arbor, Michigan 48105 1

Dr. M. Good
University of New Orleans
Department of Chemistry
Lakefront
New Orleans, Louisiana 70122 1

No. Copies

Douglas Aircraft Company
3855 Lakewood Boulevard
Long Beach, California 90846
Attn: Technical Library
C1 290/36-84
AUTO-Sutton 1

NASA-Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attn: Dr. T. T. Serafini, MS 49-1 1

Dr. J. Griffith
Naval Research Laboratory
Chemistry Section, Code 6120
Washington, D.C. 20375 1

Dr. G. Goodman
Globe-Union Incorporated
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201 1

Dr. E. Fischer, Code 2853
Naval Ship Research and
Development Center
Annapolis Division
Annapolis, Maryland 21402 1

Dr. Martin H. Kaufman, Head
Materials Research Branch (Code 4542)
Naval Weapons Center
China Lake, California 93555 1

Dr. J. Magill
University of Pittsburg
Metallurgical and Materials
Engineering
Pittsburg, Pennsylvania 22230 1

Dr. C. Allen
University of Vermont
Department of Chemistry
Burlington, Vermont 05401 1

Dr. D. Bergbreiter
Texas A&M University
Department of Chemistry
College Station, Texas 77843 1

TECHNICAL REPORT DISTRIBUTION LIST, 356B

	No. Copies
Professor R. Drago Department of Chemistry University of Illinois Urbana, Illinois 61801	1
Dr. F. Brinkman Chemical Stability & Corrosion Division Department of Commerce National Bureau of Standards Washington, D.C. 20234	1