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Phosphonitrilic Compounds. XV.[1] High Molecular Weight Poly[bis(amino)phosphazenes] and Mixed-Substituent Poly(aminophosphazenes)[2]

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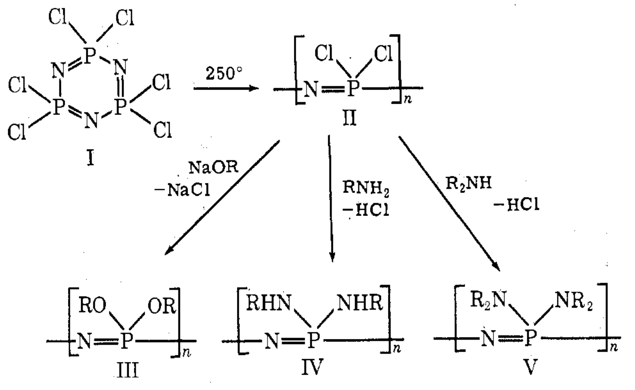
The synthesis of four new poly[bis(amino)phosphazenes] of formulas $[NP(NHCH_3)_2]_n$, $[NP(NHC_3H_7)_2]_n$, $[NP(NHC_4H_9)_2]_n$, and $[NP(NHCH_2CF_3)_2]_n$ by direct aminolysis of $(NPCl_2)_n$ is described. The replacement of chlorine in high molecular weight $(NPCl_2)_n$ is incomplete when bulky primary amines, such as isopropylamine, isobutylamine, or *sec*-butylamine, or secondary amines, such as diisopropylamine, diphenylamine, *N*-methylaniline, or diethylamine, are used as nucleophiles. With diethylamine, approximately half of the chlorine atoms are replaced nongeminally to yield $[NP(Cl)N(C_2H_5)_2]_n$. Treatment of this derivative with primary amines yields mixed substituent polymers, $[NP(NHCH_3)N(C_2H_5)_2]_n$, $[NP(NHC_2H_5)N(C_2H_5)_2]_n$, $[NP(NHC_3H_7)N(C_2H_5)_2]_n$, and $[NP(NHC_4H_9)N(C_2H_5)_2]_n$. Terpolymers which contain diethylamino, piperidino, and methylamino substituents or diethylamino, methylamino, and trifluoroethoxy groups have also been prepared.

Introduction

An unusual series of useful high polymers can be synthesized by the thermal polymerization of hexachlorocyclotriphosphazene (I) to high molecular weight poly(dichlorophosphazene) (II), followed by treatment of this intermediate with alkoxides, aryl oxides, or amines to yield poly(organophosphazenes) of structure III, IV, or V.[3-5] These products are stable elastomers, flexible film-forming materials, or glasses according to the nature of the substituent groups. For the amino-substituted polymers IV and V, derivatives have been reported in which the substituent groups are ethylamino, phenylamino, dimethylamino, and piperidino.[5] In this paper we report a detailed investigation of the reactions of other amines with poly(dichlorophosphazene) (II).

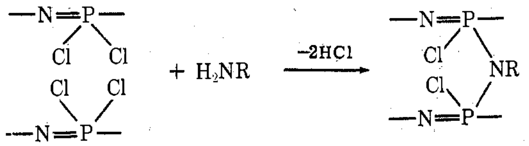


n in II ≈ 15,000

The derivatives discussed here are high molecular weight linear or branched molecules, which display markedly different properties from the numerous cyclic trimeric and tetrameric aminophosphazenes reported in the literature. Much of the fundamental interest in organophosphazene high polymers is connected with the different reactivities, substitution patterns, and physical properties which result from the presence of the long-chain skeleton.

Results and Discussion

Reactions of Poly(dichlorophosphazene) with Primary Amines.—In theory it is possible to envisage the synthesis of a wide variety of polymers with the general structure $[NP(NHR)_2]_n$ (IV) by the interaction of poly(dichlorophosphazene) (II) with different primary amines. In practice, two limitations reduce the synthetic possibilities. The first is connected with the opportunities which exist for primary amines to cross-link phosphazene chains, as shown in the scheme



Such cross-linking reactions yield insoluble, often partly substituted polymers. The second limitation results from the fact that bulky, branched primary amines do not replace all the chlorine atoms on each chain. As illustrated below, steric hindrance in the amine appears to play a large part in determining the reaction pathway.

Ammonia reacts with poly(dichlorophosphazene) in tetrahydrofuran solution at low temperatures (see Experimental Section) to yield a labile, substituted, uncross-linked polymer, presumably with the structure $[NP(NH_2)_2]_n$. This glass-like material hydrolyzes rapidly in contact with atmospheric moisture with elimination of ammonia. However, the cross-linking reaction occurs readily, especially above 25° in solvents such as toluene or tetrahydrofuran, to give insoluble, partly substituted products. It is worthwhile to compare this reaction with the ammonolysis of the trimer and tetramer $(NPCl_2)_{3 \text{ or } 4}$ where total halogen replacement occurs at low temperature in ether to give the hygroscopic solids $[NP(NH_2)_2]_{3 \text{ or } 4}$. These decompose with loss of ammonia when heated or when treated with water.[6] However, the opportunities for cross-linking

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[2] Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Illinois, Sept 1970; and reported in part in a preliminary communication, H. R. Allcock and D. P. Mack, *Chem. Commun.*, 685 (1970).

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are apparently less with cyclic trimeric or tetrameric structures than with the high polymer.

With methylamine as a reagent, cross-linking can be prevented by careful experimental technique, particularly when the temperature is maintained at 25° or below and when the substituted polymer remains in solution. Precipitation of the partly substituted polymer in a nonsolvent favors cross-linking. Excess of the reagent amine functions as the hydrohalide acceptor.

$$(NPCl_2)_n + 4nCH_3NH_2 \longrightarrow [NP(NHCH_3)_2]_n + 2nCH_3NH_2\cdot HCl$$

The syntheses of the ethylamino,[5] *n*-propylamino, *n*-butylamino, and trifluoroethylamino derivatives, $[NP(NHC_2H_5)_2]_n$, $[NP(NHC_3H_7)_2]_n$, $[NP(NHC_4H_9)_2]_n$, and $[NP(NHCH_2CF_3)_2]_n$ were accomplished in a straightforward manner by interaction of the appropriate primary amine with poly(dichlorophosphazene) with the use of triethylamine as a hydrohalide acceptor in tetrahydrofuran solvent. No problems were encountered with the formation of cross-linked polymers, and no difficulty was experienced with obtaining complete halogen replacement. However, total substitution could not be obtained when isopropylamine, isobutylamine, or *sec*-butylamine were employed as reagents.

For example, isopropylamine replaced 75% of the available chlorine in $(NPCl_2)_n$, isobutylamine replaced 80%, and *sec*-butylamine replaced 52%, under conditions where total substitution occurs with unbranched amines (see Experimental Section).

This influence by branched primary amines is reminiscent of the reactions of amines with the cyclic trimeric and tetrameric chlorophosphazenes. Thus, unbranched primary amines, such as methylamine or *n*-butylamine, yield the fully aminolyzed trimers in boiling ether or benzene,[7,8] but isopropylamine can be induced to replace all the halogen atoms in $(NPCl_2)_3$ only after prolonged reaction in boiling benzene or at 140–180° under pressure.[7] Only partial replacement of halogen occurs when isopropylamine reacts with $(NPCl_2)_4$ in organic media.[9] The reaction of isopropylamine with $(NPCl_2)_3$ yields both geminal and nongeminal products.[10] However, the hydrolytic sensitivity of the partly substituted high polymer has prevented an analysis of positional assignments for this compound. *o*-Phenylenediamine reacts with $(NPCl_2)_3$ to yield the spirocyclic tris(*o*-phenylenediamino)cyclotriphosphazene,[11] but the same reagent reacts with the high polymer $(NPCl_2)_n$ to cross-link the chains.

Reactions of Poly(dichlorophosphazene) with Secondary Amines.—The total replacement of all the halogen atoms in $(NPCl_2)_n$ can be accomplished by treatment with dimethylamine or piperidine.[5] However, diphenylamine showed no evidence of reaction with $(NPCl_2)_n$ even after the use of forcing conditions. This does not reflect the weak basicity of diphenylamine as a hydrohalide acceptor, since the same result was obtained when triethylamine was used as a dehydrohalogenation base. Treatment of $(NPCl_2)_n$ with *N*-methylaniline in boiling tetrahydrofuran resulted in the replacement of only 20–30% of the halogen atoms by dimethylamino units. The polymers resulting from this substitution were hydrolytically unstable. Diisopropylamine replaced only 41% of the available chlorine.

Diethylamine reacted with $(NPCl_2)_n$ in tetrahydrofuran at 25° to replace approximately half of the chlorine atoms by diethylamino groups. Higher reaction

$$(NPCl_2)_n + 2n(C_2H_5)_2NH \longrightarrow [NPClN(C_2H_5)_2]_n + (C_2H_5)_2NH\cdot HCl$$

temperatures did not enhance the degree of substitution appreciably. This transparent, elastomeric polymer was soluble in solvents such as benzene, tetrahydrofuran, or carbon tetrachloride. It was resistant to atmospheric hydrolysis for periods of several weeks, and it proved to be a valuable precursor for subsequent halogen replacement reactions.

The behavior of $(NPCl_2)_n$ with secondary amines generally reflects the substitution characteristics of cyclotri- and tetraphosphazenes in the presence of the same reagents. For example, nongeminal partial replacement of chlorine in $(NPCl_2)_3$ by dimethylamino occurs readily, but reactions in boiling xylene with excess dimethylamine are required before complete substitution can be effected.[12,13] With the tetramer $(NPCl_2)_4$ partial substitution occurs under mild conditions.[14] Thus, the relatively facile replacement of chlorine in $(NPCl_2)_n$ by dimethylamino groups[5] suggests that the polymer is, if anything, more reactive to dimethylamine than are the lower cyclic homologs. The ready replacement of all the chlorine atoms in $(NPCl_2)_n$ by piperidino[5] is reminiscent of the ease of total substitution of $(NPCl_2)_3$ by the same reagent under mild conditions.[15] When *N*-methylaniline reacts with $(NPCl_2)_3$ or $(NPCl_2)_4$ the results are similar to those found for the high polymer, with partially substituted products only being isolated.[16,17]

However, differences exist between the behavior of $(NPCl_2)_3$ and $(NPCl_2)_n$ in the presence of diethylamine. Total replacement of all the halogen in $(NPCl_2)_3$ by diethylamino can be effected, although a 24-hr reaction at 150° is required before total substitution occurs.[7] Forcing conditions such as these are difficult to apply to the polymeric reaction because of the need to avoid depolymerization of the skeleton to lower cyclic species.

Synthesis of Poly(aminophosphazenes) with Mixed Substituents.—The synthesis of poly(diethylaminochlorophosphazene) (VI) described above provided a novel route to the controlled synthesis of polyphosphazenes which contained two different substituents attached to each phosphorus atom. The remaining chlorine atoms in the diethylaminochloro derivative could be replaced by other nucleophiles, as illustrated in eq 1. Reagents used in this reaction included ammonia, methylamine, ethylamine, propylamine, piperidine, and sodium trifluoroethoxide.

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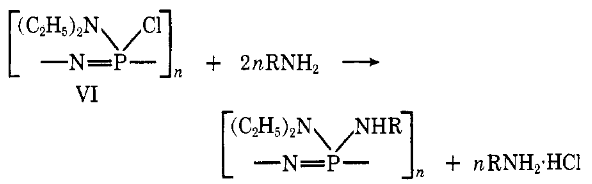

$$\underset{\text{VI}}{\left[\begin{array}{c}(C_2H_5)_2N\diagdown\;\diagup Cl\\ -N{=}P-\end{array}\right]_n} + 2n\,RNH_2 \longrightarrow \left[\begin{array}{c}(C_2H_5)_2N\diagdown\;\diagup NHR\\ -N{=}P-\end{array}\right]_n + n\,RNH_2{\cdot}HCl \qquad (1)$$

Polymer VI reacted with ammonia in tetrahydrofuran at 0–25° to yield a clear, colorless, glass-like material of structure $[NP(NH_2)N(C_2H_5)_2]_n$. The cross-linking process which was evident during attempted bisammonolysis appeared to be absent during this reaction. The mixed-substituent polymer hydrolyzed slowly in contact with atmospheric moisture with the liberation of ammonia. Treatment of VI with methylamine, *n*-propylamine or *n*-butylamine yielded the polymers $[NP(NHCH_3)N(C_2H_5)_2]_n$, $[NP(NHC_2H_5)N(C_2H_5)_2]_n$, $[NP(NHC_3H_7)N(C_2H_5)_2]_n$, or $[NP(NHC_4H_9)N(C_2H_5)_2]_n$, with no evidence being found for cross-linking or incomplete substitution.

With piperidine, some difficulty was experienced in obtaining complete replacement of chloro by piperidino groups, but the remaining chlorine could be removed by a cross-linking reaction with disodium butane 1,4-dioxide.

The synthetic versatility of this preparative route was also demonstrated by the reaction of $[NP(Cl)N(C_2H_5)_2]_n$ with sodium trifluoroethoxide to yield a mixed trifluoroethoxydiethylamino polymer of structure $[NP(OCH_2CF_3)N(C_2H_5)_2]_n$. With mild conditions, only partial replacement of the halogen occurred with sodium trifluoroethoxide, and the remaining chlorine was then removed by reaction with methylamine to yield a diethylaminomethylaminotrifluoroethoxy terpolymer.

Influence of Steric Hindrance during Substitution.—The cross-linking mechanism with primary amines is apparently controlled by steric factors. Cross-linking occurs readily when ammonia reacts with $(NPCl_2)_n$, less readily when methylamine is employed, and not at all when ethylamine, *n*-propylamine, and *n*-butylamine are employed as nucleophiles. Thus, the group R in a P–NHR unit retards attack by the ligand nitrogen atom on the phosphorus atom of a nearby chain. This evidence is consistent with an S_N2 rather than an S_N1 substitution mechanism. Steric inhibition by the group R in secondary amines also explains the substitution trends observed with those reagents. Thus, the ease of total substitution of halogen in $(NPCl_2)_n$ by base, in the order: $(CH_3)_2NH \approx C_5H_{10}N > (C_2H_5)_2NH > C_6H_5CH_3NH \gg (C_6H_5)_2NH$, roughly parallels the expected increase in steric hindrance. However, the unreactivity of diphenylamine is difficult to explain purely in terms of steric retardation. The fact that diethylamine is less reactive than dimethylamine is evidence against a direct basicity influence. Similar effects are evident during copolymer formation, where ammonia, methylamine, ethylamine, *n*-propylamine, and *n*-butylamine react completely with $[NP(Cl)(C_2H_5)_2]_n$, but where piperidine under the same conditions replaces only part of the available halogen.

Properties of the Polymers.—The polymers of structures $[NP(NHCH_3)_2]_n$, $[NP(NHC_2H_5)_2]_n$, $[NP(NH\text{-}n\text{-}C_3H_7)_2]_n$, and $[NP(NH\text{-}n\text{-}C_4H_9)_2]_n$ are clear, colorless, leathery, film-forming materials which are soluble in acidic organic media. The bismethylamino derivative is unusual in being soluble in water. The polymers are not affected by water or by prolonged exposure to the atmosphere. Although $[NP(Cl)N(C_2H_5)_2]_n$ is an elastomer, $[NP(NH_2)N(C_2H_5)_2]_n$ is a hydrolytically unstable glass. In contrast, the polymers $[NP(NHCH_3)N(C_2H_5)_2]_n$, $[NP(NHC_2H_5)N(C_2H_5)_2]_n$, $[NP(NHC_3H_7)N(C_2H_5)_2]_n$, and $[NP(NHC_4H_9)N(C_2H_5)_2]_n$ are clear, colorless, transparent, flexible, film-forming materials, with the flexibility increasing in the order: $RNH = CH_3NH < C_2H_5NH < C_3H_7NH < C_4H_9NH$. These latter polymers are soluble in a variety of organic media and in aqueous acid, and all four are stable in water and to prolonged exposure to the atmosphere. The copolymer $[NP(OCH_2CF_3)N(C_2H_5)_2]_n$ is a clear, colorless, film-forming material which is soluble in solvents such as tetrahydrofuran and trifluoroethanol. The diethylaminomethylaminotrifluoroethoxy terpolymer is a tough, flexible thermoplastic similar in properties to poly[bis(trifluoroethoxy)phosphazene].[4] Glass transition and melting temperatures are listed in Table I.

Molecular Structure of the Polymers.—The solubility of a high polymer is evidence that the material is not cross-linked. Thus, nearly all the polymers synthesized in this work have a linear or branched structure similar to that of the $(NPCl_2)_n$ precursor. To characterize a polymer adequately, information is required concerning the molecular arrangement, disposition of substituent groups along the chain, the degree of chain branching, and the crystallinity and preferred conformation of the polymer.

The general molecular structure of these polymers appears to be unambiguous. They are prepared from a precursor, $(NPCl_2)_n$, the structure of which is known[18,19] and a wide background of research on the reactions of amines with cyclic trimeric and tetrameric chlorophosphazenes strongly reinforces the view that the amino residues replace the chlorine atoms at phosphorus. Microanalyses of polymers are nearly always less definitive than those of low molecular weight compounds because of the difficulty involved in the removal of trace impurities but, as shown in the Experimental Section, the elemental compositions of the homopolymers correspond satisfactorily to the expected structures. Analyses for the polymers with mixed substituents correspond closest to structures with 52.5 or 55% diethylamino units present. The fact that the diethylamino group content is over 50% may reflect the presence of many branch points and terminal units, where diethylaminolysis is not limited to one site at each phosphorus.

Infrared spectra of the polymers were consistent with the expected structures. All the polymers exhibited a characteristic P=N "stretching" absorption between 1320 and 1100 cm^{-1}, with specific skeletal and related assignments being as follows (with frequencies in cm^{-1}): for $[NP(NHR)_2]_n$ where R is CH_3, 1255, 1200 (P–N), 950 (P–N, C–N), 1190 (C–N); n-C_3H_7, 1260 (P–N), 915 (P–N, C–N), 1190 (C–N); n-C_4H_9, 1250 (P–N), 910 (P–N, C–N), 1190 (C–N); for $[NP(Cl)N(C_2H_5)_2]_n$, 1255, 1200 (P–N), 1160 (C–N),

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TABLE I: ANALYTICAL DATA[a]

Compound	% C		% H		% N		% P		Tg	Tm	Mol wt	Intrinsic viscosity, dl/g	Partial specific volume, ml/g
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found					
$[NP(NHCH_3)_2]_n$	22.86	22.90	7.62	7.66	40.00	42.63	29.52	30.90	14	140	8.1×10^4 [d]	2.0[g]	0.71434
$[NP(NHC_3H_7)_2]_n$	44.72	44.64	9.93	9.83	26.08	25.95	19.25	19.08	4	151		1.10[h]	0.92536
$[NP(NHC_4H_9)_2]_n$	50.08	49.99	10.59	10.51	22.22	21.84	16.40	16.72	8	139		2.50[h]	0.97861
$[NP(Cl)N(C_2H_5)_2]_n$[a,b]	33.80	32.74	7.05	7.09									
$[NP(NHCH_3)N(C_2H_5)_2]_n$[c]	42.06	41.72	9.66	9.49	27.78	27.65	20.50	20.80	8	174	2.30×10^5 [d]	1.41[i]	0.86685
$[NP(NHC_2H_5)N(C_2H_5)_2]_n$[b]	45.42	44.05	9.98	9.69	25.64	25.38	18.92	19.00	−11	111	2.74×10^5 [d,e]	1.16[i]	0.91360
$[NP(NHC_3H_7)N(C_2H_5)_2]_n$[b]	48.30	48.40	10.31	10.43	23.81	23.80	17.57	18.38	−5		1.32×10^5 [d,f]	1.20[i]	0.93012
$[NP(NHC_4H_9)N(C_2H_5)_2]_n$	50.79	50.82	10.58	10.65	22.20	22.05	16.40	16.50	−6		1.55×10^5 [d]	1.41[i]	0.7013

[a] All polymers contained no residual chlorine (Beilstein test) except $[NP(Cl)N(C_2H_5)_2]_n$ for which the chlorine analysis was calcd 20.46, found 20.27. [b] Calculated analyses based on a 45% Cl or NHR, 55% $N(C_2H_5)_2$ content. [c] Calculated analysis based on 47.5% $NHCH_3$, 52.5% $N(C_2H_5)_2$ content. [d] By ultracentrifugation. [e] $\bar{M}_n$ value, 1.55×10^5 by osmotic pressure. [f] $\bar{M}_n$ value, 1.27×10^5 by osmotic pressure. [g] In water at 30°. [h] In CF_3CH_2OH at 30°. [i] In benzene at 30°.

TABLE II: REACTION CONDITIONS FOR THE SYNTHESIS OF $[NP(NHR)N(C_2H_5)_2]_n$

NHR	Amt, mol		THF, ml	Temp, °C	Time, hr	Yield,[a] %
	$[NP(Cl)N(C_2H_5)_2]_n$[a]	RHN_2				
$NHCH_3$	0.7	1.3	900	25	48	20
NHC_2H_5	0.34	2.0	1000	25	24	24
NH-*n*-C_3H_7	0.7	2.3	800	25	48	14
NH-*n*-C_4H_9	0.29	5.0	800	25	48	16

[a] Based on $(NPCl_2)_n$ used initially.

950 (P-N, C-N); for $[NP(NHR)N(C_2H_5)_2]_n$ where R is CH_3, 1240, 1205 (P-N), 1165 (C-N), 935 (P-N, C-N); C_2H_5, 1250, 1200 (P-N), 1165 (C-N), 940 (P-N, C-N); *n*-C_3H_7, 1250, 1200 (P-N), 1165 (C-N), 930 (P-N, C-N); *n*-C_4H_9, 1265, 1200 (P-N), 1165 (C-N), 930 (P-N, C-N). There was no significant skeletal ultraviolet absorption at wavelengths longer than 220 mμ, in keeping with the results derived from related alkoxyphosphazene polymers.[4]

For the mixed diethylamino-primary amino copolymers, it appears likely that the diethylamino groups are disposed nongeminally along the chain. Three items of evidence are consistent with this belief. First, the maximum degree of halogen replacement that could be obtained with diethylamine was close to 50%, and this strongly suggests that one chlorine atom per phosphorus is replaced. Second, the considerable evidence reported in the literature for the reactions of other secondary amines, such as dimethylamine[12,13] or *N*-methylaniline[17] with $(NPCl_2)_{3\text{ or }4}$ indicate a nongeminal replacement pattern, and it is reasonable to assume that this pattern persists with diethylamine.

Third, ^{31}P nmr spectra of the copolymers showed one peak only, and this is consistent with a nongeminal structure. The following are ^{31}P nmr chemical shift values (in ppm) for the homopolymers and copolymers relative to aqueous 85% H_3PO_4 (estimated standard deviation, ±0.5 ppm): $[NP(NHC_3H_7)_2]_n$, −3.9; $[NP(NHC_4H_9)_2]_n$, −4.1; $[NP(NHCH_2CF_3)_2]_n$, −1.1; $[NP(NHCH_3)N(C_2H_5)_2]_n$, −2.2; $[NP(NHC_2H_5)N(C_2H_5)_2]_n$, −4.0; $[NP(NH\text{-}n\text{-}C_3H_7)N(C_2H_5)_2]_n$, −3.1; $[NP(NH\text{-}n\text{-}C_4H_9)N(C_2H_5)_2]_n$, −3.3. In general, the polymers show chemical shifts which are more positive than those of the appropriate cyclic trimers, a result which can be attributed to the greater skeletal torsional mobility of the polymer chain.

None of the polymers prepared in this work were sufficiently crystalline to allow X-ray structural methods to be employed.

The maximum molecular weight of a polymer prepared by this synthesis route should be determined by the chain length of the $(NPCl_2)_n$ used initially. Because different polymerization runs yield $(NPCl_2)_n$ polymer with different average degrees of polymerization, some variation in the molecular weights of the final substituted polymers is to be expected. In nearly every case, the polymer molecular weights were too high for the use of vapor pressure, boiling point, or melting point depression methods, and a combination of osmotic pressure, light scattering, solution viscosity, and ultracentrifugation techniques was employed. Specific values for molecular weights are listed in Table I. The weight average molecular weights fell within the range of 8.1×10^4 to 2.74×10^5. These values are generally lower than expected from the degree of polymerization expected for $(NPCl_2)_n$, as inferred from solution viscosity and light scattering values for other substituted high polymers.[3-5] Thus, aminolysis of $(NPCl_2)_n$ appears to be accompanied by some chain cleavage. Further information about the molecular structure was derived from ultracentrifugation experiments discussed in the next section.

Ultracentrifuge Experiments.—Polymers prepared by this route show a polydisperse molecular weight distribution. If a narrow molecular weight distribution exists, the ratio $\bar{M}_w/\bar{M}_n$[20] approaches unity. Earlier work with poly[bis(trifluoroethoxy)phosphazene][4] suggested a $\bar{M}_w/\bar{M}_n$ ratio of 19, and more recent gel-permeation work with poly[bis(*p*-chlorophenoxy)phosphazene][21] suggested a value of 31. Ultracentrifuge experiments with $[NP(NEt_2)(NH\text{-}n\text{-}C_3H_7)]_n$ yielded a plot of d*n*/d*r* against *r*, and integration of the area under this curve yielded an S-shaped plot of ln *c* against r^2. By interpretation of this curve, it was deduced that the system is both polydisperse and nonideal. One explanation for this is that the degree of chain branching varies widely with the different species present. Those molecules with different degrees of branching would exhibit different partial volumes, and each set would then establish its own equilibrium distribution with respect to molecular weight. Similar results were obtained for $[NP(NHR)N(C_2H_5)_2]_n$, where R is CH_3, C_2H_5, $n\text{-}C_3H_7$, and $n\text{-}C_4H_9$.

Glass Transition Temperatures.—Glass transition temperatures are shown in Table I. The values obtained are in the −11 to +14° range—values which are much higher than those for poly(alkoxyphosphazenes) reported previously.[4] This suggests that amino substituents lower the torsional mobility of the phosphazene backbone when compared to alkoxy substituents.

Experimental Section[22]

Materials.—Hexachlorocyclotriphosphazene (El Monte Chemical Co.) was purified by extraction with concentrated sulfuric acid from heptane solution, followed by isolation of the trimer by pouring of the acid extract onto ice. A subsequent recrystallization from *n*-heptane gave material, mp 110–112°. Direct recrystallization of the commercial trimer gave material, mp 87–110°, which contained ~40% of the cyclic tetramer.

Ammonia, methylamine, and ethylamine (Matheson) were condensed into a storage flask and then distilled into the reaction flask. *n*-Propylamine, *n*-butylamine, triethylamine (Eastman), piperidine (Baker), diethylamine, and *N*-methylaniline (Aldrich) were dried over potassium hydroxide and distilled immediately before use. 2,2,2-Trifluoroethanol (Halocarbon Products) was used as received. Isopropylamine, isobutylamine, *sec*-butylamine (Eastman), and diisopropylamine (Baker) were boiled at reflux for 24 hr over potassium hydroxide pellets and were then distilled onto potassium hydroxide pellets immediately before use. Trifluoroethylamine hydrochloride (Columbia Chemical Co.) was used as received. Benzene (Baker Reagent Grade) and tetrahydrofuran (Fisher Certified Reagent) were boiled at reflux over calcium hydride and then distilled immediately before use.

Thermal Polymerization of $(NPCl_2)_3$.—Hexachlorocyclotriphosphazene (220 g), purified as described above, was placed in a 30 × 3.5 cm constricted Pyrex tube. Air was removed by vacuum pumping at 0.1 mm for 30 min followed by several melt–freeze–evacuation cycles. After the final solidification of the trimer, evacuation was continued for 30 min and the tube was then sealed. The tubes were then placed in a thermo-regulated oven at 250° for 48–96 hr. The exact polymerization time required to ensure a 75% conversion to high polymer without cross-linking depended on the presence of trace impurities[4] and especially on the amount of $(NPCl_2)_4$ present. Reproducible polymerizations were exceedingly difficult to achieve. For this reason the polymerization characteristics of each new batch of purified trimer were determined by small scale polymerization experiments prior to performing a larger scale reaction. Initially, no attempt was made to separate cyclic chlorophosphazene oligomers from the oligomer–polymer mixture. This ensured that the opportunities for cross-linking of the polymer by traces of moisture were minimized. Instead, the substituted oligomers were ultimately separated from the substituted polymer by reprecipitation after the chlorine replacement reactions had been completed.

Reactions of Poly(dichlorophosphazene) with Ammonia.—A number of reactions were performed with the use of tetrahydrofuran solutions of poly(dichlorophosphazene) and ammonia at −50, +25, and +50° with initial excess of both reagents being examined. Ammonolysis of the poly(dichlorophosphazene) was highly exothermic in all cases and the polymeric products were insoluble in the medium and very unstable hydrolytically. Ammonia was evolved when the products were exposed to the atmosphere. The fact that gelation occurred in the initial stages of substitution suggests that a cross-linking process takes place.

Poly[bis(methylamino)phosphazene], $[NP(NHCH_3)_2]_n$.—Methylamine (140 g, 4.5 mol) was distilled into a cooled flask which contained tetrahydrofuran (1000 ml). This stirred solution was allowed to warm to 0° and a solution of poly(dichlorophosphazene) (70 g, 0.60 mol) in tetrahydrofuran (1000 ml) was added dropwise. The mixture was then stirred at 25° for 24 hr, after which time additional methylamine (31 g, 1.0 mol) was added and the white suspension was stirred for a further 12 hr. Addition of the mixture to an excess of *n*-heptane induced precipitation of polymer and amine hydrochloride salt. The total precipitate was then dissolved in water and subjected to dialysis for 1 day. The polymer remaining after dialysis was isolated by freeze-drying of the aqueous solution. It was a slightly hygroscopic material, readily soluble in aqueous 95% ethanol. Analytical, solution viscosity, and molecular weight data are shown in Table I.

Poly[bis(*n*-propylamino)phosphazene], $[NP(NH\text{-}n\text{-}C_3H_7)_2]_n$.—A solution of poly(dichlorophosphazene) (35 g, 0.30 unit mol) in tetrahydrofuran (1000 ml) was added dropwise to a stirred solution of *n*-propylamine (115 g, 1.95 mol) and triethylamine (101 g, 1.0 mol) in tetrahydrofuran (1500 ml). The reaction mixture was stirred at room temperature for 24 hr, and it was then added dropwise to water to precipitate the polymer. Residual amine hydrochloride salt was removed by several washings with water. The polymer was then dried and purified further by reprecipitation from 2,2,2-trifluoroethanol solution into methanol or water. The purified polymer (6 g, 12%) was soluble in trifluoroethanol.

Poly[bis(*n*-butylamino)phosphazene], $[NP(NH\text{-}n\text{-}C_4H_9)_2]_n$.—A solution of poly(dichlorophosphazene) (35 g, 0.30 unit mol) in tetrahydrofuran (1000 ml) was added dropwise to a stirred solution of *n*-butylamine (105 g, 1.45 mol) and triethylamine (140 g, 1.40 mol) in tetrahyfrofuran (1500 ml). The reaction mixture was stirred at 25° for 24 hr before addition to excess water to precipitate the polymer. Purification from salts and oligomers was effected by repeated precipitation from 2,2,2-trifluoroethanol into acetone. The polymer (8 g, 14%) was soluble in trifluoroethanol.

Treatment of Poly(dichlorophosphazene) with Isopropylamine.—A solution of poly(dichlorophosphazene) (40 g, 0.35 mol) in benzene (600 ml) was added dropwise to a stirred solution of isopropylamine (59 g, 1.0 mol) and triethylamine (141.4 g, 1.40 mol). An immediate precipitation of amine hydrochloride took place. The reaction mixture was stirred at 25° for 24 hr and then filtered to remove the salt. The polymer which remained in solution was isolated by removal of the solvent at reduced pressure. Analytical tests revealed the presence of residual chlorine in the polymer, and this explained the hydrolytic instability and the tendency for cross-linking. Approximately

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[20] $\bar{M}_w$ is the weight average molecular weight determined by light scattering, solution viscosity, or ultracentrifugation techniques. These methods favor measurement of the higher molecular weight species present. $\bar{M}_n$ is the number average molecular weight obtained by colligative techniques which preferentially favor the lower molecular weight species (see ref 18).

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[22] Ultracentrifuge experiments were conducted with the use of a Beckman Model E analytical ultracentrifuge, with tetrahydrofuran used as a solvent for the diethylamino- aminophosphazene copolymers, trifluoroethanol for $[NP(NH\text{-}n\text{-}C_3H_7)_2]_n$ and $[NP(NH\text{-}n\text{-}C_4H_9)_2]_n$, and aqueous 95% ethanol for $[NP(NHCH_3)_2]_n$. The sedimentation equilibrium method was employed. Number average molecular weights were measured with the use of a Hewlett-Packard Model 501 high speed membrane osmometer fitted with Schleicher and Schuell 08 membranes, with toluene as a solvent at 40°. Infrared spectra of films cast on salt plates were recorded on a Beckman IR5A or a Perkin-Elmer 621 spectrometer. Solution viscosities were measured with Cannon dilution viscometers and solution density measurements were made using standard pycnometers. Glass transition temperatures were determined either by differential thermal analysis with a Du Pont instrument, with some of the values kindly provided by the Firestone Research Laboratory, or with the use of a torsional pendulum device constructed from a design suggested by Dr. J. V. Koleske of Union Carbide Corp.

75% substitution of chlorine by isopropylamine was estimated on the basis of the amine hydrochloride recovered. Similar results were obtained when poly(dichlorophosphazene) was treated with a tenfold excess of isopropylamine in tetrahydrofuran at 60° for 36 hr.

Treatment of Poly(dichlorophosphazene) with Isobutylamine and *sec*-Butylamine.—With the use of the techniques described above, poly(dichlorophosphazene) (11 g, 0.095 mol) was allowed to react with isobutylamine (51 g, 0.7 mol) in tetrahydrofuran (800 ml) at 60° for 36 hr. The precipitate consisted of a mixture of polymer and isobutylamine hydrochloride. The latter compound was removed by solution in hot water, recovered, and identified. The weight of amine hydrochloride (16.8 g) indicated ~80% replacement of chlorine in the polymer by isobutylamine. A similar reaction between poly(dichlorophosphazene) (9.2 g, 0.079 mol) and *sec*-butylamine (45 g, 0.62 mol) yielded 9.1 g of amine hydrochloride, which was indicative of 52% chlorine replacement.

Poly[bis(2,2,2-trifluoroethylamino)phosphazene].—Trifluoroethylamine hydrochloride (25 g, 0.186 mol) was added to a solution of triethylamine (40 g, 0.40 mol) in tetrahydrofuran (400 ml), and the mixture was stirred at 55° for 1 hr to liberate the free base. The mixture was cooled to 25° and to it was added dropwise a solution of poly(dichlorophosphazene) (6 g, 0.051 mol) in tetrahydrofuran (400 ml). The reaction mixture was heated at reflux and stirred for 24 hr and then cooled to 25° and filtered to removed triethylamine hydrochloride (38 g, 96%). The filtrate was reduced in volume to 150 ml and the polymer was precipitated from it by addition to excess *n*-heptane. The poly[bis(trifluroethylamino)phosphazene] (8.2 g, 66% yield) was further purified by precipitation from acetone into water (5.4 g, 44% overall yield). The polymer forms clear, colorless, brittle films which are soluble in tetrahydrofuran or acetone but are insoluble in benzene.

Treatment of Poly(dichlorophosphazene) with *o*-Phenylenediamine.—A solution of poly(dichlorophosphazene) (49 g, 0.16 mol) in tetrahydrofuran (500 ml) was added to a solution of *o*-phenylenediamine (29 g, 0.27 mol) and triethylamine (36 g, 0.36 mol) in tetrahydrofuran (1000 ml). Amine hydrochloride salt formation and gelation of the mixture occurred rapidly. The resultant cross-linked polymer was unstable to atmospheric moisture.

Treatment of Poly(dichlorophosphazene) with *N*-Methylaniline.—A solution of poly(dichlorophosphazene) (16 g, 0.14 mol) in THF (500 ml) was added to a stirred solution on *N*-methylaniline (60 g, 0.56 mol) and triethylamine (28 g, 0.28 mol) in THF (100 ml) and the mixture was heated at reflux for 3 days. The triethylamine hydrochloride salt which precipitated from solution was filtered off and dried (18 g, 0.115 mol, 42%). This corresponded to only 30–40% replacement of chlorine by *N*-methylamino. The polymeric products which remained in solution were isolated by removal of the solvent in vacuum. They hydrolyzed rapidly in contact with atmospheric moisture. Similar results were obtained when benzene was used as a reaction solvent.

Treatment of Poly(dichlorophosphazene) with Diphenylamine.—A solution of poly(dichlorophosphazene) (25 g, 0.22 mol) in benzene (600 ml) was added to a stirred solution of diphenylamine (100 g, 0.59 mol) in benzene (200 ml). The reaction mixture was stirred at 25° for 4 days and at reflux temperature for an additional 4 days. During this time, the reaction mixture darkened in color and the solution viscosity decreased, but no diphenylamine hydrochloride was formed. Similar results were obtained when triethylamine was employed as a hydrohalide acceptor.

Reaction of Poly(dichlorophosphazene) with Diisopropylamine.—A solution of poly(dichlorophosphazene) (7.3 g, 0.063 mol) in tetrahydrofuran (400 ml) was added dropwise to a stirred solution of diisopropylamine (50 g, 0.50 mol) in tetrahydrofuran (400 ml). After a 36-hr reaction at 60°, the mixture was cooled and filtered. The solid amine hydrochloride was extracted with hot water, recovered, dried and identified as diisopropylamine hydrochloride (7.2 g). This corresponded to 41.5% replacement of chlorine by the amine.

Poly(diethylaminochlorophosphazene), $[NP(Cl)N(C_2H_5)_2]_n$.—A solution of poly(dichlorophosphazene) (25 g, 0.22 unit mol) in tetrahydrofuran (600 ml) was added to a stirred solution of diethylamine (14.3 g, 2.25 mol) in tetrahydrofuran (200 ml). The reaction mixture was stirred at 25° for 2 days and then filtered to remove precipitated diethylamine hydrochloride (32 g, 53%). The polymer was isolated by precipitation of the filtrate into an excess of acetone followed by vacuum drying. It was an elastomeric, clear, colorless, film-forming material which was soluble in carbon tetrachloride, chloroform, *s*-tetrachloroethane, benzene, and tetrahydrofuran. It cross-linked slowly when exposed to moist air during several weeks. Material synthesized as precursor for subsequent substitution reactions was used as soon as possible after preparation to avoid the possibility of cross-link formation.

Poly(aminodiethylaminophosphazene), $[NP(NH_2)N(C_2H_5)_2]_n$.—A solution of poly(diethylaminochlorophosphazene) (58 g, 0.5 unit mol) in tetrahydrofuran (1000 ml) was added to a stirred, cooled solution of ammonia (43 g, 2.5 mol in tetrahydrofuran (200 ml). Volatilized ammonia was returned to the system by means of a Dry Ice condenser. The reaction mixture was stirred at 0° for 4 hr and was then allowed to warm to 25° as condensed ammonia (95 g, 5.5 mol) was distilled into the mixture over a period of 4 hr. The mixture was then stirred at 25° for 24 hr and filtered to remove precipitated salts, and the filtrate was added to methanol to precipitate the polymer. The polymer was purified by precipitation from tetrahydrofuran into hexane or heptane. Immediately after its isolation, the polymer was a clear, colorless glass, but storage in the atmosphere or in closed container resulted in slow decomposition accompanied by evolution of ammonia.

Poly(alkylaminodiethylaminophosphazenes), $[NP(NHR)N(C_2H_5)_2]_n$.—The same general synthesis procedure was used for the preparation of $[NP(NHCH_3)N(C_2H_5)_2]_n$, $[NP(NHC_2H_5)N(C_2H_5)_2]_n$, $[NP(NH\text{-}n\text{-}C_3H_7)N(C_2H_5)_2]_n$, and $[NP(NH\text{-}n\text{-}C_4H_9)N(C_2H_5)_2]_n$. Reaction conditions are listed in Table II. The following general procedure used for $[NP(NHCH_3)N(C_2H_5)_2]_n$ is typical. A reaction mixture which contained poly(diethylaminochlorophosphazene) (0.7 unit mol), precipitated diethylamine hydrochloride and unreacted diethylamine in tetrahydrofuran (600 ml) was prepared by the method described previously. Methylamine (40 g, 1.3 mol) was condensed from a cylinder and then distilled into tetrahydrofuran (300 ml), and to this solution was slowly added the aminochlorophosphazene mixture. Volatilized methylamine was returned to the reaction flask by means of a Dry Ice condenser. The reaction mixture was stirred at 25° for 2 days, then filtered to remove the precipitated salts and added to a tenfold excess of aqueous 95% ethanol to precipitate the polymer. Purification of the polymer was effected by several reprecipitations of the material from tetrahydrofuran or benzene into acetone. The polymer (21 g, 20%) was soluble in carbon tetrachloride, benzene, tetrahydrofuran, and 2,2,2-trifluoroethanol. Films of the polymer could be cast by evaporation of solutions. Analytical samples were prepared by freeze-drying of a benzene solution. The only procedural difference employed for the other three polymers was the use of methanol instead of aqueous 95% ethanol as the initial precipitation medium.

Reaction of Poly(diethylaminochlorophosphazene) with Sodium Trifluoroethoxide and Methylamine.—A solution of poly(diethylaminochlorophosphazene) (31 g, 0.2 mol) in tetrahydrofuran (1000 ml) was added to a stirred slurry of sodium 2,2,2-trifluoroethoxide (150 g, 1.25 mol) in benzene (1500 ml). The reaction mixture was stirred and heated at reflux temperature for 2 days. The tetrahydrofuran was then removed by distillation as benzene (1000 ml) was added, and the mixture was heated at reflux for an additional day. The mixture was washed with water to remove sodium chloride and unreacted sodium trifluoroethoxide, and the polymer was isolated (27 g, 15%) by precipitation of the benzene solution into methanol. A Beilstein test on the purified polymer indicated that some residual chlorine remained in the product, and an elemental analysis indicated 9.5% chlorine present. This polymer was soluble in benzene.

In order the remove the remaining halogen atoms, the polymer (22 g, 0.12 mol) was dissolved in tetrahydrofuran (1000 ml) and methylamine (32 g, 1.0 mol) was distilled into the cooled solution. The mixture was stirred at room temperature for 1 day as volatilized methylamine was returned to the reaction mixture by the use of a Dry Ice condenser. Precipitated methylamine hydrochloride was removed by centrifugation, and the polymer was isolated by precipitation of the solution into methanol. Purification was effected by several subsequent precipitations from tetrahydrofuran into methanol. The product (12 g, 6.5%) was soluble in tetrahydrofuran.

Poly(diethylaminopiperidinomethylaminophosphazene) Co-

polymer.—A filtered reaction mixture containing poly(diethylaminochlorophosphazene) (22.9 g, 0.15 mol) and diethylamine in tetrahydrofuran (1000 ml) was added to a solution of piperidine (100 ml, 1.0 mol) in tetrahydrofuran (500 ml). The mixture was stirred at 25° for 3 days and then filtered to remove amine hydrochloride (10 g, 0.09 mol). Halogen tests at this stage revealed that chlorine replacement was incomplete. The filtrate was added to a solution of methylamine (75 ml, 0.75 mol) and triethylamine (55 g, 0.55 mol) in tetrahydrofuran (500 ml). The mixture was then boiled at reflux for 1 day and filtered to remove triethylamine (2.5 g, 0.018 mol).

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The Lewis Basicity of Some Difluorophosphines toward Borane

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The previously unreported compounds CH_3SPF_2, $(CH_3S)_2PF$, $CH_3PF_2 \cdot BH_3$, $CH_3SPF_2 \cdot BH_3$, and $(CH_3S)_2PF \cdot BH_3$ have been prepared and characterized by ^{19}F, ^{11}B, ^{1}H, and ^{31}P nmr and ir spectroscopy as well as by stoichiometric data. Mass spectral data were also used to help characterize CH_3SPF_2 and $(CH_3S)_2PF$. A series of base displacement reactions established the base strengths toward borane as $CH_3PF_2 > (CH_3)_2NPF_2 > CH_3OPF_2 > CH_3SPF_2 \geq (CH_3S)_2PF$ while $^1J_{BP}$ for the fluorophosphine–borane adducts decreases in the series $(CH_3)_2NPF_2 > CH_3OPF_2 > CH_3PF_2 > CH_3SPF_2 > (CH_3S)_2PF$. The basicity of CH_3PF_2 is not mirrored by the value of the $^1J_{BP}$ coupling constant.

Rudolph and Schultz reported[1] that there is an empirical relationship between the magnitude of J_{BP} and the dative bond strength for the BH_3 adducts of a series of smoothly varying phosphine ligands such as $(Me_2N)_{3-n}PF_n \rightarrow BH_3$, $F_{3-n}H_nP \rightarrow BH_3$, and $F_2XP \rightarrow BH_3$ (X = F, Cl, Br).[1] However, the correlation did not appear to be general for the case when the phosphine belongs to different series.[1] Cowley and Damasco[2] also suggested that there is a correlation between the J_{BP} coupling constant and the base strength of a series of 15 phosphines toward BH_3. Their data for two series of phosphines (containing three and four members, respectively) were obtained from the previous literature, and for the other phosphines they performed three selected displacement reactions. From these data they concluded that J_{BP} of the borane adduct considered may be taken as a measure of the basicity of the phosphine examined toward BH_3.

We have been examining the base strength of phosphines of the type PF_2X (X = Me, MeO, Me_2N, MeS) and PFX_2 (X = MeS) toward BH_3 to see if the dative π bonding between the filled 2p orbitals of MeO, Me_2N, and MeS and the vacant P 3d or P 4p orbitals influences the basicity of the phosphine. In a previous article we suggested[3] that a dative bond of this type may be important in determining the PF bond distance and the FPF bond angle in a series of PF_2X compounds. Our studies indicate that although the stability of phosphine–borane adducts correlates with J_{BP} for a series of five phosphine–borane adducts, a 1:1 correlation between J_{BP} and base strength is not possible. The base strengths of the phosphines we examined were determined by displacement reactions. In structurally similar compounds, the entropy change accompanying coordination to a specific acid should be approximately constant and contributions to differences in entropy correspondingly small. The structures of three of the four difluorophosphines we investigated were known to be similar, and we expect no gross distortions in the structures upon coordination.[3,4]

Experimental Section

All work was carried out under inert atmosphere or by standard vacuum-line techniques. ^{31}P and ^{19}F nmr, ir, and mass spectral data were obtained by the use of previously described instrumentation.[5] ^{11}B nmr spectra were recorded with a Varian Model HA-100 nuclear magnetic resonance spectrometer operating at 32.1 MHz.

$MePF_2$,[6] $MeOPF_2$,[7a] Me_2NPF_2,[7b] and B_2H_6[8] were prepared as described in published methods and purified by either codistillation[9] or by trap-to-trap distillation.

Preparation of CH_3SPF_2 and $(CH_3S)_2PF$.—The hitherto unreported $MeSPF_2$ and $(MeS)_2PF$[10] were prepared by the interaction of PF_2Cl and CH_3SH in the presence of Me_3N. In a typical reaction 7.00-mmol samples of PF_2Cl,[7b] Me_3N[11] (dried over sodium), and MeSH (Amoco) were condensed sequentially at −196° into a previously dried 500-ml round-bottom flask equipped with a Teflon vacuum valve (Kontes). The reaction mixture was allowed to warm to 25° over a period of 5 min. An immediate reaction was indicated by formation of a white cloud. The volatile products were separated by first passing the mixture through traps held at −45 and −196° and then by codistillation of the material in the −196° trap. A 1.45-mmol sample of PF_3, a 0.04-mmol sample of PF_2Cl, and a 0.04-mmol sample of Me_3N were recovered and were identified by their gas-phase ir spectra. In addition, a 1.92-mmol sample of $MeSPF_2$ and a

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