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Phosphonitrilic Compounds. VII.[1] High Molecular Weight Poly(diaminophosphazenes)[2]

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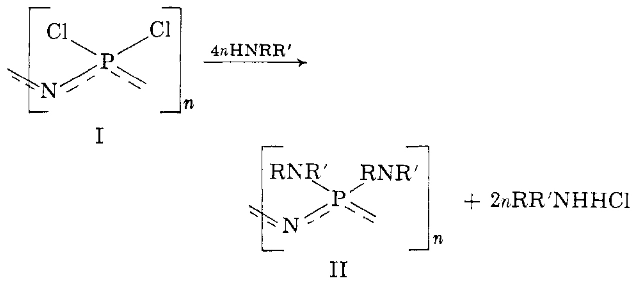
High molecular weight poly(dichlorophosphazene), $(NPCl_2)_n$, was allowed to react with aniline, dimethylamine, ethylamine, and piperidine to yield poly(diaminophosphazenes), $[NP(NRR')_2]_n$. The characterization and properties of these polymers are described. Reaction of $(NPCl_2)_n$ with ammonia or methylamine induced cross-linking of the phosphazene chains, while treatment with diethylamine, methylphenylamine, or diphenylamine did not bring about substitution. An explanation of this behavior in terms of steric hindrance involving the amine is discussed. The qualitative results are consistent with the concept that replacement of chloro by amino in polyphosphazenes involves a nucleophilic attack by the amine at phosphorus. The poly(diaminophosphazenes) act as polyelectrolytes in acidic media.

Introduction

The reactions of poly(dichlorophosphazene) (I) with alkoxides and aryloxide to yield high molecular weight poly(alkoxy- and aryloxyphosphazenes) were reported previously.[1] The present paper describes a comparable procedure for the synthesis of poly(diaminophosphazenes) (II) by the reaction of poly(dichlorophosphazene) with primary or secondary amines. These derivatives represent a new and unusual series of high polymers.



I

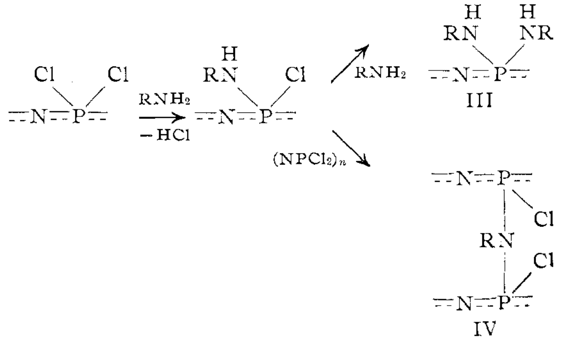
II

$n \approx 15{,}000$

Considerable work has been reported in the literature on the reactions of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, or octachlorocyclotetraphosphazene, $(NPCl_2)_4$, with amines.[4] In general, it appears that with strongly electron-supplying secondary amines, such as dimethylamine, nongeminal substitution occurs, but for some primary amines, such as aromatic amines or *t*-butylamine,[5] a geminal substitution pattern may be evident. The nongeminal orienting effect of dimethylamino can be ascribed either to deactivation of the supporting phosphorus atom by an inductive electron supply or to a steric shielding of that phosphorus atom by the bulky dimethylamino substituent. Sterically hindered secondary amines, such as diethylamine or methylphenylamine, also react with $(NPCl_2)_3$ or $(NPCl_2)_4$ to give partly substituted products.[4] However, the reactions of amines with high polymeric $(NPCl_2)_n$ have not been described. These reactions present additional complications.

Results and Discussion

Treatment of open-chain poly(dichlorophosphazene) with a primary amine could lead to the formation of open-chain disubstituted products (III) or cross-linked species (IV). With ammonia or methylamine



the cross-linking reaction occurred readily, and insoluble, partly-substituted products of type IV were formed. However, with aniline or ethylamine there was no evidence of cross-linking, and fully-substituted, high molecular weight products of structure $[NP(NHC_6H_5)_2]_n$ and $[NP(NHC_2H_5)_2]_n$ were obtained. It seems clear that the larger steric dimensions of the ethyl and phenyl groups serve to retard attack by the substituent nitrogen atom on an adjacent chain phosphorus.

With secondary amines, excessive steric hindrance retards even the initial substitution at phosphorus. For example, although reaction of I with dimethylamine or piperidine yielded fully-substituted polymers of structure $[NP(N(CH_3)_2)_2]_n$ and $[NP(NC_5H_{10})_2]_n$, replacement of even one chlorine atom per phosphorus could not be effected with diethylamine, methylphenyl-

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(1) Part VI: H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966).

(2) A preliminary reference to this work is contained in a previous communication: H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87**, 4216 (1965).

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(4) See, for instance, reviews by C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 275 (1962), and by R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).

(5) S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 5032 (1965).

amine, or diphenylamine under the reaction conditions employed. This suggests that substitution proceeds *via* an initial S$_N$2-type attack by the amine at phosphorus. Presumably each phosphorus atom in the polymer is more shielded by the adjacent repeating units than in the trimer or tetramer.

For the fully-substituted polymers, $[NP(NHC_6H_5)_2]_n$, $[NP(NHC_2H_5)_2]_n$, $[NP(N(CH_3)_2)_2]_n$, and $[NP(NC_5H_{10})_2]_n$, the infrared spectra were consistent with the expected structures and no evidence for P—OH, P=O, or P—O—P units was found. However, small amounts of these units could have remained undetected. Each polymer showed the characteristic -P-N- stretching bands near 1200 cm^{-1}. Tentative assignments for the main peaks were as follows (frequencies in cm^{-1}): NRR′ = NHC_6H_5, 1280 ($N-C_6H_5$), 1180–1220 (-P-N-), 925–960 (-P-N-), 750, 690 (aryl); $NH(C_2H_5)$, 1265, 1200 (-P-N-), 1120 (C-N), 950 (C-N or -P-N-); $N(CH_3)_2$, 1280, 1240 (-P-N-), 1180 (C-N), 980 (C-N or -P-N-); $N(C_5H_{10})$, 1248 (-P-N-), 1198 (-P-N- or C-N), 1333, 1160, 1120, 1060, 950 (piperidyl). There was no significant ultraviolet absorption at wavelengths longer than 200 mμ for $[NP(NHC_2H_5)_2]_n$ or $[NP(N(CH_3)_2)_2]_n$. Only very weak, broad absorption bands (log ϵ <0.4) were detected between 220 and 350 mμ, and these were attributed to the presence of trace impurities. The phenylamino and piperidino derivatives gave spectra which were characteristic of the side groups. The ultraviolet spectra are, therefore, consistent with a poorly delocalized skeletal π system.[1]

^{31}P nmr peaks were as follows (values in ppm at ~30°): $[NP(NHC_6H_5)_2]_n$ (CDCl$_3$), +14; $[NP(NHC_2H_5)_2]_n$ (CDCl$_3$), +26.6; $[NP(NC_5H_{10})_2]_n$ (benzene), +7.7. The dimethylamino derivative showed several broad peaks with the largest at +5.3 ppm and the highest field peak at +0.7 ppm. This could be considered evidence that a wide spectrum of species, from cyclic oligomers to high polymer, was present.[6] Proton nmr spectra were poorly resolved except for the piperidine derivative which showed two peaks at δ 1.43 and 3.0 in a ratio of 3:2.

The general experimental data indicate that the phenylamino, ethylamino, dimethylamino, and piperidino derivatives are of open-chain or macrocyclic structure. It also appears that the high side-group polarity and increased opportunities for hydrogen bonding (when NHR groups are present) decrease the flexibility of the chain, relative to the alkoxy and aryloxy derivatives. This is indicated by the relatively high glass transition temperature of the amino derivatives. The basicity of the side groups (and perhaps of the chain nitrogen atoms also) is probably responsible for the fact that the polymers behave as polyelectrolytes in acidic media. The ethylamino and dimethylamino derivatives were soluble in dilute aqueous acids. All four polymers were stable to water.

The tendency for depolymerization to cyclic oligomers above 100–150°, which was observed for the alkoxy and aryloxy derivatives,[1] was also noticeable with the poly(aminophosphazenes). This was ascribed to side-group steric hindrance.[7] However, the amino side groups appeared to be more prone to oxidative decomposition and cross-linking at moderate temperatures than did the alkoxy or aryloxy derivatives.

Experimental Section

Materials.—Polydichlorophosphazene was prepared by the procedure described previously.[1] Ammonia, aniline (Baker and Adamson), and ethylamine (Matheson) were distilled before use. Diethylamine (Eastman), bp 55°, N-methylaniline (Eastman practical), bp 196°, and piperidine (Eastman practical), bp 106–107°, were distilled through an 18-in. packed column before use. Dimethylamine (Eastman) was used as received and diphenylamine (Eastman) was recrystallized from heptane before use. Methylamine (Matheson) was dried over sodium hydroxide, refluxed over sodium, and distilled. Solvents which came into contact with $(NPCl_2)_n$ were dried rigorously by methods described previously.[1]

Analyses.—Analytical, molecular weight, and solution viscosity data are shown in Table I. The total analyses for the ethylamino, dimethylamino, and piperidino derivatives were 2 to 3% less than theory. This was ascribed to the presence of water or of mineral acids retained as polymer salts. The analyses are considered to be satisfactory in view of the experimental difficulties involved in synthesis and purification.

Poly[bis(phenylamino)phosphazene], $[NP(NHC_6H_5)_2]_n$.—A solution of polydichlorophosphazene[1] (116 g, 1.0 unit mole) in benzene (600 ml) was added to a solution of aniline (800 g, 8.6 moles) in tetrahydrofuran (600 ml), and the mixture was then boiled at reflux for 48 hr and then allowed to stand at 25° for 1 week. The precipitated aniline hydrochloride was filtered off (174 g, 1.34 moles) and polymer was isolated by dropwise precipitation of the filtrate into absolute ethanol (~8 l.). The white, fibrous polymer (70 g, 30%) was then reprecipitated from benzene solution into 95% ethanol, from tetrahydrofuran into a large excess of water, and several times from dioxane into water. Analytical samples were prepared by freeze-drying from dioxane solution. The glass transition temperature was 91° (by differential thermal analysis).

Poly[bis(ethylamino)phosphazene], $[NP(NHC_2H_5)_2]_n$.—A solution of polydichlorophosphazene (116 g, 1.0 unit mole) in toluene (1500 ml) was added slowly to a stirred solution of ethylamine (270 g, 6.0 moles) in toluene (1500 ml). Volatilized ethylamine was returned to the mixture by means of a Dry Ice condenser. The reaction was allowed to proceed at 25° for 8 days. The mixture of polymer and hydrochloride salt was filtered off, dissolved in dilute aqueous sulfuric acid, filtered, and precipitated by addition of dilute aqueous ammonium hydroxide solution. This process was repeated, and the solid polymer was washed with a large excess of water to remove ammonium sulfate and then dried under vacuum over P_2O_5. The polymer was a leathery material which was soluble in dilute aqueous mineral acids, acetic acid, and trifluoroethanol, but insoluble in water, aqueous base, benzene, and tetrachloroethane. The polymer glass transition temperature (by dta) was 30°.

Poly[bis(dimethylamino)phosphazene], $[NP(N(CH_3)_2)_2]_n$.—A solution of polydichlorophosphazene (200 g, 1.73 unit moles) in benzene (2.5 l.) was added dropwise over 2 hr to a stirred solution of dimethylamine (242 g, 5.4 moles) in benzene (1 l.) maintained at 0–5°. Volatilized dimethylamine was returned to the reaction flask by means of a Dry Ice condenser. The reaction was then allowed to proceed at 25° for 24 hr. The mixture was filtered hot to remove amine salts, and polymer (50 g) was then

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(6) Dimethylaminochlorocyclotriphosphazenes show ^{31}P peaks in the −20 to −30 ppm region: R. Keat, S. K. Ray, and R. A. Shaw, *J. Chem. Soc.*, 7193 (1965).

(7) H. R. Allcock, *Inorg. Chem.*, **5**, 1320 (1966).

Table I

Analytical Data

	C, %		H, %		N, %		P, %		Cl, %			
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Mol wt[a]	Intrinsic viscosity, dl/g
$[NP(NHC_6H_5)_2]_n$	62.88	61.74	5.28	5.55	18.33	18.08	13.51	13.49	...	0.8[b]	1,650,000	1.44 (THF) 30°
$[NP(NHC_2H_5)_2]_n$	36.10	34.6	9.03	9.07	31.5	30.39	23.3	23.13	...	0	...	0.47 (1 *M* NaCl–0.1 *N* HCl) 20°
$[NP(N(CH_3)_2)_2]_n$	36.08	34.01	9.09	8.63	31.56	30.79	23.27	23.60	...	0–0.2[b]	363,000	0.89 (1 *M* NaCl–0.1 *N* HCl) 30°
$[NP(NC_5H_{10})_2]_n$	56.32	53.27	9.45	9.3	19.71	18.78	14.52	15.43	...	1.10[b]	1,580,000	1.33 (benzene) 30°

[a] By light scattering in tetrahydrofuran (phenylamino and piperidino compounds), trifluoroethanol (ethylamino and dimethylamino compounds), or benzene (piperidino derivative). [b] Apparently due to the presence of a trace of polymer hydrochloride salt (the chlorine does not appear to result from the presence of residual P–Cl bonds since it is not hydrolyzable; some decrease in chlorine analysis can, however, be effected by prolonged treatment with dry tertiary amine). The removal of the last trace of sulfuric acid or hydrogen chloride was a serious problem with all the aminophosphazene polymers synthesized here because of the basicity of the polymers.

precipitated from the filtrate by addition to heptane. Purification was effected by precipitation of the polymer three times from solution in dilute aqueous sulfuric acid into dilute aqueous ammonium hydroxide and once from dilute acetic acid in ethanol into methanol which contained a trace of triethylamine. The polymer was then dried under vacuum over P_2O_5. It was a leathery material which was soluble in acetic acid, dilute mineral acids, and trifluoroethanol, but insoluble in benzene, chloroform, carbon tetrachloride, ethyl acetate, methanol, acetonitrile, acetone, water, dimethylformamide, and dimethyl sulfoxide. The glass transition temperature (dynamic mechanical) was −4°.

Poly[bis(piperidino)phosphazene], $[NP(NC_5H_{10})_2]_n$.—Piperidine (187 g, 2.2 moles) was added dropwise to a solution of polydichlorophosphazene (58 g, 0.5 mole) in benzene (1000 ml), and the mixture was heated at reflux for 48 hr. Piperidine hydrochloride was filtered off, and polymer was obtained from the filtrate by addition to ethanol. It was then reprecipitated from benzene into ethanol and was isolated after centrifuging. It was then redissolved in benzene and freeze-dried. The polymer was a colorless, film-forming material which was soluble in tetrahydrofuran, benzene, toluene, chlorinated hydrocarbons, formic and acetic acids, trifluoroethanol, and concentrated sulfuric acid. It was insoluble in dilute mineral acids. The glass transition temperature of the polymer was 19° (by dta).

Reaction of $(NPCl_2)_n$ with Ammonia.—Ammonia gas (422 g) was bubbled slowly over 2 days into a stirred solution of polydichlorophosphazene (200 g, 1.73 unit moles) in dry benzene (2 l.) at 25°. The initial cross-linked conglomerate eventually dispersed to a white suspension. This was filtered off, washed with 50 vol. % aqueous acetone (4 l.) to remove ammonium chloride, and dried. The residual polymer (93 g) was insoluble at 25°. It dissolved in boiling water, however, with evolution of ammonia. The precipitate, which was obtained by addition of this solution to methanol, appeared to have undergone extensive hydrolytic degradation.

Reaction of $(NPCl_2)_n$ with Methylamine.—A solution of polydichlorophosphazene (116 g, 1.0 mole) in toluene (1500 ml) was added over 30 min to a stirred solution of methylamine (155 g, 5.0 moles) in tetrahydrofuran (1500 ml). Volatilized methylamine was returned to the reaction flask *via* a Dry Ice condensor. Gelation of the mixture occurred almost immediately, but the conglomerate was dispersed by high-speed stirring for 48 hr. The polymeric product was insoluble in a wide variety of media and appeared to be cross-linked.

Reaction of $(NPCl_2)_n$ with Diethylamine, Methylphenylamine, and Diphenylamine.—When benzene solutions of polydichlorophosphazene were boiled with more than a two-molar excess of diethylamine, methylphenylamine, or diphenylamine for up to 4 days, no significant formation of amine hydrochloride salt took place. With diethylamine the small quantity of hydrochloride which did precipitate was ascribed to minor amounts of $(NPCl_2)_3$ in the equilibrium polymer mixture. With both methylphenylamine and diphenylamine, the most noticeable changes during refluxing were that the solution viscosity decreased markedly and the color darkened, presumably because of oxidation of the amine.

Acknowledgments.—We thank Dr. J. E. Lancaster and Mrs. M. Neglia for the nmr data, Dr. V. J. Lostaglio for the light-scattering results, and Mrs. R. R. Fiala for the solution viscosity measurements.