reaction mixture was maintained at 2 °C or lower during the addition. The mixture was then stirred at 0 °C for 24 h, allowed to warm to 25 °C, and stirred at this temperature for 180 h. ^{31}P NMR spectroscopy at this point showed three distinct sets of resonances, none of which could be ascribed to P–Cl units. The reaction mixture was filtered and the filtrate concentrated under reduced pressure to a volume of 300 mL. The concentrate was added to hexane to precipitate the polymer as an off-white powder. This was Soxhlet extracted with hexane and precipitated twice from THF or dioxane into pentane.

The second half of the initial reaction mixture was treated with 2-amino-4-picoline (35 g, 0.324 mol) in dry THF (500 mL). The subsequent steps were similar to those described above. The product was a white powder.

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References and Notes

(1) Hall, C. E.; Hall, O *Experienta* **1961**, *17*, 544; **1962**, *18*, 38.
(2) Cornell, R. J.; Donaruma, L. G. *J. Polym. Sci., Part A* **1965**, *3*, 827.
(3) Donaruma, L. G.; Razzano, J. *J. Med. Chem.* **1966**, *9*, 258.
(4) Donaruma, L. G.; Vogl, O., Eds. "Polymeric Drugs"; Academic Press: New York, 1978.
(5) Merigan, T. C.; Finkelstein, M. S. *Virology* **1968**, *35*, 363.
(6) Minor, W.; Alfrey, T.; Koehler, J.; Zimmerman, R. *Bacteriol. Proc.* **1971**, *225*.
(7) Lampson, G. P.; Field, A. K.; Tytell, A. A.; Nemes, M. M.; Hilleman, H. R. *Proc. Soc. Exp. Biol. Med.* **1970**, *135*, 911.
(8) Allcock, H. R.; Fuller, T. J.; Mack, D. P.; Matsumara, K.; Smeltz, K. M. *Macromolecules* **1977**, *10*, 824.
(9) Allcock, H. R.; Fuller, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2250.
(10) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 3984, 3987.
(11) Allcock, H. R.; Greigger, P. P.; Gardner, J. E.; Schmutz, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 606.
(12) Allcock, H. R.; Fuller, T. J. *Macromolecules* **1980**, *13*, 1338.
(13) Allcock, H. R.; Fuller, T. J.; Matsumura, K. *J. Org. Chem.* **1981**, *46*, 13.
(14) Einhorn, A.; Fiedler, K.; Ladisch, C.; Uhlfelder, E. *Justus Liebigs Ann. Chem.* **1909**, *371*, 142.
(15) Smitz, H. L.; Loevenhart, A. S. *J. Pharmacol. Exp. Ther.* **1924**, *24*, 159, 167.
(16) Schulemann, W. *Klin. Wochenschr.* **1924**, *3*, 676.
(17) I. G. Farbenindustrie, A. G. German Patent 582715, 1933.
(18) Fussganger, R.; Schumann, O. *Arch. Exp. Pathol. Pharmakol.* **1931**, *160*, 53.
(19) Bonica, J. J. *Curr. Res. Anesth. Analg.* **1951**, *30*, 1, 76.
(20) Weiner, B. Z.; Zilka, A. *J. Med. Chem.* **1973**, *16*, 573.
(21) Allcock, H. R.; Cook, W. J.; Mack, D. P. *Inorg. Chem.* **1972**, *11*, 2584.
(22) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1320.
(23) White, J. E.; Singler, R. E.; Leone, S. A. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2531.

Coupling of Cyclic and High-Polymeric [(Aminoaryl)oxy]phosphazenes to Carboxylic Acids: Prototypes for Bioactive Polymers

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ABSTRACT: Prototypical polymer-bound chemotherapeutic or herbicidal systems have been synthesized in which bioactive molecules are linked to poly(organophosphazenes) by peptide-coupling techniques. The synthetic procedures were developed first through the use of cyclotriphosphazene small-molecule model systems and with the initial use of simple nonbioactive carboxylic acids. These reactions were then utilized for the synthesis of high-polymeric analogues containing bioactive side groups. The sodium salts of 4-cyanophenol and phenol were allowed to react with $(NPCl_2)_3$ or $(NPCl_2)_n$ to yield derivatives of type $[NP(OPh)_x(OC_6H_4CN)_y]_{3 \text{ or } n}$. The 4-cyano groups were then reduced to 4-(aminomethyl)phenoxy units with the use of BH_3·THF. Condensation of the pendent amino groups with acetic, propionic, benzoic, acrylic, and nicotinic acids, *N*-acetylglycine, *N*-acetyl-DL-penicillamine, *p*-(dipropylsulfamoyl)benzoic acid, and 2,4-dichlorophenoxyacetic acid was accomplished with the use of dicyclohexylcarbodiimide. The physical and chemical properties of the products are discussed.

Many advantages can be foreseen for the use of synthetic macromolecules as carriers and controlled-release substrates for bioactive agents.[1] However, relatively few conventional polymers are appropriate for this purpose, primarily because of their bioincompatibility or resistance to hydrolytic breakdown. As discussed by us in other papers,[2-8] poly(organophosphazenes) possess a number of almost unique characteristics that may favor their use as carrier species. These features include the ease with which bioactive agents can be linked covalently or coordinatively to the macromolecular system and the wide choice of side-group structures that can impart water solubility, hydrophilic or hydrophobic insolubility, or, in special cases, biodegradability to nontoxic molecules.

In the present paper we describe a new option for the attachment and hydrolytic release of bioactive side groups. It makes use of an amide linkage between an aryloxy spacer group attached to the phosphazene chain and a carboxylic acid. The polymers described here are prototypes in the sense that they illustrate the range of structures that can be synthesized. However, they are water-insoluble systems that are not designed as facile biodegradable species. Biodegradability requires the use of cosubstituent groups, such as amino acid ester or imidazolyl units.[9] Water solubility requires the presence of methylamino or related cosubstituent groups.[2,10]

As discussed earlier,[11] our preferred route to the synthesis of new phosphazene high polymers involves a prior exploration of new reactions using small-molecule cyclic trimeric phosphazene models. This is the route followed in this work also. The carboxylic acids chosen for these coupling studies include a number of simple molecules such as acetic, propionic, and benzoic acids that were employed as preliminary models for reactions with more complex species. The coupling studies were then extended to reactions of the phosphazenes with acrylic and nicotinic

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acids, *N*-acetylglycine, *N*-acetyl-DL-penicillamine, *p*-(dipropylsulfamoyl)benzoic acid, and 2,4-dichlorophenoxyacetic acid. Acrylic acid was employed as a possible means for the introduction of cross-links. Nicotinic acid provided an example of a simple vitamin. *N*-Acetyl-DL-penicillamine (**13**) is an antiviral agent, and *p*-(dipropylsulfamoyl)benzoic acid (**14**) is a diuretic. 2,4-Dichlorophenoxyacetic acid (**15**) is a well-known herbicide.

Results and Discussion

Outline of Synthetic Procedures. The linkage of carboxylic acids to phosphazenes via condensation to side-group amino residues is an appealing prospect. Many aminophosphazenes such as $[NP(NH_2)_2]_x$, $[NP(NH_2)(NHR)]_x$, or $[NP(NHR)_2]_x$ are known, both as cyclic trimers or tetramers and as high polymers.[12] (*p*-Aminophenoxy)phosphazenes, $[NP(OC_6H_4NH_2)_2]_x$, have also been synthesized.[6,13] However, all attempts to bring about coupling between aminophosphazenes such as these and carboxylic acids proved to be unsuccessful. It appears that NH_2 groups linked directly to a phosphazene skeleton or attached to it through an aryloxy spacer group are deactivated toward condensation reactions.

Thus, an alternative strategy was developed in which a CH_2NH_2 unit was employed as the coupling site. The overall reaction sequence is shown in Scheme I. It involves the synthesis of (*p*-cyanophenoxy)phosphazenes, which were then reduced by means of BH_3·THF to *p*-(aminomethyl)phenoxy groups. The aminomethyl active sites were then induced to couple to a variety of carboxylic acids by DCC-mediated, peptide-coupling techniques.

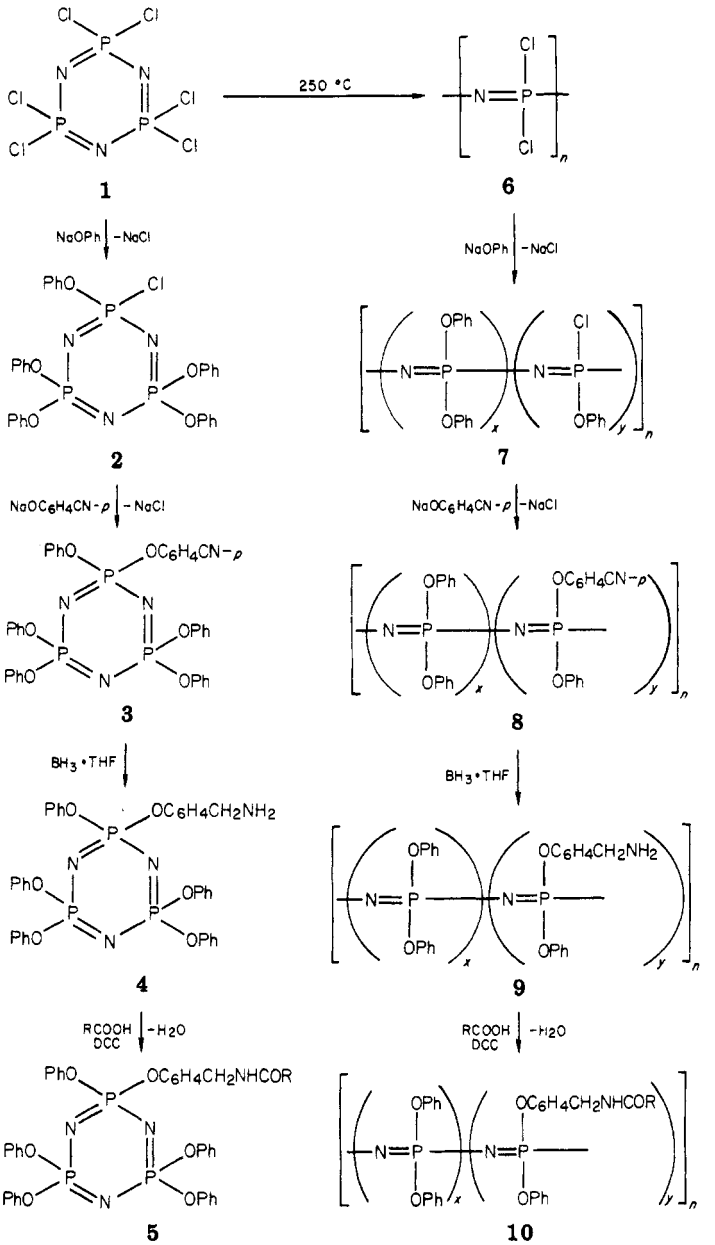
Model Compound Studies. Hexachlorocyclotriphosphazene (**1**) reacted with sodium phenoxide to yield **2**. Treatment of **2** with excess sodium 4-cyanophenoxide yielded **3**. The 4-cyano unit of **3** was reduced to a 4-aminomethyl group with sodium borohydride or a BH_3·THF complex. The latter reagent was preferred because it generates a homogeneous reaction mixture, and it was assumed that this might prove critical for a successful application of this approach to the high-polymeric analogues. Under the influence of dicyclohexylcarbodiimide (DCC) in organic media, compound **4** coupled with the nine carboxylic acids listed in Scheme I to yield products of type **5**. These were yellow, air- and water-stable oils. There seems to be little or no tendency for the formation of an *N*-acylurea derived from the carboxylic acid. This is a frequent byproduct in coupling reactions of this type.[14]

Species **2**–**5** were characterized by a combination of ^{31}P NMR, ^1H NMR, and infrared spectroscopy, mass spectrometry, and elemental microanalysis (see Table I and the Experimental Section). For example, the ^{31}P NMR spectra were singlets for compounds **4** and **5**, with a chemical shift at 9.44 ppm, irrespective of the nature of the para-substituent group. The ^1H NMR spectra were complicated, but the integrated areas of aromatic to aliphatic protons were consistent with the structures indicated. The NH proton resonance decreased in intensity and moved upfield following the conversion of **4** to **5**.

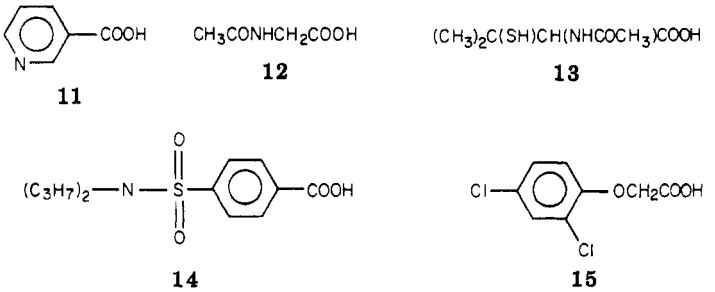
Infrared spectra contained maxima in the 1150–1200-cm^{-1} range, which were indicative of a retention of the cyclophosphazene ring. Aromatic C–H bonds were detected from peaks in the 3000–3100-cm^{-1} region, and the carbonyl groups in species **5** were evident from a distinct peak at 1705 cm^{-1}. Reduction of **3** to **4** could be monitored easily by the disappearance of the characteristic C≡N stretch at 2235 cm^{-1}.

The mass spectra of compounds **2**–**5** showed parent peaks that corresponded to the expected molecular weights (see Experimental Section).

Scheme I



RCOOH = CH_3COOH, C_2H_5COOH, C_6H_5COOH, $CH_2{=}CHCOOH$



Synthesis and Structural Characterization of the High Polymers. With the reaction conditions and characterizations established at the model compound level, it was then possible to extend the procedures to include the analogous high polymers. Hexachlorocyclotriphosphazene (**1**) was polymerized thermally, in vacuo, at 250 °C with procedures discussed previously.[15] Poly(dichlorophosphazene) (**6**) was then treated sequentially with a molar deficiency of sodium phenoxide and with sodium *p*-cyanophenoxide in boiling dioxane to yield **8**.

Table I
Elemental Microanalysis Data[a]

compd	derived from RCOOH	% C	% H	% N	% P
3		61.83	4.03	7.79	12.95
		61.70	4.08	7.73	12.90
4		61.50	4.57	7.76	12.88
		61.31	4.70	7.58	12.69
5	C_6H_5COOH	63.92	4.48	6.77	11.26
		63.72	4.68	6.60	11.15
5	11	62.40	4.35	8.45	11.24
		62.80	4.52	8.10	11.09
8		53.22	3.27	7.94	
		54.06	3.57	7.69	
9		53.16	4.15	7.90	
		55.13	4.02	8.43	
10[b]	CH_3COOH	59.14	4.76	7.51	
		56.85	4.40	8.35	
10[b]	C_2H_5COOH	61.40	5.10	8.10	
		58.96	4.30	7.60	
10[b]	C_6H_5COOH	64.16	5.01	7.41	
		63.29	6.12	8.29	
10[b]	11	58.23	5.87	9.70	
		57.62	7.74	8.99	
10[b]	12	56.02	4.67	9.80	
		55.36	4.07	6.89	
10[b]	13	57.08	5.40	8.90	
		58.93	6.15	8.63	
10[b]	$CH_2=CHCOOH$	55.72	4.09	7.84	
		56.54	4.37	7.37	
10[b]	14	59.76	6.65	7.64	
		60.22	6.12	9.70	
10[b]	15	54.59	4.28	6.26	
		54.18	4.96	7.23	

[a] Calculated values listed in first row, found values in second row. [b] Calculations assume that all the polymers have the structure $\{[NP(OPh)_2]_x[NP(OPh)(OC_6H_4CH_2NCOR)]_y\}_n$, where the x:y ratio is 1:2.

The reduction of **8** to **9** and purification of **9** did not proceed with the simplicity evident in the model compound studies. Reduction yielded a soluble polymer which became insoluble after reprecipitation. This occurred when a variety of reaction conditions was employed (use of BH_3·THF, $NaBH_4$, or $NaAlH_4$, use of THF solvent at −78, 0, or +25 °C or *p*-dioxane at 0 or +25 °C). The insolubilization was ascribed to strong hydrogen bonding in the solid state. However, the polymer could be induced to dissolve in boiling dioxane or THF over a period of several days. Thus, the phenomenon is not due to covalent cross-linking. The coupling reactions of **9** with the carboxylic acids were carried out in THF solution at 0 °C. The coupled products (**10**) were readily soluble in THF or dioxane at 25 °C.

Approximately 35% of the side groups in **10** contained the amide-linked units. This was deduced from the microanalytical data (Table I) and from the ^{31}P NMR spectrum of **8**. This spectrum contained broader peaks than that of the cyclic trimer, but species **8** showed distinct resonances at −21 ppm (from $P(OPh)_2$ groups) and at −17.3 (from $P(OPh)(OC_6H_4CN)$ residues). Following reduction of the cyano function, the peaks coalesced into a broadened resonance centered at −21 ppm.

The infrared spectra of the high polymers were consistent with structures **8**–**10**. As in the case of the trimers, reduction of the cyanophenoxy unit to the aminomethyl function could be monitored by the disappearance of the characteristic sharp absorption at 2235 cm^{-1}. All the polymers showed a characteristic P–N skeletal band at 1320–1100 cm^{-1}. The formation of the coupled products was confirmed by the appearance of a C=O absorption near 1705 cm^{-1}.

The polymers and trimers of types **10** and **5** appeared to be hydrolytically stable at 37 °C in a buffered aqueous medium at pH 7.4. This is expected in view of the hydrophobic character of the phenoxy cosubstituent groups. The induction of biological activity, either of the phosphazene-bound acids or of the free carboxylic acids released by hydrolysis, would probably be enhanced by the use of hydrophilic or hydrolytically unstable cosubstituent groups.

Experimental Section

Reagents and Solvents. Hexachlorocyclotriphosphazene (mp 110–112 °C) was obtained from a trimer–tetramer mixture (Ethyl Corp.) after two fractional vacuum sublimations at 60 °C (0.5 torr), two recrystallizations from heptane, and two additional vacuum sublimations. Phenol (Aldrich) was sublimed before use. All other reagents were obtained from Aldrich with the exception of *p*-(dipropylsulfamoyl)benzoic acid (Sigma) and were used without further purification.

Tetrahydrofuran (THF) and dioxane (Fisher) were distilled from sodium/benzophenone. Sodium hydride, as a 50% dispersion in oil (Alfa), was washed with dry heptane before use. All reactions were carried out under an atmosphere of dry nitrogen.

Analytical Techniques. Proton-decoupled ^{31}P NMR spectra were obtained in the FT mode at 40.5 MHz with a JEOL PS100FT spectrometer equipped with a Nicolet 1080 data processing system. Infrared spectra were obtained with a Perkin-Elmer 580 spectrometer. Polymer molecular weight determinations were by gel permeation chromatography with the use of a Waters Associates ALC-201 instrument. Approximate calibration of the columns was accomplished by means of narrow molecular weight polystyrene standards obtained from Waters Associates. The T_g values of the polymer samples were measured with a Perkin-Elmer DSC20 instrument. Mass spectra were obtained for the trimeric species with an AEI MS902 mass spectrometer operating at an ionization potential of 30 eV. Elemental analyses were obtained by Galbraith Laboratories.

Synthesis of 3. $N_3P_3(OPh)_5Cl$ (**2**) was prepared by a published method[16] and was recrystallized from heptane to yield white crystals, mp 68–71 °C. *p*-Cyanophenol (2.0 g, 0.0167 mol) was dissolved in THF (250 mL). This solution was added slowly to a suspension of sodium hydride (0.8 g, 0.0167 mol) in THF (100 mL). When the reaction was complete, the mixture was heated to 50 °C. The hot solution was filtered and the filtrate was transferred to a 1000-mL capacity vessel. To this solution was added rapidly a sample of **2** (10.70 g, 0.0168 mol) dissolved in THF (150 mL). The reaction mixture was heated at reflux for 72 h. The solvent was then removed by means of a rotary evaporator, and methylene chloride (100 mL) was added to the residue. The solution was extracted twice with water (2 × 50 mL). The organic layer was dried with magnesium sulfate, and the solution was concentrated by means of a rotary evaporator. Addition of pentane produced a white precipitate of **3**. Recrystallization from methanol and/or column chromatography on silica gel with methylene chloride as eluent yielded $N_3P_3(OPh)_5(OPhCN)$ as white needles, mp 106–108 °C. The ^{31}P NMR spectrum of this compound consisted of a singlet at +9.44 ppm. The total yield of the pure product was 62%.

Preparation of 4. $N_3P_3(OPh)_5(OPhCN)$ (5 g, 0.007 mol) was dissolved in dry THF (100 mL). The solution was cooled with an ice bath, and 10 mL of a 1.6 M solution of BH_3·THF[17] was added via syringe techniques (equivalent to 0.016 mol of BH_3). The solution was allowed to warm slowly to 20 °C and was stirred at room temperature for 24 h. 2-Propanol was added (**Caution**) and the THF was removed under reduced pressure. Methylene chloride was added, the resultant solution was extracted with water, and the organic layer was dried with magnesium sulfate. The solvent was then removed under reduced pressure. The resultant orange-colored oil was purified by chromatography on a silica (Flosil) column using sequentially as eluents methylene chloride, methylene chloride/ethyl acetate, and pure ethyl acetate. Compound **4**, isolated in this way, was a pale yellow oil. The yield of purified product was 78.5% (based on **3**). Structural confir-

mation was by mass spectrometry, ^1H NMR spectroscopy, infrared spectroscopy, and microanalysis (see Table I).

Preparation of Poly(dichlorophosphazene) (6). The cyclic trimer $(NPCl_2)_3$ (200 g) was polymerized in evacuated, sealed glass tubes at 250 °C for periods of 4–12 h. The tube was rocked continuously during polymerization to ensure agitation of the contents. The tube was then cooled, and residual cyclic oligomers were removed by sublimation at 55 °C (0.7 torr).

Poly[phenoxy(4-cyanophenoxy)phosphazene] (8). Poly(dichlorophosphazene) (6) (11 g, 0.095 mol) dissolved in dioxane (1000 mL) was added slowly to stirred solution of sodium phenoxide prepared from phenol (11.66 g, 0.124 mol) and sodium hydride (5.96 g, 0.124 mol) in dioxane (200 mL). The ratio of reactants was designed to bring about replacement of only 66% of the chlorine by phenoxy groups. The mixture was stirred at reflux for 48 h, cooled to 25 °C, and then treated dropwise with a solution of sodium 4-cyanophenoxide prepared previously from 4-cyanophenol (18.65 g, 0.157 mol) and sodium hydride (7.54 g, 0.157 mol) in dioxane (150 mL). The reaction mixture was stirred at reflux for 60 h, cooled to 25 °C, and filtered to remove sodium chloride. The solvent volume was reduced to 500 mL on a rotary evaporator, and the polymer was precipitated from the residue by dropwise addition to water at 25 °C. Purification was by reprecipitation of the polymer from THF into water twice, from THF into absolute ethanol twice, and from THF into pentane once. The polymer was then dried in vacuo (73% yield). Characterization data are listed in Table I.

Poly[phenoxy[4-(aminomethyl)phenoxy]phosphazene] (9). Poly[phenoxy(4-cyanophenoxy)phosphazene] (8) (5 g, 0.0067 mol) was dissolved in dry tetrahydrofuran (150 mL). The solution was cooled to 0 °C by means of an ice bath, and BH_3·THF (13.4 mL, 0.0134 mol) was added as a 1.0 M solution in THF via syringe techniques. The solution was allowed to warm to room temperature and was stirred for an additional 24 h. The reaction was quenched with 2-propanol (**Caution**), and the polymer was isolated by precipitation of the polymer from THF into water, from THF into absolute ethanol, and finally from THF into pentane. It was then dried in vacuo (yield 3.7 g, 78%).

Typical Procedure for Synthesis of Condensation Products 5. Preparation of $N_3P_3(OPh)_5(OC_6H_4CH_2NHCOPh)$. $N_3P_3(OPh)_5(OC_6H_4CH_2NH_2)$ (4) (1 g, 0.0014 mol) was dissolved in dry methylene chloride (25 mL). The solution was cooled by means of an ice bath, and benzoic acid (0.34 g, 0.0028 mol) was added. Dicyclohexylcarbodiimide (DCC) (0.43 g, 0.0021 mol) was dissolved in dry methylene chloride (10 mL) and was added in one portion. A copious white precipitate formed within 1 h. The solution was allowed to warm to room temperature and was stirred for 24 h. The mixture was reduced in volume to 10 mL and was filtered through a coarse fritted funnel to remove dicyclohexylcarbodiimide–urea. The solution was extracted with water, dried with magnesium sulfate, and evaporated to dryness to yield a yellow oil. This was purified by column chromatography on silica, using a 50:50 methylene chloride/ethyl acetate as eluent, to yield 5 as an off-white oil in approximately 62% yield (yield based on 4). The ^{31}P NMR spectra, ^1H NMR spectra, and microanalytical data for this compound were consistent with the structure postulated.

Typical Syntheses of Species 10. Synthesis of $NP(OPh)_{1.33}(OC_6H_4CH_2NHCOCH_2NHCOCH_3)_{0.66}$. Poly[phenoxy[4-(aminomethyl)phenoxy]phosphazene] (9) (1 g, 0.0014 mol) was dissolved in dry THF (50 mL). The solution was cooled to 0 °C and *N*-acetylglycine (0.491 g, 0.0042 mol) was added in one portion. Dicyclohexylcarbodiimide (0.577 g, 0.0028 mol) was dissolved in THF (15 mL) and was added in one portion. The solution was allowed to warm to room temperature. This was accompanied by the formation of a white precipitate of DCC–urea. The solution was stirred at room temperature for 24 h. The product was then isolated by precipitation of the reaction mixture into water. As before, purification was by repeated precipitation from THF into water, from THF into ethanol, and finally from THF into pentane. Characterization data are listed in Table I (yield 80%).

Summary of Characterization Data. Mass spectral parent peaks were detected for the following compounds at the m/e values given: **3**, 718; **4**, 722; **5** (RCOOH = CH_3COOH), 764; **5** (RCOOH = C_2H_5COOH), 778; **5** (RCOOH = C_6H_5COOH), 826; **5** (RCOOH = CH_2=CHCOOH), 777; **11**, 826; **12**, 821; **13**, 895; **14**, 989; **15**, 925.

For the high polymers, the following are T_g values (°C) and GPC molecular weights ($\times 10^{-5}$): **8** +1.3, 4.9–5.3; **9**, +6, 4.9–5.3; **10** (RCOOH = CH_3COOH), −4, 5.1–5.5; **10** (RCOOH = C_2H_5COOH), +3, 5.2–5.5; **10** (RCOOH = C_6H_5COOH), +10, 4.9–5.4; **10** (RCOOH = CH_2=CHCOOH), +19, 4.9–5.2; **11**, +8, 4.9–5.2; **12**, +27, 5.1–5.5; **13**, +12, 5.1–5.5; **14**, +17, 5.1–5.4; **15**, −2, 4.9–5.3.

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References and Notes

(1) Donaruma, L. G.; Vogl, O., Eds. "Polymeric Drugs"; Academic Press: New York, 1978.
(2) Allcock, H. R.; Greigger, P. P.; Gardner, J. E.; Schmutz, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 606.
(3) Allcock, H. R.; Fuller, T. J.; Mack, D. P.; Matsumura, K.; Smeltz, K. M. *Macromolecules* **1977**, *10*, 824.
(4) Allcock, H. R.; Fuller, T. J. *Macromolecules* **1980**, *13*, 1338.
(5) Allcock, H. R.; Austin, P. E. *Macromolecules* **1981**, *14*, 1616.
(6) Allcock, H. R.; Austin, P. E.; Rakowsky, T. F. *Macromolecules* **1981**, *14*, 1622.
(7) Allcock, H. R.; Austin, P. E.; Neenan, T. X. *Macromolecules*, preceding paper in this issue.
(8) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 3984.
(9) Allcock, H. R.; Fuller, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2250.
(10) Allcock, H. R.; Cook, W. J.; Mack, D. P. *Inorg. Chem.* **1972**, *11*, 2584.
(11) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(12) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972.
(13) Kober, E.; Lederle, H.; Ottman, G.; Hooks, H. *Inorg. Chem.* **1967**, *6*, 394.
(14) Klausner, Y. S.; Bodansky, M. *Synthesis* **1972**, 453.
(15) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(16) McBee, E. T.; Okuhara, K.; Morton, C. J. *Inorg. Chem.* **1966**, *5*, 450.
(17) Drago, R. S.; Gaul, J.; Zombeck, A.; Straub, D. K. *J. Am. Chem. Soc.* **1980**, *102*, 1033.