gation number (Figure 6). This drastic increase of the specific viscosity is probably caused by interchain interaction leading to the phase separation mentioned in the previous paragraph.

Conclusion

From these results it can be concluded that polymerization of the reverse micellar system does not proceed intramicellarly but rather by a mechanism analogous to that described for water-soluble monomers solubilized in a reverse micellar system. Viscosity measurements show that polymerization leads to a stabilization of the inverse micellar system. Further addition of water after polymerization leads to a drastic increase in the viscosity finally resulting in gelation.

Experimental Section

Synthesis of Monomer I. Monomer I was synthesized by coupling *N*-didodecyl-*N*-methyl-*N*-(2-hydroxyethyl)ammonium chloride with methacryloyl chloride by using general methods. *N*-Didodecyl-*N*-methyl-*N*-(2-hydroxyethyl)ammonium chloride was synthesized as described elsewhere.[18]

Polymerization. Monomer I was photopolymerized by using 4,4′-azobis(4-cyanovaleric acid) as the initiator. A typical sample contained the desired amounts of initiator and water and 0.05 M of monomer solubilized in either toluene or benzene. The samples were then degassed with nitrogen for 0.5 h and then illuminated with 350-nm lamps for 4 h.

Fluorescence decay curves of degassed solutions were determined by using a single-photon counting apparatus coupled to a PDP 11/23 computer. Several statistical criteria were used[19] to judge the goodness of the fit. A Perkin-Elmer Lamda 5 UV–vis spectrophotometer was used for the UV absorption measurements.

Viscosity measurements were performed by using an Ubbelohde viscosimeter.

GPC chromatograms were taken on a Perkin-Elmer Series 10 liquid chromatograph by using styragel columns of 10^5, 10^4, 10^3, and 10^2 Å. The flow rate was 5 mL/min. An IR detector locked at 5.7 μm was used to detected the polymer. Chloroform with 10^{-3} M tetrabutylammonium bromide was used as the solvent since this is a polar solvent, which inhibits the formation of aggregates. The salt was added to avoid the polymer remaining on the column. Polystyrene standards with molecular weight of 10^5, 10^4, and 3600 were used for the calibration.

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Registry No. I, 114199-09-6; I (homopolymer), 114199-10-9.

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Glyceryl Polyphosphazenes: Synthesis, Properties, and Hydrolysis

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ABSTRACT: Methylene-, isopropylidene-, and methoxymethylene-protected glyceryl units have been linked to cyclic and high polymeric phosphazenes. The structures and physical properties of these protected glyceryl-substituted phosphazenes were investigated by ^{31}P NMR, ^{1}H NMR, and IR spectroscopy and thermal analysis. Hydrolytic deprotection reactions in acidic media yielded the water-soluble cyclic trimeric and high polymeric glycerylphosphazenes. Cross-linking of the protected high polymers was accomplished by γ irradiation. The deprotected polymer cross-linked in the presence of adipoyl chloride or hexamethylene diisocyanate to yield systems that absorbed water to form hydrogels. Slow hydrolysis of poly(diglycerophosphazene) occurred in neutral aqueous media at 37 °C to yield glycerol, phosphoric acid, and ammonia.

Introduction

Water-soluble synthetic polymers are of interest as models for biological macromolecules and for their possible uses in biomedicine. Prominent among the biomedical uses are applications that involve the formation of hydrogels that can be utilized as membranes, structural materials, or matrices for the immobilization of bioactive agents.[1-3]

Particular interest has been shown in polymers that bear hydroxyl units in the side-group structure. Such units provide sites for cross-linking or binding to bioactive agents, for example, via treatment with cyanogen bromide.

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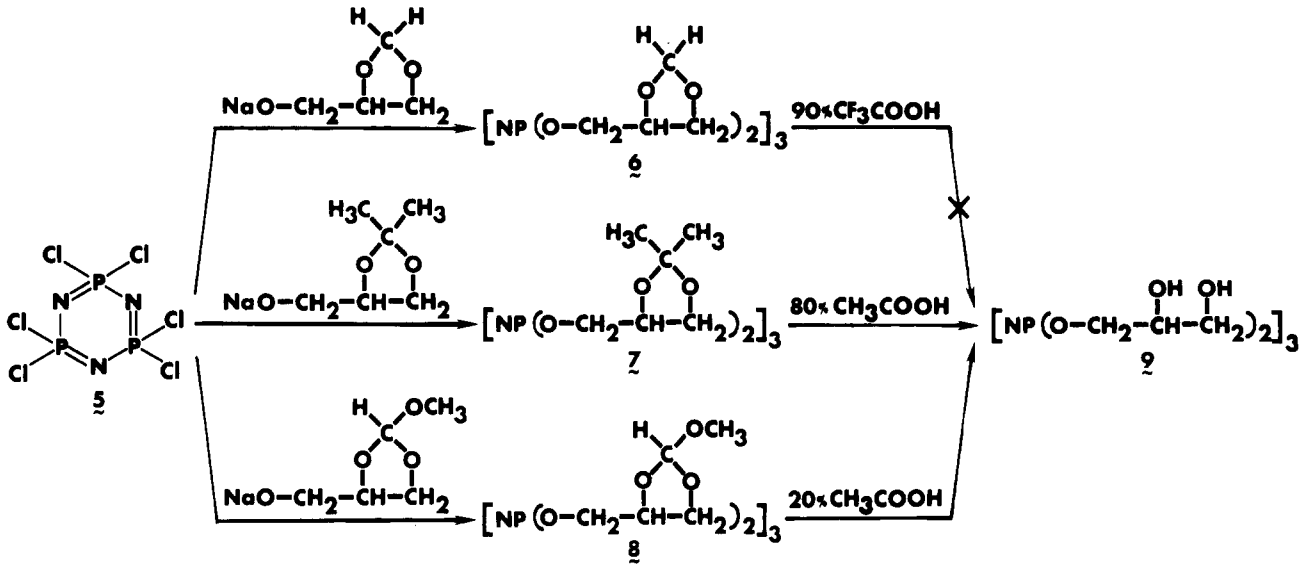
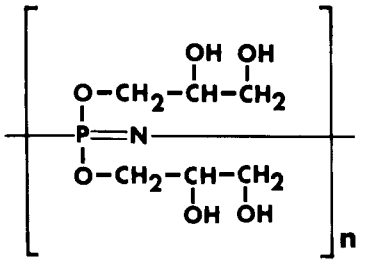
Scheme I



Polysaccharides such as agarose, cellulose, or dextran are used frequently as hydrogels.[4] However, synthetic polymers are perhaps more useful than biopolymers for hydrogel studies because they allow better reproducibility and often permit a more subtle tailoring of specific properties.[5] Poly(vinyl alcohol),[6] poly(hydroxyethyl methacrylate),[7] poly(ethylene oxide),[8] and polymers based on acrylamide[9] have been used widely for hydrogel formation.

In earlier work we have shown that certain poly(organophosphazenes) are soluble in water and can be cross-linked to form membranes or hydrogels. These include poly[bis(methylamino)phosphazene], $[NP(NHCH_3)_2]_n$,[10] and the related mixed-substituent derivatives with methylamino and trifluoroethoxy or phenoxy side groups,[10] poly[bis((methoxyethoxy)ethoxy)phosphazene], $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$,[11] and the glucosyl derivative, $[NP(OC_6H_{11}O_4)_2]_n$.[12] Moreover, we have shown that a wide variety of bioactive molecules that range from antibacterial agents,[13] platinum antitumor compounds,[14] anticoagulents,[15] catecholamines,[16] and oligopeptides[17] or enzymes[18] can be linked to polyphosphazenes to form biomedically active conjugates.

In this paper we describe an extension of these principles to the synthesis of polyphosphazenes that bear glyceryl side groups (1). Two primary reasons for our interest in



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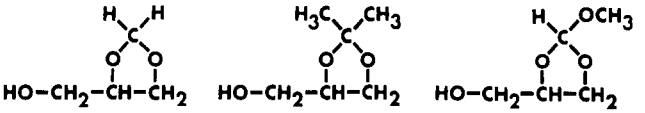
these polymers were (a) the presence of hydroxyl groups in the side units was expected to generate water solubility and provide possible sites either for cross-linking or for the attachment of bioactive agents and (b) the molecular structure of the polymer might allow hydrolytic breakdown to the biologically innocuous products glycerol and phosphate, together with small amounts of ammonia.

In the following sections we discuss (1) the development of synthetic methods for the linkage of glyceryl units to a phosphazene ring or high polymeric chain, (2) characterization of the reaction intermediates and products, (3) cross-linking reactions, especially those that result in the formation of hydrogels, and (4) an examination of the hydrolysis behavior and hydrolysis products.

Results and Discussion

Overall Synthetic Approach. The method of synthesis involved the replacement of chlorine atoms in poly(dichlorophosphazene) by glyceryl units by using the nucleophilic substitution method discussed in earlier papers.[19-21] Because glycerol is a trifunctional reagent, it was necessary to first protect two of the hydroxyl groups to prevent cross-linking reactions. This was accomplished by the formation of glycerol formal (2),[22] isopropylidene-



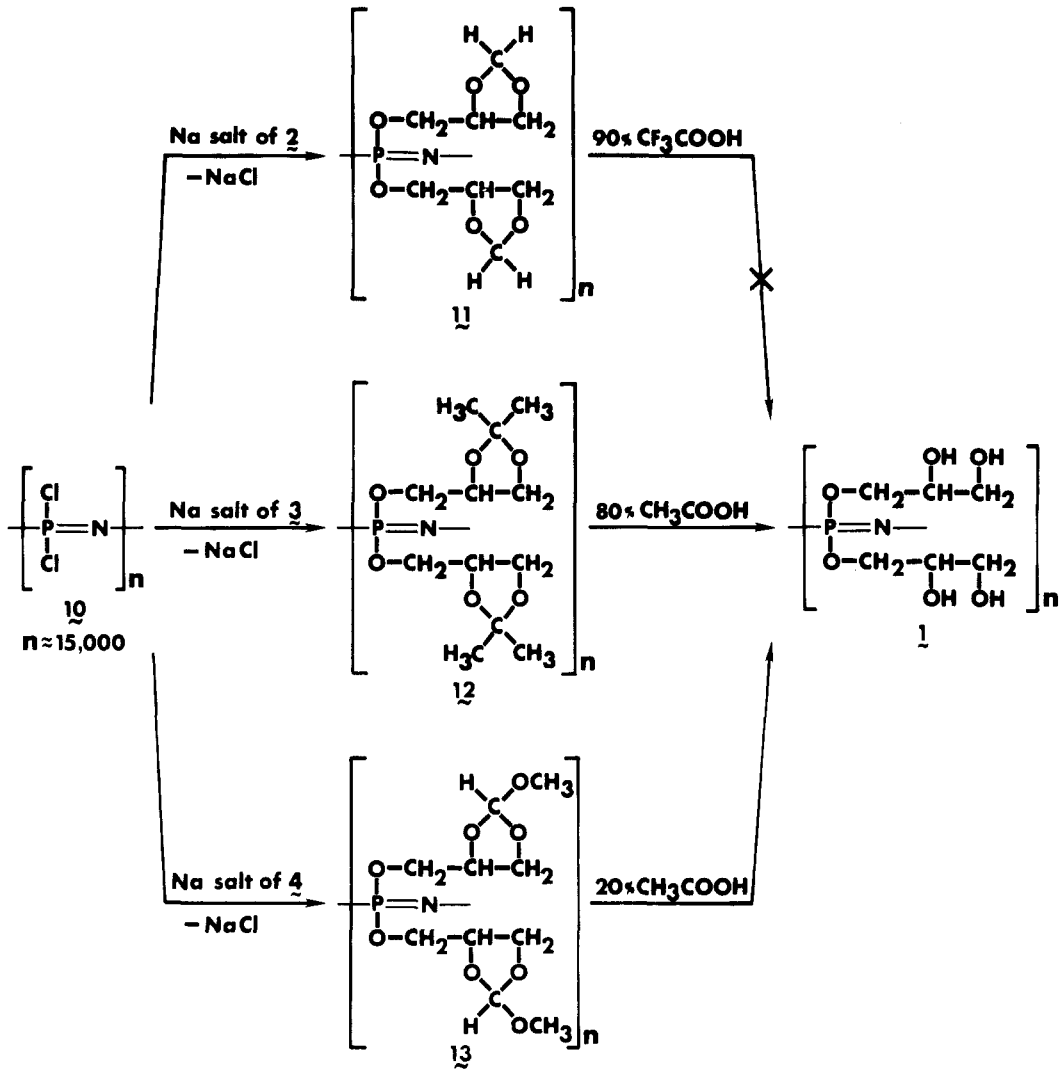
2 3 4

glycerol (3),[23] and 2-methoxy-1,3-dioxolane-4-methanol (4),[24] conversion of these to the sodium salts, and subsequent reaction with poly(dichlorophosphazene). After characterization of these protected intermediates, it was necessary to determine conditions that would bring about deprotection without decomposition of the trimer or polymer. Throughout these transformations, the reactions at the cyclic trimer level were viewed as models for the more challenging macromolecular systems.

Model Reactions with Cyclic Trimers. Glycerol was protected by reaction with formaldehyde to yield glycerol formal (2),[25] by the reaction with acetone to form isopropylideneglycerol (3),[23] and by the reaction with trimethyl orthoformate to yield 2-methoxy-1,3-dioxolane-4-methanol (4).[24] An excess of the sodium salts of these three compounds was then allowed to react with hexachlorocyclotriphosphazene (5), with total replacement of the chlorine atoms by the protected glycerol derivatives. These reactions yielded three different protected glyceryl-substituted trimers, 6, 7, and 8. The general synthetic strategy is outlined in Scheme I.

The structures of compounds 6, 7, and 8 were examined by a combination of infrared, ^{31}P NMR, and ^1H NMR spectroscopy and mass spectrometry. For example, the ^{31}P NMR spectrum of compound 6 consisted of a singlet at +17.5 ppm; the ^1H NMR spectrum contained a doublet at +4.8 ppm and a multiplet at +4.2 to +3.4 ppm. The ^{31}P NMR spectrum of compound 7 showed a clean singlet

Scheme II



at +17.9 ppm, and the ^{1}H NMR spectrum showed a doublet at 1.4 ppm and a multiplet at +4.3 to +3.5 ppm. The ^{31}P NMR spectrum of compound **8** also consisted of a singlet at +18.0 ppm, and the ^{1}H NMR spectrum comprised a doublet at +5.7 ppm, multiplet at +4.5 to +3.4 ppm, and a doublet at +3.2 ppm.

Removal of the methylene, isopropylidene, and methoxymethylene groups was attempted by treatment with various acidic reagents such as trifluoroacetic acid,[26] boron trichloride,[27] HCl/THF,[28] and *p*-toluenesulfonic acid[29] and an ion-exchange resin.[30] The conditions required for deprotection were quite critical. Thus, treatment of **6** with 90% trifluoroacetic acid removed only 25% of the protecting groups after 5 h at 25 °C. But treatment with HCl/THF at 100 °C led to general decomposition. No satisfactory conditions were found for the deprotection of **6**. On the other hand, although compound **7** decomposed in contact with trifluoroacetic acid, it could be deprotected cleanly by treatment with 80% acetic acid[31] (see Experimental Section). Compound **8** was deprotected during 10 h in the presence of aqueous 10% or 20% acetic acid.

The authenticity of the deprotected trimer **9** was established by a combination of infrared, ^{31}P NMR, and ^{1}H NMR spectroscopy and by mass spectrometry. For example, the infrared spectrum contained an O–H stretch at 3500–3200 cm^{-1}, a P=N band at 1250 cm^{-1}, and a C–O stretch at 1120 cm^{-1}. The ^{31}P NMR spectrum consisted of a singlet at +19.7 ppm. Deprotection resulted in the loss of the doublet a +1.4 ppm found in **7** and attributed to the two isopropylidene methyl groups. The mass spectrum of **9** contained a molecular ion peak at 675 (theoretical value = 675).

Synthesis of the High Polymers. Poly(dichlorophosphazene) (**10**) was prepared by the well-established thermal polymerization of the cyclic trimer **5**.[19-21] Polymer **10** was then allowed to react with the sodium salts of the protected glycerols **2**–**4** in a sequence similar to that described for the cyclic trimers. These reactions are summarized in Scheme II.

The structures of the protected glycerophosphazene high polymers **11**–**13** were established by infrared, ^{31}P NMR, and ^{1}H NMR spectroscopy and by elemental microanalysis (Table I).

Deprotection of polymer **11** proved to be as difficult as for its small-molecule counterpart, **6**. Treatment with 90% trifluoroacetic acid for 50 h failed to displace the protective groups. Exposure of **11** to HCl/THF at 100 °C for 2 h brought about general decomposition of the polymers. However, as with the analogous trimer, deprotection of polymer **12** was accomplished by treatment with aqueous 80% acetic acid at 25 °C. As described in the Experimental Section, the reaction time was critical, with high yields of **1** being obtained up to 35 h of reaction, and decomposition to phosphate occurring after this point. Polymer **13** failed to undergo deprotection in the presence of 0.01 or 0.1 N hydrochloric acid—a surprising result in view of the known sensitivity of methoxymethylene-protected glycerol to dilute acid.[32] However, as with the

Table I
Characterization Data for High Polymers

polymer		analysis[a] %C	%H	%N	%Cl	^{31}P NMR,[b,c] ppm	^{1} NMR, ppm	IR, cm^{-1}
11	calcd	38.25	5.58	5.58		s at −7.9	d at 4.8	P=N str at 1250
	found	38.32	5.34	5.31	0.05		m at 4.1–3.5	C–O str at 1050
12	calcd	46.9	7.17	4.56		s at −7.6	m at 4.3–3.5	P=N str at 1250
	found	46.68	7.27	4.70	0.03		d at 1.4	C–O str at 1050
13	calcd	38.59	5.79	4.50		s at −7.4	d at 5.8	P=N str at 1250
	found	38.54	6.08	4.48	0.02		m at 4.3-3.5	C–O str at 1050
							d at 3.1	
1	calcd	29.89	5.81	5.81		s at −4.9	m at 4.3–3.5	O–H str at 3500–3200
	found	29.68	5.53	5.74				P=N str at 1250

[a] Analytical data were obtained by Galbraith Laboratories, Knoxville, TN. [b] All samples were decoupled. Chemical shift positions were relative to aqueous 85% H_3PO_4. A D_2O capillary lock was used. [c] s = singlet; d = doublet; m = multiplet; str = stretch.

analogous trimer, polymer **13** underwent clean deprotection with aqueous 10% or 20% acetic acid. The characterization data for the deprotected polymer **1** are shown in Table I.

Properties of the Polymers. The protected polymers **11–13** are noncrystalline elastomeric materials at room temperature, with glass transition temperatures of −19.1 (**11**), −34.5 (**12**), and −25.7 °C (**13**). The gel permeation chromatography (GPC) average molecular weights of all three polymers were higher than 1×10^6. Polymers **11–13** are insoluble in water but are soluble in THF, from which they can be cast as films. Although a related polymer, $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$, is an excellent solid electrolyte medium,[33] polymer **12** allows only a very low conductivity of salts such as lithium triflate, perhaps because of the chelating action of the vicinal oxygen atoms toward cations.[34]

The deprotected polymer **1** was hygroscopic in the solid state and was soluble in water. Its T_g value was −19.2 °C. Under certain conditions, the deprotection process can result in some chain cleavage. For example, the treatment of polymer **12** with 80% acetic acid reduced the GPC average molecular weight from $>1 \times 10^6$ to 1×10^5. However, the deprotection of polymer **13** by 20% acetic acid yielded polymer **1** without any significant decrease in average chain length.

Cross-Linking Reaction of Polymers 11–13 and 1. Poly(organophosphazenes) that possess aliphatic carbon–hydrogen bonds in the side-group structure are susceptible to radiation-induced cross-linking reactions.[10,11,35] In earlier work we showed that polyphosphazenes with methylamino or (methoxyethoxy)ethoxy side groups cross-link during γ irradiation.[10,11] Polymer **1** did not undergo cross-linking in the solid state when irradiated with up to 2 MRad of γ radiation. The concentration of C–H groups may be too low to permit efficient cross-linking. However, polymers **11** and **12** cross-linked when irradiated with 2 MRad of γ rays. The cross-linked polymers swelled in organic solvents such as THF or dioxane, but they did not dissolve. Treatment of cross-linked **11** with 80% of trifluoroacetic acid or of **12** with 80% acetic acid resolubilized the polymers as the protecting groups were removed.

The presence of free hydroxyl units in the side groups of polymer **1** offered an opportunity for chemical cross-linking. Treatment of **1** in organic media (dimethylformamide, DMF) with adipoyl chloride or hexamethylene diisocyanate, in the presence of 4-(dimethylamino)pyridine as a base, brought about cross-linking in both cases to yield polymers that absorbed water to generate stable hydrogels.

Biomedical Implications. Two aspects of this chemistry are of interest from a biomedical viewpoint. First, the capacity of **1** to cross-link and form hydrogels offers the prospect that this system could be used for the diffusion-controlled release of bioactive agents. Clearly, the rate of diffusion should depend (beyond a certain point) on the degree of cross-linking. Second, the prospect exists that **1** can undergo hydrolytic breakdown in aqueous media to the innocuous products glycerol and phosphate, with the concurrent release of ammonia. This reaction would open possibilities for the bioerosion of this polymer in solution or of hydrogels derived from it.

In fact, polymer **1** was found to hydrolyze to glycerol and phosphate in water at 100 °C. The hydrolysis was detectable after 12 h and was complete after 150 h. At 37 °C the hydrolysis was essentially complete after 720 h. Preliminary experiments with the diffusion release of 2-(*N*-benzyl-*N*-(2-(*N*,*N*-dimethylamino)ethyl)amino)pyridine hydrochloride (tripelennamine hydrochloride)[36] from hydrogels derived from **1** suggested that diffusion-controlled release followed by polymer hydrolysis are possible. We also recognize that the chemistry exists for the covalent linkage of a wide range of bioactive molecules to polymer **1** via the pendent hydroxyl groups.

Experimental Section

Equipment. The ^{31}P NMR spectra were obtained in the Fourier transform mode with a JEOL FX90Q NMR spectrometer. The ^{1}H NMR spectra were obtained with the same spectrometer operated at 90 MHz. Infrared spectra were recorded by means of a Perkin-Elmer 580 spectrometer. Gel permeation chromatography was carried out with the use of a Hewlett-Packard HP1090 liquid chromatograph with an HP1037A refractive index detector, an HP3329A integrator, and an HP9121 disk drive. The system was controlled by a Hewlett-Packard HP83B computer. Glass transition temperatures (T_g) were recorded with the use of Perkin-Elmer DSC-7 unit with a PE7500 computer. A polarizing optical microscope was used to check for crystallinity. Mass spectra were obtained for the cyclic trimeric species with use of an AEI MS902 mass spectrometer operated at an ionization potential of 30 eV. A Hewlett-Packard Model 8450A UV–vis spectrometer was used for the UV spectra.

Materials. Toluene (VWR Scientific) was freshly distilled under nitrogen from sodium benzophenone ketyl. Hexachlorocyclotriphosphazene (**5**, mp 110–113 °C) was obtained from a tetramer–trimer mixture (Ethyl), which was purified by two fractional vacuum subliminations at 60 °C (0.5 Torr), two recrystallizations from hexane, and two further vacuum subliminations. Poly(dichlorophosphazene) (**10**) was prepared by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C.[19,20] Acetic acid (Fisher), glycerol (Aldrich), *p*-toluenesulfonic acid (Aldrich), hydrochloric acid (Fisher), boron trichloride (Aldrich), trifluoroacetic acid (Aldrich), and sodium spheres (Aldrich) were used as received. Trimethyl orthoformate, glycerol formal (**2**), potassium carbonate, adipoyl chloride, hexamethylene diisocyanate, 4-(dimethylamino)pyridine, and tripelennamine hydrochloride were obtained from Aldrich and were used as received.

Preparation of Protected Glyceryl Derivatives. Isopropylideneglycerol (**3**) was prepared by methods described by

other workers.[23] Species **4** was prepared in the following way. Glycerol (92 g, 1 mol) and trimethyl orthoformate (106 g, 1 mol) were stirred in a 1-L two-necked flask at 90 °C. Methanol (2 mol) was distilled out of the mixture. The reaction mixture was then distilled over potassium carbonate (85 °C, 1 Torr), and the impurities were removed by evaporation in vacuo. A colorless, transparent oil was obtained. This compound was characterized by ^{1}H NMR and IR spectroscopy and mass spectrometry (a molecular ion peak at 134).

Preparation of Compound 6. Glycerol formal (23.34 g, 0.224 mol) in toluene (300 mL) and sodium spheres (3.96 g, 0.17 mol) were stirred in a 1-L three-necked flask and refluxed for 8 h. Hexachlorocyclotriphosphazene (**5**) (5 g, 0.014 mol) was dissolved in toluene and was added slowly to the sodium salt solution. The mixture was stirred at reflux for 40 h. The ^{31}P NMR spectrum of the mixture contained a singlet at +17.5 ppm. The solution was then allowed to cool to room temperature, and the final compound was isolated by column chromatography. A transparent oil (yield 80%) was obtained. The mass spectrum showed a molecular ion peak at 753.

Preparation of Compound 7. Sodium spheres (1.452 g, 0.0632 mol) were added to 100 mL of dry toluene. The protected glycerol **3** (12.30 g, 0.094 mol) was then added to the suspension, and the mixture was stirred at reflux for 6 h. To the brown solution was added compound **5** (2 g, 5.75 mmol), and the mixture was stirred at reflux for 48 h. The ^{31}P NMR spectrum of the solution showed a singlet at +17.9 ppm. The solution was filtered through a 2.5-cm layer of silica gel, and the solvent was removed under reduced pressure. The product (**7**) was purified by column chromatography with an ingradient solvent system of hexane, methylene chloride, and THF. A colorless oil was obtained (yield 71%). The mass spectrum contained a molecular ion peak at 921.

Preparation of Compound 8. To a suspension of sodium spheres (2.89 g, 0.103 mol) in toluene (200 mL) was slowly added 2-methoxy-1,3-dioxolane-4-methanol (**4**) (27.6 g, 0.206 mol). The addition was carried out at 0 °C, and care was taken since the reaction was vigorous. After the addition, the mixture was allowed to warm to room temperature. A light brown, transparent solution was obtained after 6 h. Compound **5** (3 g, 8.6 mmol) was added to the solution, and the mixture was stirred at reflux for 60 h. The ^{31}P NMR spectrum of the solution contained a singlet at +18.0 ppm. The viscous product was obtained after column chromatography.

Deprotection of Compound 7. One representative reaction will be described. Compound **7** (0.2 g, 0.218 mmol) was dissolved in a mixture of acetic acid (4 mL) and water (1 mL). The solution was stirred at 25 °C for 12 h, during which time a slight shift of the ^{31}P singlet to +19.7 ppm indicated the formation of **9**. The yield of **9** rose from 68% after 2.5 h to 96% after 12 h, as determined by the extraction of **9** with diethyl ether from the residue left after removal of the aqueous acetic acid. The product was a viscous oil. Prolonged treatment of **7** with acetic acid beyond 12 h brought about general decomposition of **9**, as evidenced by the growth of a ^{31}P NMR peak at 0.9 ppm, which indicated the presence of phosphate.

Preparation of Polymer 11. Poly(dichlorophosphazene) (**10**) (5 g, 0.043 mol) was dissolved in dry toluene (300 mL). The polymer solution was slowly added to the sodium salt of glycerol formal (26.92 g, 0.26 mol). The mixture was stirred at reflux for 6 h, after which time the polymer precipitated from solution. The ^{31}P NMR spectrum of the polymer in THF showed a singlet at −7.9 ppm. The solution was allowed to cool, and the polymer was isolated by filtration. The product was purified by reprecipitation from THF into water (twice) and hexane (three times). An elastomeric polymer was obtained, and the yield was 85%.

Preparation of Polymer 12. Isopropylideneglycerol (33.5 g, 0.056 mol) was dissolved in 100 mL of dry toluene and was treated with sodium spheres (3.97 g, 0.1724 mol). The mixture was stirred at reflux for 6 h. To the sodium salt of compound **4** was slowly added a solution of polymer **10** (5 g, 0.043 mol) dissolved in 200 mL of dry toluene. The ^{31}P NMR spectrum of the solution showed a singlet at −7.6 ppm. The solution was concentrated by evaporation in vacuo. The polymer was isolated by precipitation into hexane. Further purification was carried out by reprecipitation from THF into water (three times) and from THF into hexane (twice). The product was dried overnight under vacuum. A white and elastomeric polymer was obtained (yield 91%).

Preparation of Polymer 13. Sodium spheres (3.97 g, 0.172 mol) were suspended in dry toluene (200 mL), and to this solution was added compound **4** (46 g, 0.344 mol) at 0 °C. The reaction mixture was stirred for 12 h, and a transparent solution was obtained. To the sodium salt was added polymer **10** (5 g, 0.043 mol) dissolved in toluene (200 mL). The mixture was stirred at reflux for 20 h. The ^{31}P NMR spectrum indicated that the solution had a clean singlet at −7.4 ppm. The polymer was isolated by precipitation into hexane and was further purified by reprecipitation into water, ethanol, and hexane. A white and elastomeric polymer (**13**) was obtained in 94% yield after drying.

Deprotection of Polymer 12. After several trial reactions it was found that aqueous 80% acetic acid at 25 °C was the best reagent for deprotection of **12**. Polymer **12** (0.5 g, 2.2 mmol) was added to 10 mL of 80% acetic acid. The polymer dissolved only slowly, and 5–6 h were required to bring about complete solution. The reaction was followed by ^{31}P NMR spectroscopy: the peak in the spectrum moved gradually from −7.5 to −5 ppm over a reaction time of 7–35 h. During this same time the yield of **1** rose from 25% to 80%. After 37 h of reaction a peak at 0.5 ppm appeared and grew in size. This was attributed to phosphate formed by skeletal degradation.

Deprotection of Polymer 13. Polymer **13** (1 g, 2.106 mmol) was added to 20 mL of 20% acetic acid, and the mixture was stirred at room temperature for 25 h. The solution was diluted with 100 mL of deionized water and was dialyzed in a cellulose tube for 72 h. After dialysis against water, the solution was concentrated by evaporation in vacuo. The ^{31}P NMR spectrum of the transparent and hygroscopic polymer consisted of a singlet at −4.9 ppm. The hydrolysis yield was 100%, as determined by ^{1}H NMR spectroscopy.

Cross-Linking Reactions with Polymer 1. The deprotected polymer **1** (1 g, 4.1 mmol) was dissolved in dry DMF (6 mL). To the polymer solution was added the base 4-(dimethylamino)-pyridine (60 mg). Hexamethylene diisocyanate (60 μL) was then added quickly. The reaction mixture was then shaken vigorously. After 2 h, the solution began to gel, and after 2.5 h, the mixture was completely gelled. The final product was washed several times with water and was stored in water. The cross-linking reaction with adipoyl chloride was carried out in a similar manner.

Drug Delivery from Hydrogel. Polymer **1** (0.4 g, 1.76 mmol) was dissolved in 5 mL of dry DMF. To the polymer solution was added tripelennamine hydrochloride (50 mg). The solution was stirred vigorously. Hexamethylene diisocyanate (0.05 mL) was added quickly, and the mixture was poured into a Petri dish. The solvent was removed in a controlled-atmosphere casting chamber. After drying, the polymer was immersed in water. Every 2 h, the absorbance of the solution at 306 nm was measure by UV spectroscopy. The measurement was carried out until the solution showed no difference of absorbances (26 h).

Hydrolytic Degradation of Polymer 1. Polymer **1** (0.2 g, 0.83 mmol) was dissolved in 15 mL of pure water (boiling deionized water). The solution was heated at 100 °C and was stirred for 150 h. The degradation was monitored by ^{31}P NMR spectroscopy. After the ^{31}P NMR spectrum changed to a singlet at +0.3 ppm, the solution was cooled and the water was removed by evaporation. The degradation products were separated by column chromatography with THF and methanol as an eluent mixture (3:1). After separation, the products were characterized by ^{1}H NMR and IR spectroscopy. The same reaction was carried out at 37 °C for 720 h. A temperature-controlled water bath was used to maintain constant temperature.

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Registry No. **2**·Na, 114564-11-3; **3**·Na, 33145-48-1; **4**·Na, 114564-13-5; **5**, 940-71-6; **6**, 114564-10-2; **7**, 114581-46-3; **8**, 114564-12-4; **9**, 100211-24-3; triplennamine hydrochloride, 154-69-8.

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Polymers and Polymer–Metal Complexes Containing Pendent 2,2′:6′,2″-Terpyridinyl Ligands

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ABSTRACT: Homopolymers and styrene copolymers derived from 4′-vinyl-2,2′:6′,2″-terpyridinyl were prepared in chlorobenzene at 60 °C by using azobis(isobutyronitrile) (AIBN) initiation, and monomer reactivity ratios were determined for the styrene copolymers. These polymeric systems containing pendent terpyridinyl ligands readily formed complexes with Co, Cu, and Zn cations. Although vinylterpyridinyl cobalt and ruthenium complex monomers did not undergo homopolymerization with AIBN initiation, they readily formed styrene copolymers under these polymerization conditions. Removal of the metal ions from these polymer–metal complexes occurred readily on washing the complex with acid.

Polymers containing pendent chelating ligands are of special interest for potential applications as sequestration agents for a variety of metal ions[1] and for the formation of polymer–metal complexes that may behave as redox polymers and homogeneous or heterogenous catalysts.[2,3] Polymer–metal complexes containing 2,2′-bipyridinyl pendent ligands have outstanding properties as redox polymers in chemically modified electrodes[4] and also act as efficient light-harvesting systems in solar energy conversion applications.[5] Poly(vinyl-2,2′-bipyridinyls) were found[6] to be effective sequestration agents for transition metals.

Our interest in terpyridinyl chemistry[7] suggested that incorporation of a vinyl group into various positions on the terpyridinyl nucleus would provide a group of monomers whose homopolymers and styrene copolymers should be of special interest in a number of applications. The established, greater stability[8] of (2,2′:6′,2″-terpyridinyl)metal complexes when compared to the stability of those derived from 2,2′-bipyridinyl indicated that many of the stability problems encountered with polymer–transition metal complexes derived from poly(vinyl-2,2′-bipyridinyl) would be avoided by the use of the terpyridinyl ligand in analogous polymer environments. We have recently found[9] that (vinylterpyridinyl)metal complexes readily undergo electropolymerization yielding modified electrodes containing stable polymer–metal complexes that show interesting electrocatalytic properties. In this publication we show that 4′-vinyl-2,2′:6′,2″-terpyridinyl readily forms homopolymers as well as styrene copolymers using AIBN initiation. The corresponding monomeric metal complexes of cobalt and ruthenium also formed polymer–metal complexes on copolymerization with styrene.

Homopolymers of 4-Vinyl- and 4′-Vinyl-2′:6′,2″-terpyridinyls. Poly(4-vinyl-2,2′:6′,2″-terpyridinyl) (**3**) and poly(4′-vinyl-2,2′:6′,2″-terpyridinyl) (**4**) were prepared from 4-vinyl-2,2′:6′,2″-terpyridinyl (**1**) and 4′-vinyl-2,2′:6′,2″-terpyridinyl (**2**), respectively, in sealed glass tubes in the presence of a catalytic amount of AIBN in chlorobenzene at 60 °C for 18–24 h. The use of chlorobenzene as solvent resulted in better solubility of the developing polymer and subsequent molecular weight enhancement. The polymers were purified by repeated precipitation into either *n*-hexane or ether from either chlorobenzene or chloroform. The polymers **3** and **4** were isolated as off-white, amorphous materials. Polymer **4** was analyzed thermogravimetrically in a nitrogen atmosphere. The transition onset point was reached at 310 °C, and between 310 and 360 °C the polymer lost most of its weight, and the experiment afforded a char yield of 25%.

Spectroscopic Studies. Homopolymers **3** and **4** were

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