was prepared on the glass wall of a round flask. Oxygen-free water was added to this, and the mixture was then mixed in a Vortex mixer. It was ultrasonicated and homogenized in an ice water bath under nitrogen atmosphere. Thus prepared porphyrin/lipid liposome solution was incubated at room temperature for a few hours and then was allowed under nitrogen atmosphere to polymerize under ultraviolet irradiation for 1–4 h to give the porphyrin/lipid copolymerized liposome. Complete polymerization was confirmed by UV and ^{13}C NMR spectroscopical measurements: disappearance of the absorption peak (muconyl type, **1a–f** 254 nm; itaconyl type, **2a–f** 228 nm) and the characteristic NMR signal (muconyl type (diene, 1), δ_C 127.9, 128.5, 140.7, 141.0 ppm; itaconyl type (vinylydene, 2) 122.2, 130.9 ppm; double-bond carbon of the lipid (**3**) 118.4, 128.2, 145.2–146.0 (d) ppm).

Physicochemical Measurements. The porphyrin/lipid copolymerized liposome was separated from the aqueous medium by ultracentrifugation (45 000 rpm, 4 h, at 10 °C, ultracentrifuge Hitachi 65p-7). A GPC elution curve was measured with a Sepharose 4B (aqueous type) and Sepharose LH-60 (methanol type) (Pharmacia Fine Chemical, 20 mm ϕ × 700–2000 mm, solvent water and methanol), respectively, and a TOYO Pearl HW-60 (water type) (Toyosoda, 20 mm ϕ × 700–1500 mm, water). The transmission electron microscopy (Hitachi H-500) of the porphyrin/lipid copolymerized liposome was carried out by a negative staining method using uranyl acetate. A fluorescence spectrum of the porphyrin/lipid copolymerized liposome was measured by using excitation at 430 nm with a fluorescence spectrophotometer (Japan Spectroscopic JASC FP-550). The relative light intensity of the porphyrin/lipid copolymerized liposome solution was measured with a static light-scattering apparatus (Union-Giken, LS-1000).

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Registry No. **1a**, 117179-15-4; **1a/3** (copolymer), 117248-10-9; **1b**, 117097-89-9; **1b/3** (copolymer), 117097-90-2; **1c**, 117098-01-8; **1c/3** (copolymer), 117180-35-5; **1d**, 117179-13-2; **1d/3** (copolymer), 117248-15-4; **1e**, 117097-93-5; **1e/3** (copolymer), 117182-16-8; **1f**, 117097-94-6; **1f/3** (copolymer), 117180-36-6; **2a**, 117179-16-5; **2a/3** (copolymer), 117248-11-0; **2b**, 117097-91-3; **2b/3** (copolymer), 117097-92-4; **2c**, 106252-35-1; **2c/3** (copolymer), 106252-36-2; **2d**, 117097-95-7; **2d/3** (copolymer), 117180-37-7; **2e**, 117097-96-8; **2e/3**, 117182-17-9; **2f**, 106252-37-3; **2f/3**, 106252-38-4; **3**, 76282-07-0; **4a**, 117098-02-9; **4b**, 117098-03-0; **4c**, 117098-04-1; **4d**, 117097-97-9; **4e**, 117097-98-0; **4f**, 117097-99-1; **5a**, 106252-43-1; **5b**, 117098-00-7; **5c**, 88088-83-9; muconic acid chloride, 20578-72-7; muconic acid, 505-70-4; itaconic acid, 97-65-4; methacrylic acid chloride, 920-46-7; oxygen, 7782-44-7.

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Alcohol Derivatives of Poly(methylphenylphosphazene)

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ABSTRACT: A series of polyphosphazenes with alcohol functional groups attached to the backbone phosphorus by two-carbon spacer groups were prepared by deprotonation/substitution reactions at the pendant methyl groups in poly(methylphenylphosphazene). The polymeric anion, prepared in THF at −78 °C by using *n*-BuLi, was treated with aldehydes and ketones and subsequently quenched with aqueous ammonium chloride, to give $[Ph(Me)P{=}N]_x\{Ph[CH_2C(OH)RR']P{=}N\}_y$ where R = H, Me; R′ = Me, H, Ph, $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (ferrocene), or C═CHCH═CH-S (thiophene); and *x*:*y* ranges from 1:1 to 1:2. These new polymers were characterized by elemental analysis; size-exclusion chromatography; IR spectroscopy; thermal analysis (DSC); and ^1H, ^{31}P, and ^{13}C NMR spectroscopy.

Introduction

The synthesis of polyphosphazenes has most generally been accomplished by substitution of poly(halophosphazenes) which are prepared by ring opening of the cyclic halogenated phosphazenes.[1] This ring-opening/substitution process has been used to prepare a large variety of alkoxy-, aryloxy-, and amino-substituted polymers. A variation of this involves ring opening of cyclic phosphazenes with both halo and organo substituents.[2] More recently, a condensation polymerization method[3] has been developed which produces poly(alkyl/arylphosphazenes) with all substituents attached to the backbone by direct

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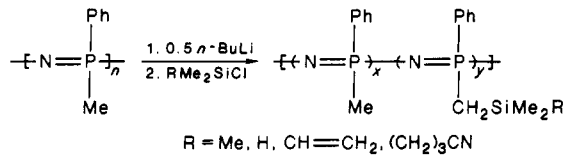
Table I
Analytical, Size-Exclusion Chromatography (SEC), and Thermal Analysis (DSC) Data

polymer	% C[a]	% H[a]	% N[a]	% substitution[b]	M_w[c]	T_g, °C
1	60.37 (60.54)	6.54 (6.25)	9.00 (9.05)	37	114000 (75000)	49
2	65.57 (65.39)	6.03 (5.84)	8.07 (7.89)	38	112000 (75000)	73
3	60.90 (61.48)	5.58 (5.40)	5.48 (6.00)[d]	45	199000 (135000)	92
4	59.46 (59.40)	5.57 (5.32)	7.18 (7.70)	43	187000 (135000)	73
5	61.02 (61.42)	6.60 (6.54)	9.14 (8.73)	37	75000 (75000)	55
6	63.40 (64.44)	6.23 (6.02)	8.19 (8.50)	23	88000 (75000)	52
7	61.85 (62.02)	5.94 (5.66)	6.39 (6.39)[e]	36	154000 (135000)	87[f]

[a] Calculated values in parentheses are based on percent substitution from ^{1}H NMR integration. [b] Determined by integration of the ^{1}H NMR spectra. [c] Values for the parent polymer in parentheses. [d] Fe analysis: 10.34 (10.76). [e] Fe analysis: 9.38 (9.17). [f] With only 23% substitution, the T_g was 65 °C.

P–C linkages. Thus far, the latter process is limited by the fact that reactive functional groups in the appropriate silicon–nitrogen–phosphorus precursors often hinder or complicate their thermal polymerization.[4] We are, therefore, investigating the derivatization[5,6] of preformed poly(alkyl/arylphosphazenes) in order to prepare new, thermally stable phosphazene materials with reactive functional groups.

In poly(methylphenylphosphazene), $[Ph(Me)P{=}N]_n$, both the phenyl and the methyl substituents are potential sites for derivatization. Thus far, we have shown that a portion of the methyl groups are readily deprotonated by treatment with *n*-BuLi at −78 °C, producing a polymer anion intermediate which reacts with electrophiles. For example, a series of silylated polymers[5] $[Ph(Me)P{=}N]_x$-$[Ph(RMe_2SiCH_2)P{=}N]_y$ (eq 1) and ferrocenyl substituted



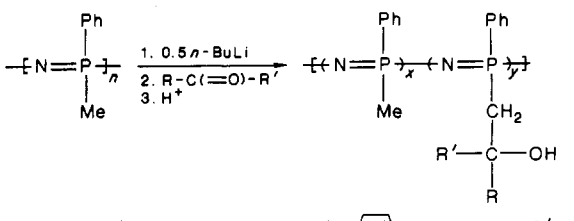
(1)

R = Me, H, CH=CH$_2$, (CH$_2$)$_3$CN

polymers[6] $[Ph(Me)P{=}N]_x\{Ph[CH_2C(OH)RR']P{=}N\}_y$ [R = H, Me; R′ = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$] have been synthesized by this approach. The work reported here further investigates the scope of the deprotonation/substitution method for the synthesis of new polyphosphazenes. A series of polyphosphazenes with RR′C(OH) substituents attached to the backbone through a CH_2 spacer group have been prepared by treating the deprotonated polymer intermediate with aldehydes and ketones.

Results and Discussion

The deprotonation of ca. half of the methyl substituents on poly(methylphenylphosphazene) was carried out in THF at −78 °C by using one-half equivalent of *n*-BuLi. Upon treatment of the intermediate polymer anion with aldehydes or ketones and subsequent quenching of the resulting alkoxide anion with a mild proton source, new polyphosphazenes containing the OH functional group were prepared (eq 2). These copolymers were soluble in



(2)

1, R = H, R′ = Me
2, R = H, R′ = Ph
3, R = H, R′ = Fe
4, R = H, R′ = S
5, R = Me, R′ = Me
6, R = Me, R′ = Ph
7, R = Me, R′ = Fe

a variety of organic solvents such as chlorinated hydrocarbons and THF and were easily purified by precipitation into hexanes, followed by drying under vacuum. While polymers **1**, **2**, **4**, **5**, and **6** were white materials that formed brittle films similar to those from the parent polymer, the ferrocene-containing polymers, **3** and **7**, had the characteristic orange color typical of most ferrocene compounds.

Elemental analysis and integration of the ^{1}H NMR spectra were used to determine the degree of substitution for each polymer. With the exception of **6**, more than 35% of the backbone methyl groups were derivatized, corresponding to a 70–90% reaction yield based on the amount of *n*-BuLi used. These results were reproducible for each aldehyde and ketone studied. The isolated yields of the purified polymers were typically better than 85% based on formula weights calculated for the degree of substitution listed in Table I. The best agreements between elemental analyses data and ^{1}H NMR data pertaining to the degree of substitution were obtained when the integration of the phenyl to methyl regions was used rather than phenyl or methyl signals relative to the CH_2 or OH signal. Simple algebraic manipulations were used to account for overlapping resonances in the spectra.

The presence of the alcohol functionality was confirmed by the observation of the O—H stretching frequency between 3280 and 3350 cm^{-1} in the IR spectra of each of these new polymers. No residual C=O signals were detected. Relatively little structural information was provided by the ^{31}P NMR spectra which were very similar to that of the parent polymer with broad, partially resolved resonances near 0 ppm. On the other hand, the ^{1}H and ^{13}C spectra were more definitive (Table II). In many cases the CH_2 and OH protons were identified in the ^{1}H NMR spectra. The ^{13}C NMR spectra, however, provided conclusive evidence for the incorporation of the carbonyl compounds into the phosphazene. With the aid of spectra obtained by using a DEPT pulse sequence,[7] all signals in the ^{13}C NMR spectra were easily assigned. In the DEPT spectra the PCH_2-derivatized carbons were clearly distinguished from carbon atoms attached to an odd number of protons. Furthermore, the chemical shifts of the quaternary carbons in polymers **3**, **4**, and **7** and the *C*OH in the polymers obtained from the ketones (i.e., **5**, **6**, and **7**) could be identified because they did not appear in the DEPT spectra. Proton-coupled ^{13}C NMR spectra of the aldehyde products (i.e., **1**, **2**, and **4**) clearly established the identity of the HCOH signal and the corresponding J_{HC} value.

Significant molecular weight increases (ca. 10–50%) relative to the parent polymers (Table I) were observed by SEC analysis. The molecular weight distributions (typically M_w/M_n ca. 1.4–2.0) were also similar to those of the parent polymers. These data indicate that no significant chain degradation or crosslinking occurred during the derivatization process and further substantiate the

Table II
NMR Spectroscopic Data[a,b]

polymer	signal	^{1}H δ	^{13}C δ	^{31}P δ
1	CH_3COH	0.9–1.8	24.6	−0.2, 3.8
	CH_3P	0.9–1.8	20.8–22.5	
	PCH_2	0.9–1.8	42.7–44.4	
	$HCOH$	3.7–3.9	62.9 (J_{HC} = 142 Hz)	
	C_6H_5	7.6, 7.1	127.7, 130.4, 131.5, 137.7–140.0	
2	CH_3P	0.9–2.3	20.22–22.71	2.4
	PCH_2	0.9–2.3	42.6–45.1	
	$HCOH$	4.6	68.9 (J_{HC} = 139 Hz)	
	OH	6.1		
	C_6H_5	7.1, 7.6	125.5, 126.7, 128.0, 130.2, 131.4, 137.7, 144.6	
3	CH_3P	0.9–2.2	20.5–22.1	0.5, 2.7
	PCH_2	0.9–2.2	42.4	
	$C_5H_4FeC_5H_5$	3.8, 3.9	65.7, 67.3, 67.6, 68.4	
	$HCOH$	4.5	65.0	
	OH	5.9		
	$HOCC$		92.2	
	C_6H_5	7.2, 7.7	127.9, 130.3, 131.5, 136.1, 138.2, 140.1	
4	CH_3P	0.8–2.3	19.5–22.6	2.0, 4.9
	PCH_2	0.8–2.3	42.5–45.1	
	$HCOH$	4.8–5.0	65.6 (J_{HC} = 142 Hz)	
	$HOCCS$		149.2	
	$(CH)_3S$	6.4, 6.7	122.4, 123.8, 128.2	
	C_6H_5	7.1, 7.6	127.9, 130.2, 131.4, 135.1–139.4	
5	CH_3P	0.9–2.1	21.0–22.7	−1.1, 0.6, 2.7
	$(CH_3)_2C$	0.9–2.1	31.6	
	PCH_2	0.9–2.1	45.4–47.2	
	COH	6.17	69.2	
	C_6H_5	7.1, 7.7	127.6, 129.6, 130.5, 131.3, 138.2–140.6	
6	CH_3P	1.3–2.4	21.0–22.9	−1.1, 1.9
	CH_3C	1.3–2.4	33.1	
	PCH_2	1.3–2.4	45.9–47.7	
	COH		72.5	
	C_6H_5	7.0, 7.1, 7.7	124.7, 125.6, 127.5, 129.6, 130.5, 131.6, 140.6–137.9, 148.8	
7	CH_3P	0.9–2.3	20.9–22.8	−0.9, 1.3
	CH_3C	0.9–2.3	30.7	
	PCH_2	0.9–2.3	47.7	
	$C_5H_4FeC_5H_5$	3.9, 4.0	65.2, 65.6, 68.4, 68.4	
	COH	6.5	69.8	
	$HOCC$		100.9	
	C_6H_5	7.1, 7.7	127.6, 129.6, 130.5, 131.4, 138.1, 140.7	

[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C NMR spectra and from H_3PO_4 for ^{31}P NMR spectra. Solvent: $CDCl_3$. [b] Broad resonances unless coupling constants are listed.

viability of using deprotonation/substitution reactions on poly(methylphenylphosphazene)[5] for the preparation of functionalized polymers.

As was noted previously for acetylferrocene,[6] more highly substituted derivatives could be prepared by carrying out the ketone quenching reactions at higher temperatures, conditions which should favor attack of the polymer anions at the carbonyl carbon over deprotonation of the methyl group attached to the carbonyl carbon. Nonetheless, the highest degree of substitution for acetophenone reactions remained lower than for the other ketones. The aldehyde reactions were more straightforward at low temperatures.

The glass transition temperatures (Table I) of these new polyphosphazenes were higher than that of the parent polymer (37 °C)[3b] and show the expected trends,[8] with T_g values increasing as the size of the substituents increases. The one exception is compound **6** where the T_g was lower than that of the closely related polymers with phenyl (**2**) or dimethyl (**5**) substituents. This is undoubtedly due to the fact that a significantly lower degree of substitution was achieved for **6** (23% vs ca. 37% for **2** and **5**). Similarly, the T_g for a ferrocenyl derivative analogous to **7** with only 23% substitution was 22 °C lower than that of the polymer with 36% substitution.

In addition to demonstrating the utility of the deprotonation/substitution reactions, the synthesis of these alcohol-functionalized polymers provides a number of potential routes for controlled cross-linking of the polymers and for the attachment of a wide variety of substrates with biological, electrical, and catalytic properties. Noteworthy in this context is the thiophene derivative **4** reported here.[9] Preliminary experiments have also shown that oxidation and dehydration reactions can be carried out on these alcohols. Hence, the poly(alkyl/arylphosphazenes) are beginning to demonstrate a rich derivative chemistry which promises to greatly expand the range of applications of this polymer system.

Experimental Section

Materials. Poly(methylphenylphosphazene), $[Ph(Me)PN]_n$, was prepared by the published procedure[3,10] and was dried under vacuum at 50 °C for at least 24 h. Tetrahydrofuran was freshly distilled from Na/benzophenone immediately prior to use. Hexanes, *n*-BuLi (hexane solution), acetone (analytical grade), acetophenone, ferrocenecarboxaldehyde, acetylferrocene, and thiophenecarboxaldehyde were used as obtained from commercial sources. Acetaldehyde and benzaldehyde were distilled before use.

Equipment. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on an IBM WP-200SY FT NMR spectrometer in $CDCl_3$. Positive ^{1}H NMR and ^{13}C NMR shifts are downfield from the external reference Me_4Si while positive ^{31}P NMR shifts are downfield from the external reference H_3PO_4. The DEPT pulse sequence used

to obtain some of the ^{13}C NMR spectra is described in the literature.[7] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106. The size-exclusion chromatography measurements were performed on a Waters Associates GPC II instrument with a Nelson Analytical data handling system by using 500-, 10^4-, 10^5-Å μ Styragel columns. The SEC operating conditions consisted of a mobile phase of THF containing 0.1% $(n\text{-Bu})_4N^+Br^-$, a flow rate of 1.5 mL/min, a temperature of 30 °C, and a sample size of 0.05 mL of 0.1% solution. IR spectra were recorded as thin films on a Perkin-Elmer 283 infrared spectrometer. Differential scanning calorimetry (DSC) measurements were made on a Du Pont Model 910 instrument under nitrogen against an aluminum reference from 0 or −140 °C to 150 °C.

Synthesis. In a typical procedure, a three-necked round-bottom flask equipped with a magnetic stirrer, nitrogen inlet, and a septum was charged with 2.0 g (14.6 mmol) of $[Ph(Me)PN]_n$ and ca. 20 mL of dry THF. The solution was cooled to −78 °C and then *n*-BuLi (3.0 mL/2.5M) was added slowly via syringe. After the mixture was stirred for 1 h at −78 °C, a solution of benzaldehyde (0.80 mL, 7.9 mmol) in 20 mL of THF was added and the mixture was allowed to warm slowly to room temperature. After the reaction mixture was stirred at room temperature for at least 1 h, ca. 2 mL of a saturated solution of ammonium chloride was added to quench the alkoxide ion. This mixture was poured into H_2O and THF was removed on a rotary evaporator. The precipitated polymer was recovered from the water and was purified by dissolving in THF and reprecipitating into hexanes, a process that was repeated two times. The ferrocene derivatives were further purified by Soxhlet extraction with hexanes and ethanol. All polymers were dried overnight in a vacuum oven at 50 °C. The yields of the purified polymers were in excess of 82% based on the degree of substitution determined by integration of the ^1H NMR spectra. Analytical and SEC molecular weight data are listed in Table I and NMR spectroscopic data are given in Table II. The IR spectra of 1–7 exhibited a strong OH stretching vibration between 3280 and 3350 cm^{-1}.

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An Ionically Cross-Linkable Polyphosphazene: Poly[bis(carboxylatophenoxy)phosphazene] and Its Hydrogels and Membranes[1]

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ABSTRACT: Hexachlorocyclotriphosphazene and poly(dichlorophosphazene) react with the sodium salt of ethyl *p*-hydroxybenzoate to give small molecule cyclic and high polymeric phosphazenes with aryloxy ester side groups. The structures and physical properties of both classes of compounds were investigated by ^{31}P NMR, ^1H NMR, and infrared spectroscopies and by thermal analysis. Reaction of these compounds with potassium *tert*-butoxide brought about complete hydrolysis of the ester groups to yield aqueous media-soluble, carboxylic acid bearing cyclic and high polymeric phosphazenes. The carboxylic acid bearing high polymer formed ionic cross-links when treated in aqueous media with salts of di- or trivalent cations, such as calcium chloride, copper bromide, copper sulfate, or aluminum acetate, to yield hydrogels and membranes. Aluminum ions proved to be more efficient cross-linking reagents than the divalent cations. The cross-linked gels were stable in neutral or strongly acidic aqueous media, but the cross-linking process was reversed in basic aqueous solutions of excess monovalent cations.

Introduction

The design and synthesis of new macromolecules for the preparation of membranes is one of the major challenges of modern polymer chemistry. At present a variety of polymeric membranes are used in applications as diverse as gas separations, microfiltration, hyperfiltration, hemodialysis, electrodialysis, controlled drug delivery, and genetic engineering.[8–15] The need for new membrane materials in biomedical engineering is particularly acute.

The synthetic polymers that are currently used as membranes can be divided into two categories: (1) neutral polymers such as polyethylene, poly(methyl methacrylate),[12] poly(organosiloxanes), and cellulose[13] and (2) ionic polymers such as poly(acrylic acid),[14] sulfonated polystyrene,[14] and perfluorinated ionomers.[15] The consideration of a polymer for incorporation into membranes

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