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Notes

Carboxylic Acid, Ester, and Lithium Carboxylate Derivatives of Poly(methylphenylphosphazene)

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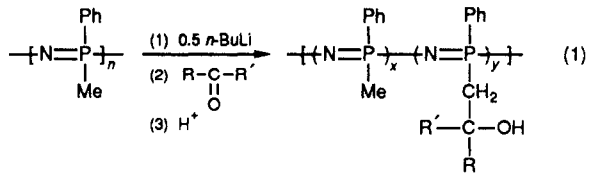
Introduction

Polyphosphazenes, $[R_2PN]_n$, are an unusual class of polymers in that the properties of this system can be varied over a very wide range through the incorporation of different substituents on the phosphorus. While literally hundreds[1] of polyphosphazenes with alkoxy, aryloxy, and amino groups have been prepared, phosphazene polymers with all substituents attached to the backbone by direct P–C bonds are relatively new and few in number.[2] As part of our ongoing studies of this type of phosphazene, i.e., the poly(alkylarylphosphazenes), we are investigating methods of diversifying the functional groups R on phosphorus. We have found that the deprotonation of methyl substituents on preformed poly(methylphenylphosphazene), $[Ph(Me)P{=}N]_n$, followed by reaction of the resulting ion with various electrophiles, provides access to P–C-substituted polymers with reactive functional groups.[3-5] For example, we recently reported the use of this deprotonation–substitution process to prepare a series of polyphosphazenes with alcohol substituents attached to the phosphorus through a CH_2 spacer group (eq 1).[4,5] We have also prepared graft copolymers by using the intermediate anion for the initiation of addition polymerization of styrene and for the ring opening of hexamethylcyclotrisiloxane.[6,7]



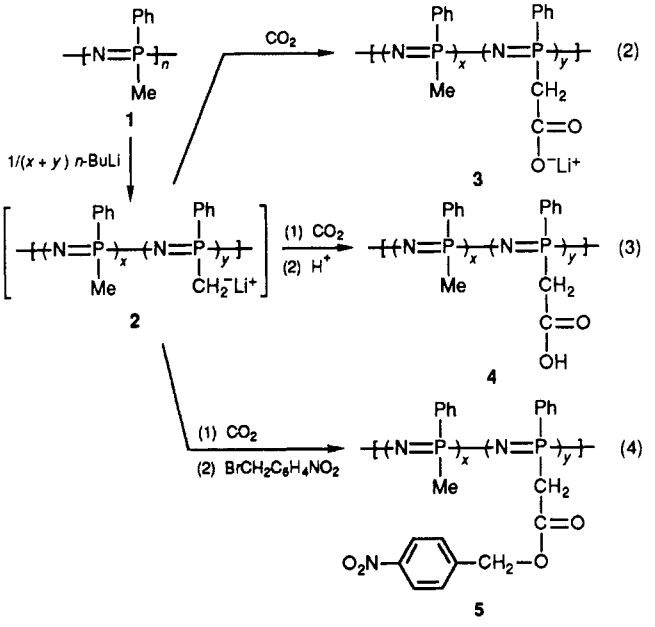
(1)

In this paper we report the use of the deprotonation–substitution process for the preparation of polyphosphazenes with carboxylate, carboxylic acid, and ester functional groups. The synthesis, characterization, and simple properties of these new phosphazenes, one of which is the first water-soluble P–C-substituted polyphosphazene, are discussed.

Results and Discussion

A series of carboxylated derivatives of $[Me(Ph)PN]_n$ in which 10, 25, and 50% of the PN monomer units contained either $CH_2COO^-Li^+$, CH_2COOH, or $CH_2COOCH_2C_6H_4$-4-NO_2 groups was prepared by initial formation of the anionic polymer intermediate by deprotonation of the appropriate number of PMe groups in the parent polymer with *n*-BuLi. Treatment of the viscous THF solution of the polymer anions **2** at −78 °C with anhydrous, gaseous carbon dioxide produced the THF-insoluble carboxylate salts, **3a–c** (eq 2; Scheme I), which could be isolated by simple removal of the solvents. Treatment of these salt slurries with aqueous solutions of HCl or with *p*-nitrobenzyl bromide resulted in the acid and ester derivatives **4a–c** and **5a–c**, respectively (eq 3 and 4; Scheme I).

Scheme I[a]



[a] **a**: $x = 9, y = 1$. **b**: $x = 3, y = 1$. **c**: $x = 1, y = 1$.

The salt derivatives **3a** and **3b** were insoluble in THF, hydrocarbons, and water but soluble in 1:1 mixtures of THF and water. Polymer **3c**, on the other hand, was quite water soluble and insoluble in organic solvents. All of the salts, **3a–c** formed extremely viscous gels in chlorinated hydrocarbons, which facilitated their characterization by NMR spectroscopy. The acid derivatives, **4a–c**, and the esters, **5a–c**, were soluble in THF and chlorinated hydrocarbons, and polymer **4c** showed some tendency to dissolve in H_2O. The new polymers were off-white ma-

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

polymer	% C[a]	% H[a]	% N[a]	M_w[b]	T_g, °C	T_{onset}, °C	T_{50}, °C
3a	59.58 (60.01)	5.67 (5.60)	9.82 (9.86)		[c]	311	335
3b	57.97 (58.21)	5.55 (5.22)	9.77 (9.36)		[c]	370	403
3c	55.50 (55.57)	5.31 (4.66)	8.27 (8.64)		[c]	320	494
4a	60.17 (60.26)	5.79 (5.70)	9.90 (9.90)	85 000	58	300	342
4b	57.96 (58.79)	5.58 (5.44)	9.16 (9.46)	103 000	78	270	330
4c	56.69 (56.61)	5.23 (5.07)	8.89 (8.80)	119 000	108	254	315
5a	59.50 (60.43)	5.52 (5.53)	9.97 (9.94)	105 000	48	266	319
5b	58.14 (59.43)	5.32 (5.13)	9.27 (9.63)	130 000	70	265	338
5c	56.60 (58.28)	4.95 (4.67)	9.05 (9.27)	177 000	85	258	299

[a] Calculated values in parentheses. [b] M_w value for the parent polymer was 77 000. [c] The T_g values for **3a–c** were estimated as 39, 36, and 51 °C, respectively. See text for discussion.

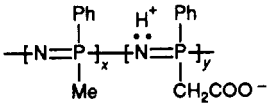
Table II
Representative NMR and IR Spectroscopic Data

		NMR data[a]			
polymer	signal	^1H, δ	^{13}C, δ	^{31}P, δ	IR data: ν, cm^{-1}
3b[b]	P–CH_3	0.5–1.6	18.9–23.0	1.2	1698 (br) C=O
	P–CH_2	2.0	44.7		1235 (s) P=N
	P–Ph	6.5–8.0	127.5, 129.3, 130.7, 138.2, 138.6, 139.9, 140.7, 141.1		
	C=O		174.8		
4c	P–CH_3	0.8–1.8	19.3–21.0	−1.5, 6.0	2650 (br) P–(*N–H*)–P
	P–CH_2	3.0	42.3–44.7		1740 (br) C=O
	P–Ph	6.5–8.7	127.9, 130.2, 130.8, 135.4, 136.7		1250 (vs) P=N
	C=O		169.8		
5b	P–CH_3	0.8–2.6	20.3–22.7	1.1, −5.3	1740 (br) C=O
	P–CH_2	2.8–3.4	42.8–45.1		1238 (vs) P=N
	OCH_2	4.8 (vbr)	64.6		
	P–Ph	6.7–8.8	123.3, 127.7, 130.3, 137.2, 137.9		
	C=O		168.3		

[a] Chemical shifts downfield from Me_4Si for ^1H and ^{13}C NMR spectra and from H_3PO_4 for ^{31}P NMR spectra. Solvent, $CDCl_3$. [b] NMR spectra recorded on a swollen gel in $CDCl_3$.

terials that formed brittle films upon slow evaporation of solvents. Purification typically involved precipitation from THF into water or from CH_2Cl_2 solutions into hexane, followed by drying in a vacuum oven. The salts were especially difficult to dry, presumably due to coordination of the lithium cation to THF or H_2O. In the case of **3c**, even extended periods of drying failed to give analytically pure samples when this polymer had been exposed to water. However, when these samples were protonated to form the corresponding acid **4c**, satisfactory elemental analyses were obtained. Clean samples of the polymer **3c** were obtained by simple removal of the reaction solvent THF followed by drying at least 48 h in a vaccum oven at 65 °C. ^1H NMR analysis indicated that THF remained if shorter drying periods were used.

Elemental analysis (Table I) of the new polymers and the integrations of the phenyl and aliphatic C–H regions of the ^1H NMR spectra (Table II) indicated that the degree of substitution for each polymer was approximately that expected from the stoichiometry of the *n*-BuLi used in the reaction. The ^{13}C NMR spectra of the new polymers (Table II) each contained the characteristic signals for the C=O carbons (δ 168–175) as well as the expected PCH_2, PMe, and PPh resonances. The ^{31}P NMR (Table II) spectra, on the other hand, are more interesting. While each of the salt derivatives gave only a single signal at δ 1.2, the spectra of the acids and esters showed at least two signals. For the esters, two well-separated and relatively sharp signals were observed. The relative intensities of these signals (i.e., δ 1 and δ −5) for **5a–c** were approximately 9:1, 3:1, and 1:1, indicating that the signal at 1 ppm corresponds to phosphorus with underivatized methyl groups and the signal at −5 ppm is due to the PCH_2COOR phosphorus. The spectra for the acids were considerably broader with approximate peak maxima at δ −1.5 and 6.0. The 25% substituted acid, **4b**, contained a third signal that appeared as a shoulder at ca. δ 4 on the downfield signal. The broad nature of these signals and the downfield shift suggest that the acid polymers may actually exist in a self-protonated, zwitterionic form



Similar chemical shifts and broad signals have been observed when the parent polymer $[Me(Ph)PN]_n$ is partially protonated.[6]

The IR spectra (Table II) provide conflicting information about the acid derivatives. Evidence for the zwitterionic form comes from the observation of a broad signal at 2650 cm^{-1} for each of the acids, **4**. Absorptions in this region have been attributed to an N–H stretching frequency in other phosphazene systems.[8] It should be noted, however, that this is not outside the range of hydrogen-bonded OH groups in carboxylic acids. Moreover, the carbonyl stretching frequency of the acids at 1740 cm^{-1} is more typical of carboxylic acids than of carboxylate salts.

Size-exclusion chromatographic analysis of the new polymers indicated that the molecular weights of the acid and ester derivatives were significantly higher than that of the parent polymer and within the range of the theoretical molecular weights based on the mass and number of acid or ester moieties attached to the derivative. No molecular weight data were obtained for the salts due to their insolubility in appropriate solvents.

The glass transition temperatures (Table I) for the new polymers were determined by differential scanning calorimetry. For the esters and acids, the values were higher than the T_g value for the parent polymer (37 °C). This

may be attributed to the incorporation of larger groups in the case of the esters and to hydrogen bonding in the acids. Moreover, increasing the degree of substitution caused a corresponding increase in the T_g values. The transitions in the DSC scans for the salts, **3**, however, were poorly defined and were difficult to interpret. Successive heating and cooling of the DSC samples, as well as extended drying of the polymers, failed to alleviate this problem. Hence, the rather low values listed in the footnote in Table I represent only estimates of the inflection point in these broad transitions.

Thermal gravimetric analysis data (in air) for the derivatives **3–5** are summarized in Table I. The acids, **4**, appear to become less stable with the incorporation of more COOH moieties. In general, the salts, **3**, have slightly higher decomposition temperatures, while the stability of the esters is similar to the acids.

Several attempts were made to prepare the acid chlorides using thionyl chloride or phosphorus chlorides. Even in the presence of amine scavengers of the HCl byproducts of these reactions, severe degradation of the polymer backbone was observed. The acids, **4**, were also treated with *N,N'*-dicyclohexylcarbodiimide (DCC) in the presence of simple alcohols in order to prepare esters, but even after several days of mild heating there was no evidence that reaction had occurred.

Finally, in order to determine if the salt derivatives, **3**, could be cross-linked by dications, an aqueous solution of the salt **3c** was added to a solution of $CuCl_2$. Precipitation occurred immediately as a result of ionic cross-linking. Similar cross-linking to form phosphazene hydrogels was reported recently.[9]

Experimental Section

Materials. Poly(methylphenylphosphazene), $[Ph(Me)PN]_n$, was prepared by the published procedure[2b,10] and was dried under vacuum at 50 °C for at least 24 h. Tetrahydrofuran was freshly distilled from Na–benzophenone immediatley prior to use. Hexanes used for precipitations were purchased commercially and were purified by distillation from CaH_2. Carbon dioxide was obtained by sublimation of dry ice and was passed through both $CaCO_3$ and P_2O_5. Both *p*-nitrobenzyl bromide and *n*-BuLi (hexane solution) were used as obtained from commercial sources.

Equipment. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on an IBM WP-200SY FT NMR spectrometer in $CDCl_3$ or D_2O. Positive ^1H NMR and ^{13}C NMR spectroscopic shifts are downfield from the external reference Me_4Si while positive ^{31}P NMR resonances are downfield from the external reference H_3PO_4. Elemental analyses were performed 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 using 500-, 10^4-, 10^5-, and 10^6-Å μStyragel 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. The system was calibrated with a series of narrow molecular weight polystyrene standards in the range of ca. 10^3–10^6. IR spectra were recorded as thin films or as $CHCl_3$ solutions on Perkin Elmer 283 or Perkin Elmer Series 1600 Fourier transform infrared spectrometers. Differential scanning calorimetry (DSC) measurements were made on a Du Pont Model 910 instrument under nitrogen against an aluminum reference from 0 °C or −140 to +150 °C, and the inflection point is listed for all transitions. Each experiment was repeated at least once on the same sample. Thermal gravimetric analyses were performed on a Du Pont TGA Model 951 instrument equipped with a Du Pont 1090 Thermal Analyzer data station. The polymer samples (ca. 50 mg) were heated at a rate of 10 °C/min from ambient temperature to 900 °C under a constant flow of air.

Isolation of Lithium Carboxylate Salt Derivatives, 3. In a typical procedure, a three-neck 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 (e.g., 3.0 mL/2.5 M for **3c**) was added slowly via syringe. After the mixture was stirred for 1.5 h at −78 °C, a large excess of CO_2 was allowed to bubble through the solution (ca. 3 h), and the resulting viscous gellike slurry was allowed to warm slowly to room temperature and was stirred overnight. This mixture was then poured into hexane to facilitate complete precipitation. The solvents were decanted, and the remaining polymer was added to distilled water. At this point polymers **3a** and **3b** formed a milky suspension. Concentration of the suspension on a rotary evaporator resulted in precipitation of these polymers. After washing twice with more distilled water, the polymers were dried overnight in a vacuum oven at 50 °C. Polymer **3c** was soluble in water and was simply precipitated from the reaction mixture into hexane and then dried in a vacuum oven at 65 °C for at least 48 h. Purified yields ranged from 63 to 75%.

Synthesis of Carboxylic Acid Derivatives, 4. Poly(methylphenylphosphazene) was deprotonated and carboxylated as described above. After the mixture was stirred under an atmosphere of CO_2 overnight, distilled H_2O (ca. 100 mL) was added to aid in dissolving the white precipitate that had formed. Then THF was removed from the solution on a rotary evaporator and the remaining aqueous suspension was acidified (pH 6) with dilute (ca. 20%) HCl. A fine white powder precipitated. After addition of 100 mL of CH_2Cl_2 to the slurry, the mixture was stirred overnight. The CH_2Cl_2 layer was separated, and the aqueous solution was extracted with CH_2Cl_2 (3 × 25 mL). The CH_2Cl_2 layers were combined and washed twice with distilled water. The CH_2Cl_2 solution was concentrated and was added dropwise to ca. 800 mL of hexane. The solvents were decanted, and the white precipitate was dried overnight in a vacuum oven at 60 °C. The polymers prepared in this manner were identified as **4a–c** (see Tables I and II). Purified yields were between 63 and 95%.

Synthesis of Ester Derivatives, 5. The lithium carboxylate intermediate was prepared as described above. After passage of CO_2 and stirring overnight at room temperature, additional THF (10 mL) and $4\text{-}NO_2C_6H_4CH_2Br$ (0.31 g, 1.5 mmol for **5b**) were added. The mixture was refluxed for 3 days. Then THF was removed at reduced pressure, and distilled water (ca. 50 mL) was added. The aqueous mixture was extracted three times with CH_2Cl_2. The combined CH_2Cl_2 portions were dried over anhydrous $MgSO_4$ and concentrated. The polymer was precipitated by dropwise addition of the CH_2Cl_2 solution into hexane. The polymer was dried overnight a vacuum oven at 50 °C. Yields were typically between 65 and 80%.

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References and Notes

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