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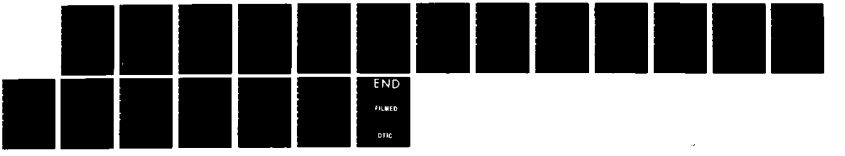

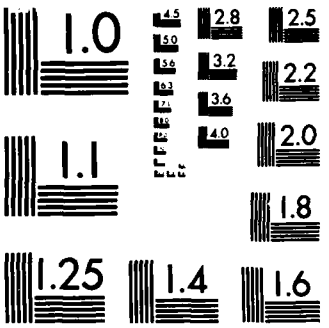

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Polyphosphazenes with Etheric Side Groups: Prospective Biomedical and Solid Electrolyte Polymers

by

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ABSTRACT:

Poly(organophosphazenes) have been synthesized with alkyl-ether-alkoxy groups attached to the phosphorus atoms of the skeleton. These species are water-stable and either water-soluble or hydrophilic polymers. Specific members of this series form complexes with metal salts, which are excellent solid electrolyte materials. Mixed substituent polymers with hydrophobic trifluoroethoxy and alkyl-ether alkoxy side groups have also been prepared and these are of interest as membranes and biomedical materials.

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Polyphosphazenes with Etheric Side Groups: Prospective Biomedical and Solid Electrolyte Polymers

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Abstract: Poly(organophosphazenes) have been synthesized with alkyl-ether-alkoxy side groups attached to the phosphorus atoms of the skeleton. These species are water-stable and either water-soluble or hydrophilic polymers. Specific members of this series form complexes with metal salts, which are excellent solid electrolyte materials. Mixed substituent polymers with hydrophobic trifluoroethoxy and alkyl-ether alkoxy side groups have also been prepared and these are of interest as membranes and biomedical materials.

One of the main characteristics of the poly(organophosphazene) system is the ease with which different organic side groups can be incorporated into the macromolecular structure. This is a consequence of the substitutive mode of synthesis used for these polymers, as described in a number of earlier publications.[1-17] The method involves the prior synthesis of a reactive, high polymeric poly(dihalophosphazene) intermediate, such as 1, by a ring-opening polymerization of the corresponding cyclic trimer, followed by replacement of the halogen atoms by one or more of a wide variety of organic or organometallic nucleophiles.

This approach has yielded a large number of different polymers in which the physical, chemical, and biological properties are determined mainly by the

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nature of the side groups. Some of these polymers have been utilized in technology,[4,14,15] and others are being evaluated for biomedical uses.

One aspect of this field that is of particular interest is the design and synthesis of polyphosphazenes that are amphiphilic, hydrophilic, or soluble in aqueous media and which are appropriate for biomedical uses. Another interest involves the use of such polymers as "solid electrolytes". For this application polymers are needed that are solvents for salts and have a high reorientational freedom at room temperature or at low temperatures.

In earlier publications we described the synthesis of water-soluble polyphosphazenes with methylamino[16] or glucosyl[17] side groups. Here, we discuss the synthesis and properties of a new class of polyphosphazenes that possess etheric alkoxy side groups linked through oxygen to the inorganic backbone. These side groups confer hydrophilicity or water-solubility on the polymers. Also, as reported in a recent communication,[18] polymers of this type are promising solid state electrolyte materials for energy storage applications.

Results and Discussion

Synthesis of Single-Substituent and Mixed-Substituent Polymers. The synthesis method used is summarized in Scheme I. Specifically, poly(dichlorophosphazene) (1) was allowed to react with the sodium salt of an etheric alcohol, or sequentially with first one alkoxide and then with the second. The sequential cosubstitution method allowed the ratio of the cosubstituents to be varied over a wide range. In most cases, the cosubstituent introduced first was a trifluoroethoxy group, but, as shown in Table I, the initial substituent can be an etheric alkoxy group.

Thus, single substituent polymers (2) were prepared in which OR was $-OCH_2CF_3$ (polymer 5), $-OCH_2CH_2OCH_3$ (6), $-O(CH_2CH_2O)_2CH_3$ (7), $-O(CH_2CH_2O)_7CH_3$ (8), $-O(CH_2CH_2O)_{12}CH_3$ (9), and $-O(CH_2CH_2O)_{17}CH_3$ (10). Mixed substituent species, 4, were synthesized in which OR and OR' were varied as shown in Table I. In each case, OR refers to the substituent group introduced first. In principle, some fine-tuning of the side group sequencing can be achieved by the order in which the substituents are introduced. The trifluoroethoxy side groups confer hydrophobic character. Hence, polymers that contain both trifluoroethoxy and etheric alkoxy side groups should show amphiphilic behavior.

An initial concern was that the ratio of substituent groups defined by the composition of 3 might not be retained in the final polymer (4) if displacement of one alkoxy group by another occurred. However, variations in the order of introduction of $-OCH_2CF_3$ and $-OCH_2CH_2OCH_3$ groups did not affect the final side group ratios (although it might affect the sequence distribution). Hence, metathetical exchange of one organic group by another did not appear to be a problem under the reaction conditions employed in this work.

Structural Characterization. The main means used for structural characterization were elemental microanalysis, ^1H NMR spectroscopy, and ^{31}P NMR spectroscopy. A critical feature of the microanalysis data was the amount of residual chlorine in polymers 2 and 4. Typically, 0.10% or less of chlorine was detected. This provided an initial indication that the replacement of chlorine by the organic groups was essentially complete. Microanalytical data are listed in Table II. However, because the purification procedure involves treatment with water, residual P-Cl bonds could be converted to POH or P(O)-NH units. Hence, the ^{31}P NMR spectra were of special interest.

The ^{31}P NMR spectra of all the polymers prepared in this work consisted of one peak, in the -7 to -8 ppm region. The existence of only one ^{31}P NMR peak in the spectra of the mixed substituent polymers was presumably a consequence of the near coincidence of the chemical shifts for RO-P-OR, RO-P-OR', and R'O-P-OR' units. Thus, it was not possible to deduce whether the distribution of different side groups was geminal or non-geminal, nor was it possible from these spectra to estimate the ratios of the two substituent groups. No evidence was found from the ^{31}P NMR spectra that detectable quantities of P-Cl or P(O)-NH units were present.

However, the ^{1}H and ^{13}C NMR spectra allowed the side group ratios to be estimated with some confidence, and these agreed with the microanalytical results. Chemical shift values are shown in Table III.

Properties. Polymers 6-10 and 11, 14, 15, 17, and 18 were soluble in water. Species 12, 13, and 16 were hydrophilic but not soluble in water. The water-soluble species are excellent candidates for surface tension modification uses. As discussed in earlier publications, polymer 5 is insoluble in water and is extremely hydrophobic.

The glass transition temperatures, Tg, are listed in Table II. They fall in the range, -55°C to -84°C, and are indicative of a high degree of reorientational mobility of the chains. As pointed out in previous papers, the polyphosphazene skeleton is one of the most flexible macromolecular backbones known and this can give rise to glass transition temperatures as low as -80°C or -90°C if small or highly flexible side groups, such as F, OCH_3, or OCH_2CH_3 are attached to the skeleton.[3,4] Evidence exists that this flexibility is mainly a consequence of torsional freedom of the backbone bonds, supplemented perhaps by P-N-P bond angle distortion. Rigid, bulky side groups lower the torsional mobility of the chain segments and raise the Tg

accordingly, Also listed in Table II are the melting points, T_m, associated with the sidechains of the alkyl-ether alkoxy polymers. As the length of the sidechain increases, the T_m shifts to higher temperatures, which indicates that the polymer is taking on more of the character of poly(ethylene oxide).

Clearly, on the basis of the Tg values measured for polymers 6 and 7, the alkoxy ether side groups used in this work are themselves inherently flexible and do not seriously impede the reorientational freedom of the inorganic skeleton. Because these polymers are non-crystalline, they are elastomers at temperatures down to their Tg. This combination of molecular flexibility, low Tg, and hydrophilicity makes them ideal candidates for use as solid state electrolytes in energy storage devices.

Thus, polymers 6-10 have been examined as electrolyte host materials. All formed single-phase complexes with lithium salts and gave systems with ionic conductivities higher than those of similar systems formed by poly(ethylene oxide). As was pointed out in a recent communication,[18] with lithium triflate as an ionic conductor dissolved in polymer 7 or 8, the conductivity at room temperature is three orders of magnitude higher than has been found for complexes of poly(ethylene oxide).

We ascribe this behavior to the ability of the alkoxy ether side groups to complex the cations (in the manner well known for crown ethers). At the same time, the reorientational freedom of the polymers permits ions to be transported rapidly from site to site (in a "hand to hand" manner) that closely mimics the behavior of ions in a liquid electrolyte. This is a striking illustration of the "liquid" character of the elastomeric state. The use of such polymers in batteries and other electrical devices is currently being investigated.

The behavior of these polymers as biomedical materials has also been examined.[19] For the mixed-substituent polymers, increasing amounts of the hydrophobic side group, CF_3CH_2O-, appear to improve the blood compatibility. The use of these polymers as membrane materials is also being studied.

Experimental Section

Equipment. ^1H NMR spectra were recorded on a Bruker WP-200 spectrometer operating at 200 MHz in the Fourier transform mode. The data were processed by means of the WP-200 spectrometer computer. All data are for samples in CD_3OD. ^{31}P NMR spectra were recorded on a Varian CFT-20 spectrometer operating at 32 MHz in the Fourier transform mode. The data were processed by use of the computer of the CFT-20 spectrometer. All spectra were recorded for samples in THF. Approximate polymer molecular weights were determined by gel permeation chromatography with the use of a Waters Associates ALC-201 instrument, with a Styragel column and water as the elution solvent for 6 and 7, or THF for 5. Approximate calibration of the columns was accomplished by means of narrow molecular weight distribution polystyrene standards obtained from Waters Associates. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tn. Samples were dried for at least 72 h over phosphorus pentoxide in a vacuum desiccator before analysis.

Reagents. Most experimental manipulations were performed under an atmosphere of dry nitrogen (Burdett). Tetrahydrofuran (THF) (MCB Omnisolv) was distilled under nitrogen from sodium benzophenone ketyl. 2-Methoxyethanol, 2-(2-methoxyethoxy)ethanol (Aldrich) and trifluoroethanol (Halocarbon) were dried over molecular sieves before use. Carbowax 350, 550, and 750 (Union Carbide), corresponding to the side chains on polymers 8, 9, and 10, respectively, were dried before use. Sodium spheres (Aldrich) were used as received. Hexachlorocyclotriphosphazene (Ethyl Corp.) was sublimed and recrystallized from hexane.

Poly(dichlorophosphazene) (1) was prepared by the thermal polymerization of $(NPCl_2)_3$ at 250°C (Scheme II). An average of 50-60% conversion to the linear polymer was obtained.

Synthesis of Poly[bis(trifluoroethoxy)phosphazene] (5). This polymer was prepared by a method reported earlier.[1] The polymer was recovered by precipitation into water and was then purified by Soxhlet extraction with 95% ethanol. The ^{31}P NMR spectrum consisted of a sharp singlet at -7.2 ppm, which was indicative of total halogen replacement. The polymer was a white film-forming material. Yield: 17.6 g (88%).

Synthesis of Poly[bis(2-methoxyethoxy)phosphazene] (6). A solution of poly(dichlorophosphazene) (20 g, 0.17 mol) in THF (400 mL) was added over a 0.5 h period to a stirred suspension of sodium 2-methoxyethoxide, prepared from sodium spheres (7.82 g, 0.34 mol) plus 2-methoxyethanol (30.4 g, 0.40 mol) in warm THF (400 mL). The reaction mixture was heated for 24 h at reflux temperature, and was then cooled to room temperature. The polymer was recovered by precipitation into heptane, and was then purified by means of dialysis against water for 5 days and was isolated first by filtration of the solution, centrifugation, and then by solvent evaporation. A ^{31}P NMR spectrum consisted of a sharp singlet at -8.0 ppm, which was indicative of total halogen replacement. The GPC molecular weight was higher than 1×10^6. Yield: 12 g (60%).

Synthesis of Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (7). A solution of poly(dichlorophosphazene) (20 g, 0.17 mol) in THF (400 mL) was added over a 0.5 h period to a stirred suspension of sodium 2-(2-methoxyethoxy)ethoxide, prepared from sodium spheres (7.82 g, 0.340 mol) and 2-(2-methoxyethoxy)ethanol (48 g, 0.40 mol) in warm THF (400 mL). The reaction mixture was heated for 24 h at reflux temperature and was then cooled

to room temperature. The polymer was recovered by precipitation into heptane and was purified by dialysis against water for 5 days. The solution was then filtered, centrifuged, and the polymer obtained by solvent evaporation. In order to reduce the electrical conductivity of the carrier polymer, further purification was accomplished by twice passing an aqueous solution of 7 through the ion exchange columns, Dowex 50W-X10 in the H^+ form and Dowex 1-X8 in the OH^- form. This treatment removes residual salts. A ^{31}P NMR spectrum consisted of a sharp singlet at -7.7 ppm, which was indicative of total halogen replacement. The GPC molecular weight was greater than 1×10^6. Yield: 12.8 g (64%).

General Synthetic Route to 8-10. All polymeric compounds of structure 8-10 were prepared in the same manner. The following procedure is typical. Carbowax 550 (methoxypolyethylene glycol) (125 g, 0.23 mol) was dried azeotropically with a benzene/absolute ethanol solution (100 mL/50mL, 3 times) and then with a benzene solution (100 mL, 2 times). The glycol was then dissolved in THF (150 mL) and was added slowly to a NaH slurry (11 g, 0.28 mol, as a 60% dispersion in oil) in THF (800 mL). This solution was stirred for 10 h at 45°C and was then filtered via Schlenk techniques. To this black solution was added slowly (over a 1.5 h period) poly(dichlorophosphazene) (4.4 g, 0.038 mol) dissolved in THF (400 mL). This solution was stirred for 36 h at 65°C. The polymer was purified by removal of the excess solvent under reduced pressure and by dialysis against water (5 days) and methanol (4 days). The solution was then centrifuged and solvent was removed by evaporation. The ^{31}P NMR spectrum consisted of a singlet at -8.1 ppm. The GPC molecular weights of 12-14 were higher than 1×10^6.

General Synthetic Route to 11-16. All polymeric compounds of structure 11-16 were prepared in the same manner. The following procedure is typical. To a solution of poly(dichlorophosphazene) (16.08 g, 0.139 mol) dissolved in

THF (500 mL) was first added sodium trifluoroethoxide, prepared from sodium spheres (3.2 g, 0.14 mol) and trifluoroethanol (14.2 g, 0.142 mol) in THF (375 mL). The reaction mixture was heated for 24 h, and then sodium 2-methoxyethoxide, prepared from sodium spheres (5.5 g, 0.24 mol) and 2-methoxyethanol (22 g, 0.29 mol) in THF (450 mL) was added. The reaction mixture was then heated for an additional 24 h. Excess THF was removed under reduced pressure and the remaining viscous solution was precipitated into water to isolate the polymer. The resultant polymer was purified by three reprecipitations from THF into water. The ^{31}P NMR spectrum consisted of a broad singlet at -7.7 ppm. Yield: 8.0 g (30%). The characterization data for these and related compounds are listed in Tables II and III.

General Synthetic Route to 17 and 18. The polymeric compounds of structures 17 and 18 were prepared in the same manner. The following procedure is typical. Carbowax 550 (methoxypolyethylene glycol) (13.4 g, 0.024 mol) was dried azeotropically with a benzene/absolute ethanol solution (100 mL/50 mL, 3 times) and then with a benzene solution (100 mL, 2 times). The glycol was dissolved in THF (250 mL) and this solution was added to a NaH slurry (1.2 g, 0.030 mol, as a 60% dispersion) in THF (300 mL). This solution was stirred for 10 h at 45°C and then filtered via Schlenk technique. To this salt solution was added slowly (over a 1.5 h period) poly(dichlorophosphazene) (2.8 g, 0.024 mol) dissolved in THF (200 mL). The mixture was stirred for 24 h at 65°C and was then cooled to room temperature. This solution was added to the sodium salt of 2-(2-methoxyethoxy)ethanol, prepared from the alcohol (10 g, 0.083 mol) and sodium spheres (1.9 g, 0.083 mol), and the mixture was stirred for 24 h at 65°C. The polymer was isolated by removal of the excess solvent under reduced pressure. It was purified by dialysis against water (4 days) and methanol (4 days). This solution was then centrifuged and the

solvent allowed to evaporate. The ^{31}P NMR spectrum consisted of a singlet at -7.7 ppm. The GPC molecular weights of these polymers were found to be higher than 1×10^6. Other characterization data for these compounds are listed in Tables II and III.

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19. Several of these polymers were evaluated for their blood compatibility behavior with the use of a Lindholm cell.[20] In these tests the polymer surface contact area was approximately 7 cm^2. The temperature was 25°C. To each cell was added 2 mL of freshly drawn bovine blood, and the cells were tilted until clotting occurred. Measured clotting times in parentheses in min were 5 (>45), 6 (<5), 7 (<5), 11 (40), 12 (40), 13 (>45), 14 (<5), 15 (40), and 16 (30). Thus, the hydrophobic fluoroalkoxy side group appears to play the major role in raising blood compatibility of these polymers.

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Table I

Mixed-Substituent Polymers

	OR	OR'
11	$-OCH_2CH_2OCH_3$ (69%)	$-OCH_2CF_3$ (31%)
12	$-OCH_2CF_3$ (35%)	$-OCH_2CH_2OCH_3$ (65%)
13	$-OCH_2CF_3$ (60%)	$-OCH_2CH_2OCH_3$ (40%)
14	$-OCH_2CF_3$ (35%)	$-O(CH_2CH_2O)_2CH_3$ (65%)
15	$-OCH_2CF_3$ (58%)	$-O(CH_2CH_2O)_2CH_3$ (42%)
16	$-OCH_2CF_3$ (82%)	$-O(CH_2CH_2O)_2CH_3$ (18%)
17	$-O(CH_2CH_2O)_{12}CH_3$ (50%)	$-O(CH_2CH_2O)_2CH_3$ (50%)
18	$-O(CH_2CH_2O)_{12}CH_3$ (30%)	$-O(CH_2CH_2O)_2CH_3$ (70%)

Table II

Analytical and Glass Transition Data

Compound		%C	%H	%N	T_g (°C)[a]
5[1,3]					-66
6	calcd	36.92	7.18	7.18	-75
	found	36.74	7.39	7.08	
7	calcd	42.40	7.77	4.95	-84
	found	41.94	7.84	4.95	
8	calcd	49.79	8.85	1.94	-67[b]
	found	49.21	8.39	2.02	
9	calcd	52.40	8.91	1.22	-63[b]
	found	50.37	8.26	1.26	
10	calcd	51.35	8.68	0.87	-59[b]
	found	51.42	8.45	1.14	
11	calcd	30.74	5.19	6.67	-61
	found	30.78	5.17	6.68	
12	calcd	30.11	5.01	6.64	-62
	found	29.87	5.03	6.51	
13	calcd	25.70	3.62	6.35	-61
	found	25.91	3.81	6.17	
14	calcd	35.11	5.80	5.20	-64
	found	35.13	6.13	5.25	
15	calcd	30.03	4.42	5.47	-57
	found	30.26	4.51	5.44	
16	calcd	24.41	2.96	5.64	-55
	found	24.25	2.99	5.60	
17	calcd	46.47	8.02	1.94	-67[b]
	found	46.48	8.19	2.68	
18					-69

[a] As determined by differential scanning calorimetry.

[b] T_m for 8 was -12°C; fo 9, +12°C; for 10, +30°C; and for 17, +1°C. Species 6 and 7 showed no evidence of a crystalline melting transition from D.S.C. analyses.

Table III

NMR Data

Polymer	^{31}P (ppm)	^{1}H (ppm)[a,b]					
		a	b	c	d	e	... x
5	-7.2	4.4					
6	-8.0	4.1	3.6	3.4			
7	-7.7	4.1	3.7	3.5	3.7	3.3	
8	-7.0	4.1	← 3.7-3.5[c] →			3.3	
9	-8.0	4.1	← 3.7-3.4[c] →			3.3	
10	-8.5	4.1	← 3.8-3.4[c] →			3.3	
11	-7.7	4.1	3.6	3.4			
12	-7.7	4.1	3.6	3.3			
13	-7.8	4.1	3.6	3.3			
14	-7.8	4.1	← 3.5-3.4[c] →				
15	-7.8	4.1	← 3.6-3.4[c] →				
16	-7.8	4.1	← 3.6-3.4[c] →				
17	-7.7	4.1	← 3.8-3.4[c] →			3.3	
18	-7.7	4.1	← 3.8-3.4[c] →			3.3	

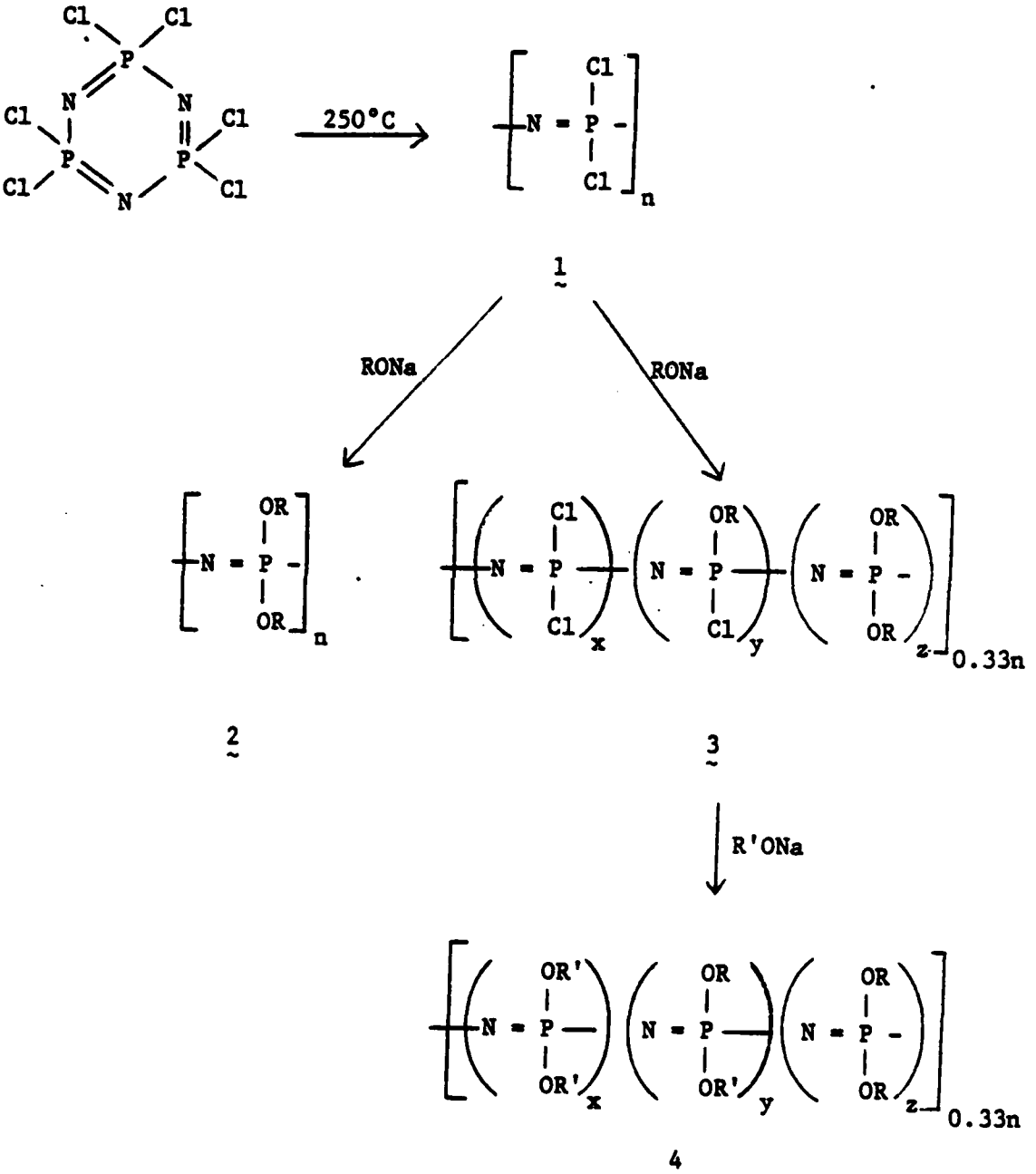
[a] The ^{1}H chemical shift positions are given in order from the site closest to the point of attachment to the phosphorus.

[b] The ^{1}H chemical shift of the methylene protons in the $-OCH_2CF_3$ cosubstituent for polymers 11-16 is 4.4 ppm.

[c] This region of the spectrum consisted of an envelope of overlapping peaks.

[d] The following ^{13}C shift positions are given in sequence from the site closest to the point of attachment to the phosphorus. The chemical shifts were: 65.9, 72.7, ←71[c] →58.9, respectively.

Scheme I



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