perature (25 °C) by means of a temperature-controlled water bath. The assay of trypsin was performed spectrophotometrically following the standard assay procedure described by Glassmeyer.[40] The reactants (15.4 mL of 0.1 M phosphate buffer, 4.6 mL of DMF, and 38.5 mg of BANA) were added to the trypsin. The reaction mixture was shaken for 30 s, and the UV absorbance of the clear solution was measured at 406 nm. The polymeric conjugate was washed three times with phosphate buffer solution to remove remaining reactants. The same amount of reactants was added and the mixture was shaken for 1 min. The absorbance was recorded again at 406 nm. This assay procedure was repeated for an extended reaction time. An almost linear assay response was obtained in all instances.

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Registry No. G-6-PDH, 9001-40-5; BrCN, 506-68-3; HNO_2, 7782-77-6; NaOPh, 139-02-6; NaH, 7646-69-7; PhOH, 108-95-2; NBu_4Br, 1643-19-2; poly[bis(*p*-aminophenoxy)phosphazene], 101760-93-4; poly(diphenoxyphosphazene), 28212-48-8; glutaric dialdehyde, 111-30-8; trypsin, 9002-07-7; poly(dichlorophosphazene), 26085-02-9.

Supplementary Material Available: Spectra of glucose-6-phosphate plus NADP (Figure 11a), gluconate-6-phosphate plus NADPH (Figure 11b), BANA (Figure 12a), and *p*-nitroaniline (Figure 12b) (2 pages). Ordering information is given on any current masthead page.

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(46) One unit will oxidize 1.0 μmol of G-6-P to 6-phosphogluconate per min at pH 7.8 at 30 °C, using NADP as a coenzyme.

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

Harry R. Allcock,*† Paul E. Austin,† Thomas X. Neenan,† John T. Sisko,† Peter M. Blonsky,‡ and Duward F. Shriver*‡

Departments of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and Northwestern University, Evanston, Illinois 60201.
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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

† The Pennsylvania State University.
‡ Northwestern University.

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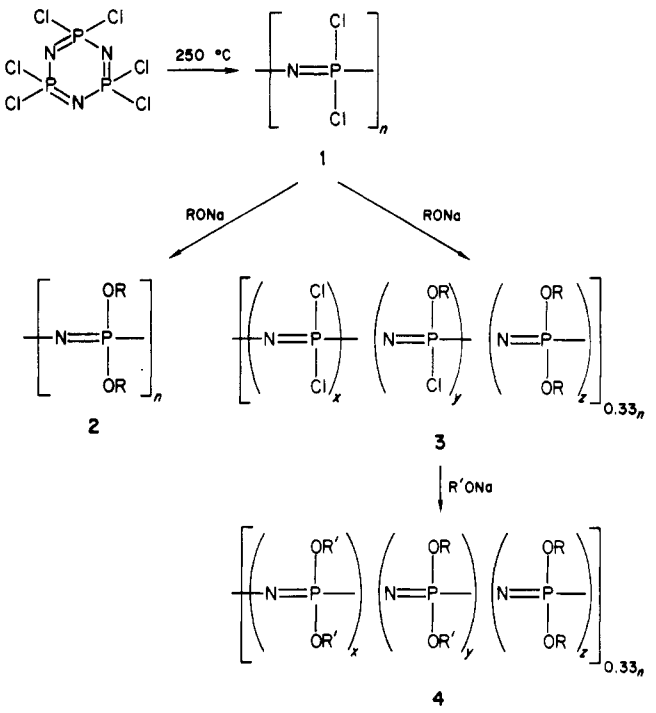
Scheme I



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 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 appropriate for biomedical uses. Another interest involves the use of such polymers as "solid electrolytes". For this purpose 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 paper,[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.

Table I
Mixed-Substituent Polymers[a]

compd	-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%)

[a] Percentages of substituent groups shown are based on analyses of the final, purified polymers with the use of a best-fit combination of ^1H NMR and elemental microanalytical data.

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 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', R'O–P–OR' units. Thus, it was not possible to deduce whether the distribution of different side groups was geminal or nongeminal, 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 ^1H 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, 17, and 18 were soluble in water. Species 12, 13, and 16 were hydrophilic but not soluble in water. Compounds 11, 14, and 15 were insoluble

Table II
Analytical and Glass Transition Data[a]

compd		% C	% H	% N	T_g,[b] °C
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[c]
	found	46.48	8.19	2.68	
18					−69

[a] Microanalyses for chlorine indicated that this element did not exceed 0.2%. The stability of these polymers to prolonged exposure to water was also consistent with the absence of P–Cl bonds. [b] As determined by differential scanning calorimetry. [c] T_m for 8 was −12 °C; for 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 DSC analyses.

Table III
NMR Data

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

[a] ^1H chemical shift positions are given in order from the site closest to the point of attachment to the phosphorus. [b] ^1H 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, and ←71[c]→58.9, respectively.

in water but could be induced to dissolve in some aqueous media. 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, T_g, are listed in Table II. They fall in the range −55 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 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 T_g accordingly. Also listed in Table II are the melting points, T_m, associated with the side chains of the alkyl ether alkoxy polymers. As the length of the side chain 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 T_g 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 noncrystalline, they are elastomers or leathery materials at temperatures down to their T_g. This combination of molecular flexibility, low T_g, 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 paper,[18] with silver or lithium triflate as an ionic conductor dissolved in polymer 7 or 8, the conductivity at room temperature is 3 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 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 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 were 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 Polymer Laboratories column and THF as the elution solvent. 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 I). 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).[21] 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; it was then purified by means of dialysis against water for 5 days and isolated 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).[21] 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 and centrifuged, and the polymer was 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 pH 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 higher 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 (methoxypoly(ethylene glycol)) (125 g, 0.23 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 (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.[22] 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 (methoxypoly(ethylene glycol)) 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 (13.4 g, 0.024 mol) 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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Registry No. **1**, 26085-02-9; **5**, 28212-50-2; **6**, 101653-85-4; **7**, 98973-15-0; **8**, 101653-86-5; $NaOCH_2CF_3$, 420-87-1; $NaOCH_2CH_2OCH_3$, 3139-99-9; $NaO(CH_2CH_2O)_2CH_3$, 19278-10-5; $NaO(CH_2CH_2O)_7CH_3$, 101653-87-6; $NaO(CH_2CH_2O)_nCH_3$, 31494-81-2.

References and Notes

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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 minutes 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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(21) The use of a slight excess of alkoxide relative to P-Cl bonds leads to complete chlorine replacement by the shorter alkoxy chains (n = 1 or 2). However, larger excesses of alkoxide are needed for the longer glyme units (up to four equivalents per P-Cl unit). We have also found that the addition of 1-2 g of $(n\text{-Bu})_4NBr$, as a "phase-transfer catalyst" to these types of reactions, is an aid to obtaining complete substitution.
(22) This method of isolation is possible because the trifluoroethoxy groups generate an insolubility in aqueous media.

Water-Soluble Copolymers. 17. Copolymers of Acrylamide with Sodium 3-Methacrylamido-3-methylbutanoate: Synthesis and Characterization

C. L. McCormick* and K. P. Blackmon

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406. *Received November 19, 1985*

ABSTRACT: The copolymerization of acrylamide (AM) with sodium 3-methacrylamido-3-methylbutanoate (NaMAMB) has been studied in the range from 25 to 90% AM in the feed. The value of r_1r_2 has been determined to be 0.24 for the AM-NaMAMB pair. The copolymer compositions have been determined from elemental analysis and ^{13}C NMR. The molecular weights as measured by low-angle laser light scattering of the copolymers were found to decrease with increasing NaMAMB content and ranged from 2×10^6 to 7×10^6. Second virial coefficients were also obtained from the light scattering data and ranged from 3.1×10^{-4} to 3.5×10^{-4} mL·mol/g^2. The copolymer microstructures, including run numbers and sequence distributions, were calculated from the reactivity ratios. These model structures are utilized for assessment of structure/dilute solution property relationships reported in a subsequent paper in this series.

Introduction

An increasingly large number of water-soluble polymers are being studied for a wide range of potential applications.[1-4] Of growing importance are copolymers of acrylamide for use as water-soluble viscosifiers and displacement fluids in enhanced oil recovery.[5-10] However, a serious limitation of many polyelectrolytes, including those derived from hydrolyzing polyacrylamide, is the severe loss of viscosity in the presence of mono- and multivalent electrolytes. Even more catastrophic is the exhibition of phase separation in the presence of multivalent electrolytes ($CaCl_2$) as is common with many such polyelectrolytes.

The aim of our continuing research[11-16] is to prepare model water-soluble polymers with large hydrodynamic dimensions in electrolyte solutions that are stable against phase separation in the presence of divalent ions, e.g., $CaCl_2$. In two previous papers[15,16] we reported the synthesis, characterization, and solution properties of copolymers of acrylamide (AM) with sodium 3-acrylamido-3-methylbutanoate (NaAMB). In this paper we report the synthesis, structural characterization, and molecular weight studies of charged copolymers of acrylamide (AM) with sodium-3-methacrylamido-3-methylbutanoate (NaMAMB). The introduction of a methyl group on the α-carbon of this monomer promised stiffening of the resulting polymer backbone with marked inhibition of rotation about the C-C bonds.[17] Furthermore, a more rigid molecule could increase hydrodynamic volume in solution.

Experimental Section

Materials. Sodium 3-methacrylamido-3-methylbutanoate (NaMAMB) was prepared by neutralization of 3-methacrylamido-3-methylbutanoic acid (MAMBA). MAMBA was synthesized via a Ritter reaction involving equimolar amounts of methacrylonitrile and 3,3-dimethylacrylic acid in the presence of water and a large excess of concentrated sulfuric acid. The synthesis of MAMBA followed the procedure set forth by Hoke and Robins.[18] The crude MAMBA was recrystallized twice from a mixture of methyl ethyl ketone and petroleum ether prior to use (mp 69-70 °C). Anal. Calcd for $C_9H_{15}NO_3$: C, 58.38; H, 8.11; N, 7.57. Found: C, 57.99; H, 8.41; N, 7.46. IR N-H stretch, 3350; CH_2=C, 2980; aliphatic C-H, 2930; amide C=O, 1690 (s), 1530 (m); acid C=O, 1710 cm^{-1}. Acrylamide (AM) from Aldrich Chemical Co. was recrystallized twice from acetone and vacuum-dried at room temperature prior to use (mp 83-84 °C). Potassium persulfate from J. T. Baker Co. was recrystallized twice from deionized water prior to use.

Poly(sodium 3-methacrylamido-3-methylbutanoate) and Poly(acrylamide-*co*-sodium 3-methacrylamido-3-methylbutanoate). The homopolymer of sodium 3-methacrylamido-3-methylbutanoate (NaMAMB) and the copolymers of acrylamide (AM) with NaMAMB were prepared in aqueous solution at 30 °C using 0.1 mol % potassium persulfate as the initiator. Each reaction was conducted in a 1000-mL, three-necked flask equipped with a mechanical stirrer and nitrogen inlet tube. A designated amount of MAMBA was partially dissolved in deionized water followed by the addition of an equimolar amount of NaOH. A designated amount of acrylamide dissolved in deionized water was then added to the neutralized MAMBA solution, and the pH of the entire mixture was adjusted to 9.0 ± 0.1 by dropwise addition of 0.5 M NaOH. The pH adjustment was performed to ensure that all of the carboxylated monomer was in the sodium salt form. Each reaction mixture was then deaerated with oxygen-free nitrogen for 20 min. The designated quantity of potassium persulfate initiator, dissolved in deionized water, was injected into the reaction vessel. The total monomer concentration in each reaction was held constant at 0.456 M. After designated reaction intervals, the resulting polymer was diluted with deionized water and precipitated into reagent-grade acetone. The polymers were further purified by reprecipitation into acetone followed by freeze-drying and then vacuum-drying for 2 days. Conversions were determined gravimetrically. Table I lists reaction parameters for the copolymerization of AM with NaMAMB and the homopolymerization of NaMAMB. IR: MAMB homopolymer, N-H stretch (br), 3400; C-H, 2970; amide C=O, 1650; sodium salt

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