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Alkanesulfonation of Cyclic and High Polymeric Phosphazenes

Harry R. Allcock,* Eric H. Klingenberg, and Mark F. Welker

Department of Chemistry, The Pennsylvania State University,
University Park, Pennsylvania 16802

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ABSTRACT: A method for sulfonating aminophosphazenes with the use of 1,3-propanesultone is described. The alkanesulfonation reactions were first developed with small molecule phosphazene cyclic trimers as models for high polymeric phosphazenes. High molecular weight poly(aminophosphazenes) were then sulfonated using similar techniques. The structure and properties of the alkanesulfonated polymers were examined by DSC, intrinsic viscosity, and ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy. This synthetic approach to sulfonated polymers is valuable for the development of new biomedical materials, membranes, reversibly cross-linkable polymers, surfactants, and polyelectrolytes.

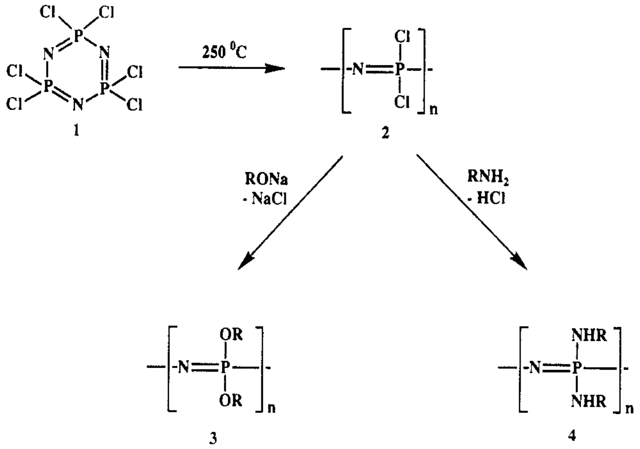
Introduction

The design and synthesis of hydrophilic or water-soluble polymers is of considerable technological interest in areas as diverse as metal chelation, antistatic materials, and adhesion.[1,2] Hydrophilicity is also an important factor in the surface behavior of biomedical materials.[3] Of the various functional groups that can impart hydrophilic character to a polymer, the sulfonic acid group is one of the most useful. Polymers that bear sulfonic acid groups are used in ion-exchange resins, nonthrombogenic biomaterials, reverse osmosis membranes, antistatic materials, and bacteriostats.[4-14] The main objective of this work was to develop a new strategy for the sulfonation of polyphosphazenes.

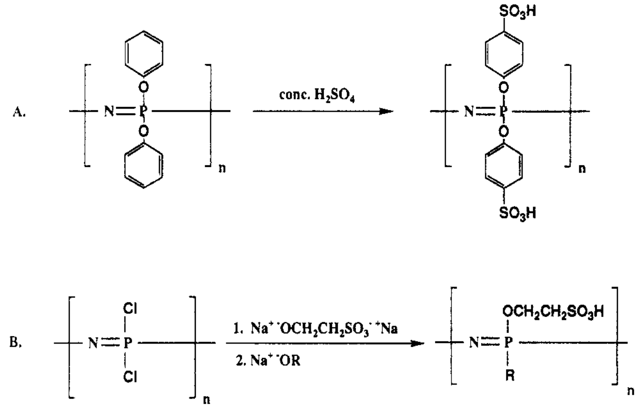
Polyphosphazenes are a broad class of macromolecules based on the repeating unit $(NPR_2)_n$. One of the main methods for the synthesis of these polymers is illustrated in Scheme I. Poly(dichlorophosphazene) (**2**) reacts with a wide variety of nucleophiles to yield high molecular weight organic-derivatized polymers with properties that vary widely with the side group structure. The stability of the phosphorus-nitrogen backbone makes this class of macromolecules particularly suitable for side-group and surface modification.

The sulfonation of phosphazenes via reactions with sulfuric acid was studied in earlier phases of our program. Specifically, the molecular level and surface sulfonation of aryloxy- and (arylamino)phosphazenes was accomplished through the use of concentrated sulfuric acid (Scheme II, reaction A).[15] (Aryloxy)polyphosphazenes can also be sulfonated via the use of sulfur trioxide as shown by Monotoneri, Gleria, and co-workers.[16,17] However, polyphosphazenes that contain etheric side groups (which are widely used in biomedical and polymeric electrolyte research) decompose under acidic conditions. Sulfonated polymers that contain etheric side groups have been synthesized by Shriver and co-workers by the reaction of sodium oxyethanesulfonate with poly(dichlorophosphazene), followed by treatment with a second etheric nucleophile (Scheme II, reaction B).[18] This method has two limitations. First, the nucleophile has only a limited solubility in the etheric solvents used for the reaction. Second, the use of a difunctional reagent results in cross-linking of the polymer chains. Although these cross-links may be broken by the addition of a second nucleophile, this introduces an unwanted complication to the process.

Scheme I



Scheme II



$R = CH_2CH_2OCH_2CH_2OCH_3$

This reaction is also limited by the premature precipitation of the polymers from solution.

Thus, an alternative general route to sulfonated phosphazenes was sought. 1,3-Propanesultone (**5**) is a commercially available sulfonating reagent that can react with a wide variety of amines to produce alkanesulfonated products in high yield.[19,20] The reaction of **5** with amines has been shown to proceed under mild reaction conditions, with the structures of the sulfonated products determined mainly by the amine used. Sulfonic acid derivatives are produced when primary or secondary amines react with **5**. Tertiary amines interact with **5** to produce zwitterionic species. In principle, high polymers containing amino groups can be sulfonated in the same way.

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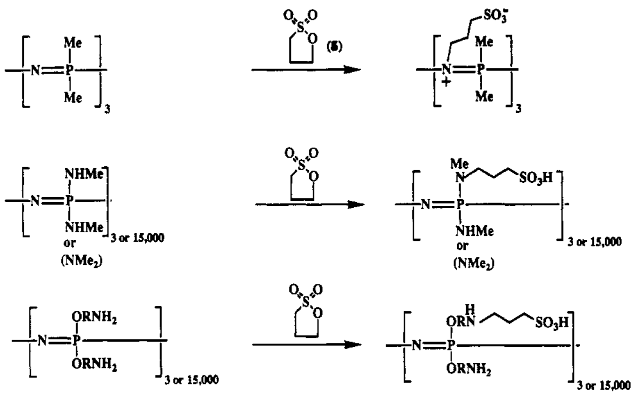
Scheme III



R = Alkoxy spacer

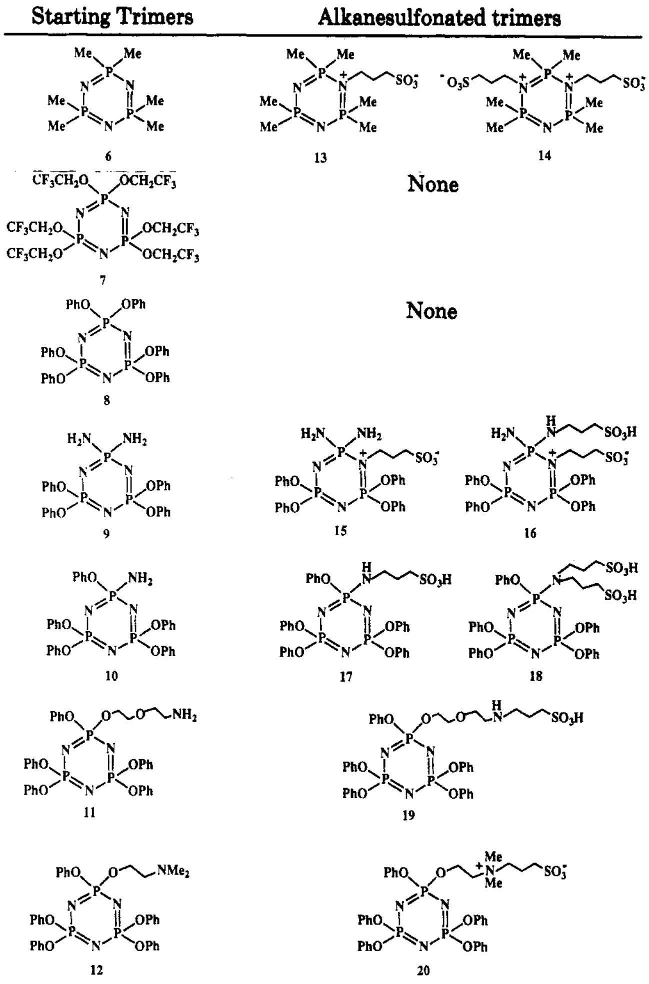
The use of phosphazenes as macromolecular substrates for alkanesulfonation with **5** provides an appealing system for the preparation of sulfonated polymers. The properties of the sulfonated phosphazenes can be tailored by a choice of different primary, secondary, or tertiary amino groups, by variations in the degree of sulfonation, and by the use of different organic cosubstituent groups.

In this paper we describe the reactions of various aminophosphazenes with **5**. The sulfonation reactions were first studied with the use of cyclotriphosphazenes as small molecule models. These model studies were conducted at three levels: (1) with cyclic trimers that contain no amino side groups, and in which the ring nitrogen atoms are the only basic sites; (2) with cyclic trimers that contain amino groups linked directly to the phosphorus atoms of the ring; and (3) with cyclic trimers that bear amino side groups linked to the phosphorus atoms through alkoxy spacer groups. The techniques were then extended to the corresponding high polymers. A general synthetic approach to these reactions is shown in Scheme III.

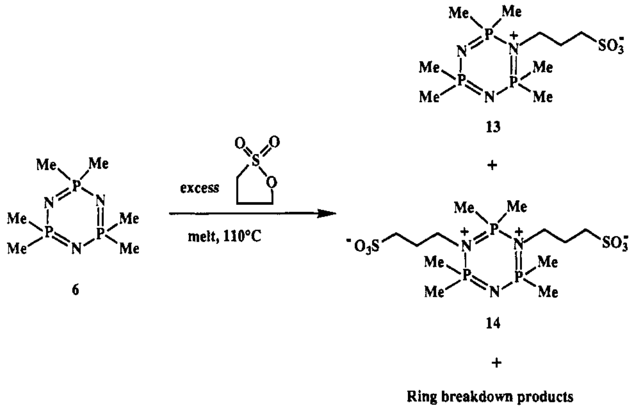
Results and Discussion

Small-Molecule Cyclotriphosphazene Studies. (a) Model Compounds with No Amino Side Groups. For sulfonation reactions with cyclotriphosphazenes that bear no amino side groups, the reactions of cyclic trimers **6**–**8** (Chart I and Table I) with **5** were examined. Trimers **7** and **8** did not undergo sulfonation with **5** in solution or in the melt at 100 °C. The steric bulk and electron withdrawing properties of the side groups may explain this result. Both the trifluoroethoxy and phenoxy side groups can withdraw electrons from the phosphazene ring, a process that makes the ring nitrogen atoms less nucleophilic than, for example, that in a free amine. However, **6** reacts rapidly with **5** in the melt at 100 °C to give the mono- and dizwitterionic products (Scheme IV), identified by ^{31}P NMR spectra and positive ion fast atom bombardment (+FAB) mass spectrometry (Table II). Thus, species **13** and **14** were detected in the ^{31}P NMR spectra as two AB_2 spin systems in close proximity to each other. Compound **13** was formed first ($\delta_A = 41.6$ ppm and $\delta_B = 29.95$ ppm, $J_{AB} = 12.8$ Hz), with compound **14** ($\delta_A = 41.4$ ppm and $\delta_B = 30.25$ ppm, $J_{AB} = 14.6$ Hz) appearing immediately thereafter. ^{31}P NMR experiments also suggest that the monozwitterionic product is readily converted to the dizwitterion. Apparently, the formation of the dizwitterion is followed by a breakdown of the molecule since the intensity of a phosphate peak in the ^{31}P NMR spectra (0 ppm) increases as the reaction continues beyond this point.

Chart I. Structures of the Starting Cyclotriphosphazenes and Their Alkanesulfonated Products



Scheme IV



(b) Model Compounds with Amino Groups Linked Directly to the Phosphazene Ring. Cyclic trimer **9**, which contains geminal NH_2 groups, reacts with **5** in refluxing THF to give both mono- and dialkanesulfonated products (Scheme V). A ring nitrogen atom adjacent to the amino-substituted phosphorus atom reacted first, as determined from ^{31}P NMR spectra. Thus, the formation of an ABX spin system in the ^{31}P NMR spectrum indicated that three different phosphorus environments were present ($\delta_A = 6.1$ ppm, $\delta_B = 19.6$ ppm, and $\delta_C = 14.8$ ppm). This would be expected if alkanesulfonatation occurs at a ring nitrogen atom adjacent to the P–NH_2 unit to yield the zwitterion **15**. An initial reaction at this site is not unexpected, since ring nitrogen atoms are often more basic than exocyclic nitrogen atoms.[21-23] Two different possibilities exist for the introduction of the second propanesulfonic acid functionality: (1) at the other ring nitrogen atom adjacent to

Table I. Characterization Data for the Starting Cyclotriphosphazenes

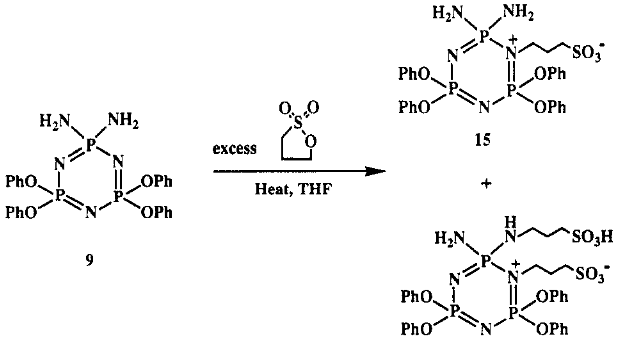
compd	Mp (°C)	NMR (ppm) ^{31}P	^{1}H	^{13}C	mass spec found (calc)
$N_3P_3Me_6$ (6)	194	24.4	1.4	23.4	348 (348)
$N_3P_3(OCH_2CF_3)_6$ (7)	49	-17.7	4.4	124.2 64.0	729 (729)
$N_3P_3(OC_6H_5)_6$ (8)	115	-9	7.3	121.2 125.0 130.1 150.0	693 (693)
$N_3P_3(OC_6H_5)_4(NH_2)_2$ (9)	104	7.8, 16.3 J_{AB} = 67 Hz	2.2, 7.2	121.1 125.2 130.0 150.0	539 (539)
$N_3P_3(OC_6H_5)_5NH_2$ (10)	65	9.3, 18.7 J_{AB} = 76 Hz	2.2, 7.3	121.0 125.1 130.1 150.0	616 (616)
$N_3P_3(OC_6H_5)_5OCH_2CH_2OCH_2CH_2NH_2$ (11)	oil	9.9, 8.4 J_{AB} = 75 Hz	3.0, 3.7, 4.1, 7.3	41.3, 67.2 68.0, 71.1 121.0 124.9 130.1 150.0	704 (704)
$N_3P_3(OC_6H_5)_5OCH_2CH_2NMe_2$ (12)	oil	9.65, 13.3 J_{AB} = 84 Hz	2.0, 2.2, 3.4, 7.3	48.1, 52.3 69.2 121.0 124.7 130.1 150.0	688 (688)

Table II. Characterization Data for Alkanesulfonated Cyclotriphosphazenes

compd	^{31}P NMR[a] (ppm) υ_A	υ_B	υ_C	mass spec found (calc)
$[N_3P_3Me_6]^+[CH_2CH_2CH_2SO_3]^-$ (13)	41.6 J_{AB} = 12.8 Hz	29.95		366 (366)
$[N_3P_3Me_6]^{2+}[CH_2CH_2CH_2SO_3]_2^{2-}$ (14)	41.4 J_{AB} = 14.6Hz	30.25		488 (488)
$[N_3P_3(OC_6H_5)_4(NH_2)_2]^+[CH_2CH_2CH_2SO_3]^-$ (15)	6.1 J_{AB} = 82 Hz	19.6 J_{BC} = 67 Hz	14.8 J_{AC} = 62 Hz	661 (661)
$[N_3P_3(OC_6H_5)_4(NH_2)(NHCH_2CH_2CH_2SO_3H)]^+[CH_2CH_2CH_2SO_3]^-$ (16)	4.7 J_{AB} = 76 Hz	19.3 J_{BC} = 67 Hz	14.4 J_{AC} = 56 Hz	783 (783)
$N_3P_3(OC_6H_5)_5(NHCH_2CH_2CH_2SO_3^{-+}Na)$ (17)	12.5 J_{AB} = 76 Hz	23.4		785 (785)
$N_3P_3(OC_6H_5)_5N(CH_2CH_2CH_2SO_3^{-+}Na)_2$ (18)	13.6 J_{AB} = 74 Hz	27.2		930 (930)
$N_3P_3(OC_6H_5)_5(OCH_2CH_2OCH_2CH_2NHCH_2CH_2CH_2SO_3H)$ (19)	7.5 J_{AB} = 81 Hz	22.8		826 (826)
$N_3P_3(OC_6H_5)_5(OCH_2CH_2CH_2NMe_2{}^+CH_2CH_2CH_2SO_3^-)$ (20)	9.4 J_{AB} = 83 Hz	13.4		811 (811)

[a] The ^{31}P NMR assignments are tentative.

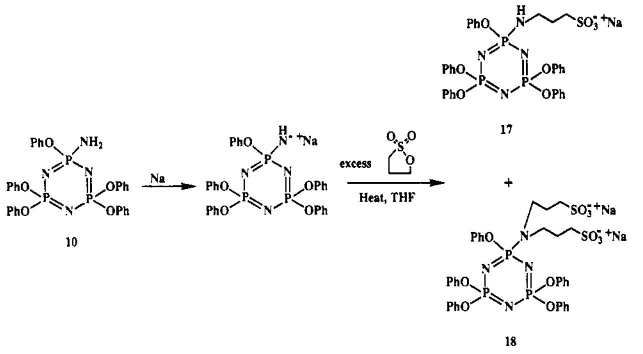
Scheme V



the amino-substituted phosphorus or (2) at one of the exocyclic nitrogen atoms. Feistel and Rapko have shown that it is possible to alkylate endocyclic nitrogen atoms in preference to ring nitrogen atoms.[24] ^{31}P NMR spectra suggested that the second reaction occurs at one of the exocyclic ring nitrogen atoms. Alkanesulfonation at the second ring nitrogen atom should lead to the formation of only two different phosphorus environments, with a ^{31}P NMR spectrum of the AB_2 type. However, the ^{31}P NMR spectrum obtained was of the ABX type (δ_A = 4.7 ppm, δ_B = 19.3 ppm, and δ_C = 14.4 ppm), which suggests that three different phosphorus environments are still present. Alkanesulfonation at the ring nitrogen atom between the phosphorus atoms that are not linked to amino groups is considered to be unlikely, because of both steric hindrance and the electron withdrawing ability of the phenoxy groups. Therefore, the second site for alkanesulfonation is believed to be one of the exocyclic amino groups, and this would yield three distinct phosphorus environments. The reaction of 9 with excess 5 gave not only the mono- or direacted products but also several multiply sulfonated species.

In an attempt to control the degree of sulfonation, cyclic trimer 10, with only one NH_2 side group, was employed (Scheme VI). Attempts to alkanesulfonate 10 with 5 in refluxing THF solutions were not successful. However, the sodium amide of 10 reacted with 5 to yield both the

Scheme VI



mono- and dialkanesulfonated products (17 and 18), which were detected by ^{31}P NMR spectra and +FAB mass spectra ($M^+ = m/z$ 785 and 930, respectively). The inability of 10 to react with 5 may again be the result of the steric bulkiness and electron withdrawing ability of the phenoxy side groups. The high reactivity of the sodium amide of 10 toward 5 apparently overcomes the electronic and steric retardation created by the phenoxy side groups. No evidence was found for ring nitrogen atom reactions based on an analysis of the ^{31}P NMR spectra. Thus, the ^{31}P NMR spectra were consistent with the apparent simultaneous formation of both the mono- and dialkanesulfonated products.

(c) Model Compounds with the Amino Side Groups Linked through Alkoxy Spacers to the Ring. Spacer groups between the exocyclic nitrogen atoms and the electron withdrawing phosphazene ring should reduce the influence of the phosphazene ring and allow side chain sulfonation to occur under milder reaction conditions. This occurred when compounds 11 and 12 reacted with 5 during a period of 2–3 days at 50 °C. Compound 11 reacted with 5 to produce the ionic amphiphile 19. However, 12 reacted to give the zwitterionic product 20. The alkanesulfonated products were examined by ^{31}P NMR, ^{13}C NMR, ^{1}H NMR, and mass spectrometry and were shown to be 19 and 20, respectively. For example, for the reaction product from 11, integration of the propyl proton peaks in the ^{1}H NMR spectra (1.8 (m), 2.65 (t), and 3.3 (t)) and the ethyleneoxy methylene protons (2.9 (t), 3.7 (m), and 4.1 (t)) indicated that only the monoalkanesulfonated product (19) was formed. ^{31}P NMR spectra for both products 19 and 20 suggest that alkanesulfonation takes place at the exocyclic amino groups. Reaction at the ring nitrogen atoms would generate an ABX spin system. However, only AB_2 spin systems were detected after alkanesulfonation.

(d) Properties of the Alkanesulfonated Cyclic Trimers. Sulfonation of the trimers changed their solubility dramatically. Compounds 6 and 10–12 are insoluble in water. However, the corresponding alkanesulfonated products show an increased solubility in polar media. Compounds 13–18 are soluble in water. Compounds 19 and 20 do not dissolve in water but readily absorb water from the atmosphere. ^{1}H NMR spectra of 19 and 20 in deuterated chloroform show a significant broadening of the propyl proton peaks (1.8, 2.65, and 3.3 ppm) and a water peak at 5 ppm. The water could be removed by extensive drying under vacuum at 40 °C.

Macromolecular Reactions. All the macromolecular reactions were performed in the solution state. The polymer alkanesulfonation reactions were examined at the same three levels as in the small-molecule model studies. Thus, alkanesulfonation was first examined with polymers that contained no amino side groups. Second, polymers were studied that contain amino side groups linked directly to the phosphorus atoms of the backbone. Third, polymers were used that contain amino groups linked to the polymer backbone through alkoxy spacer groups.

(a) Polymers Bearing No Amino Side Groups. Polymer 27 did not react with 5 even after 14 days in refluxing THF solution. As discussed for the small-molecule systems, the reaction may not occur because the side groups withdraw electron density from the phosphazene backbone, making the backbone nitrogen atoms less basic. This, together with the inhibiting effects of side group steric hindrance, may explain the resistance to alkanesulfonation.

(b) Polymers Containing Amino Groups Linked Directly to the Backbone. Alkanesulfonation of $[NP(NMe_2)_{1.12}(NHMe)_{0.88}]_n$ (21) with excess 5 takes place in refluxing THF. Approximately 15% of the amino side groups were alkanesulfonated after 2 days, as estimated by ^{1}H NMR spectroscopy. The reaction terminated when the reacted polymer precipitated from solution.

The resultant propanesulfonated polyphosphazene, $[NP(NMe_2)_{0.88}(NHMe)_{0.85}(NMe_2{}^+CH_2CH_2CH_2SO_3{}^-)_{0.27}(NMeCH_2CH_2CH_2SO_3H)_{0.03}]_n$ (22), was soluble in water, methanol, and DMSO. The polymer swelled in ethanol and 2-propanol. It was insoluble in most common organic solvents such as THF, diethyl ether, toluene, or hexane. This is in contrast to the starting polymer (21), which is insoluble in water and methanol but is soluble in THF and dioxane.

Polymer 22 was examined by ^{31}P NMR and ^{1}H NMR spectroscopy. In principle, alkanesulfonation could take place at three possible sites—at the backbone nitrogen atoms, at the dimethylamino nitrogen atoms, or at the monomethylamino nitrogen atoms. The reaction occurred in part at the dimethylamino groups to give zwitterionic units, as shown by the ^{1}H NMR spectra. A shift occurred in the dimethylamino group proton resonance from 2.4 to 3.2 ppm, which corresponds to the formation of the zwitterion. Integration of the methyl proton peak at 3.2 ppm and the methylene proton peak at 3.6 ppm for the propanesulfonate group suggested that 90% of alkanesulfonation had occurred at the dimethylamino sites. The remaining 10% may involve the monomethylamino groups. Evidence for the presence of $-SO_3H$ units was the sensitivity of polymer 22 to divalent cations.[25,26] Addition of calcium ions to an aqueous solution of polymer 22 caused gelation, presumably a consequence of ionic cross-linking.

(c) Polymers Containing Amino Groups Linked to the Backbone through Alkoxy Spacer Groups. The alkanesulfonation of polymers 23–26, with the general structure $[NP(OCH_2CF_3)_x(OCH_2CH_2OCH_2CH_2NH_2)_y]_n$ ($x + y = 2$) (Chart II and Table III), occurred at room temperature over a period of 5 days, with methanol used as the solvent, to produce alkanesulfonated derivatives 28–31. In principle, the different monomer units illustrated in Scheme VII could exist. However, it was not possible to identify each specific monomer unit by ^{31}P NMR spectroscopy because of overlapping of the peaks. In each case only ca. 50% of the NH_2 sites were alkanesulfonated. Attempts to obtain a fully alkanesulfonated polymer from 23 by raising the reaction temperature to 40 °C and increasing the amount of 5 used, did not increase the extent of reaction. This may be a consequence of competing side reactions between 5 and methanol.[27,28] All four alkanesulfonated polymers 28–31 were studied by DSC, intrinsic viscosity, and ^{31}P, ^{13}C, and ^{1}H NMR methods. The polymers had characteristic chemical shifts in the ^{1}H NMR spectra of 1,3-propanesultone residues (1.8, 2.65, and 3.3 ppm) and in the ^{13}C NMR spectra (26.5,

Table III. Characterization Data for the Starting Polymers

compd	NMR (ppm) ^{31}P	^{13}C	^{1}H	[η]^a	T_g (°C)	elem anal. found (calc)
$[NP(OCH_2CH_2OCH_2CH_2NH_2)_2]_n$ (**23**)	−8.5	41, 67, 68, 71	3.0, 3.5, 3.7, 4.1	0.53	−18	C: 38.15 (37.90) H: 7.79 (7.90) N: 16.57 (17.31)
$[NP(OCH_2CF_3)_{0.4}(OCH_2CH_2OCH_2CH_2NH_2)_{1.6}]_n$ (**24**)	−9	41, 64, 67, 68, 71, 124	3.0, 3.5, 3.7, 4.1, 4.4	0.48	−19	C: 33.51 (34.02) H: 7.22 (6.70) N: 13.87 (14.23)
$[NP(OCH_2CF_3)_{0.86}(OCH_2CH_2OCH_2CH_2NH_2)_{1.14}]_n$ (**25**)	−9.2	41, 64, 67, 68, 71, 124	3.0, 3.5, 3.7, 4.1, 4.4	0.45	−20	C: 29.45 (30.02) H: 6.12 (5.40) N: 11.00 (11.65)
$[NP(OCH_2CF_3)_{1.76}(OCH_2CH_2OCH_2CH_2NH_2)_{0.24}]_n$ (**26**)	−8.3	41, 64, 67, 68, 71, 124	3.0, 3.5, 3.7, 4.1, 4.4	0.32	−28	C: 21.47 (21.37) H: 2.03 (2.21) N: 6.87 (6.72)
$[NP(OCH_2CF_3)_2]_n$ (**27**)	−8	64, 124	4.4	1 × 10^6 ^{b}	−67	

^{a} Viscosity measurements were done in methanol at 32 °C with an Ubbelohde viscometer. ^{b} Measured by gel permeation chromatography.

Table IV. Characterization Data for the Alkanesulfonated Polymers

compd^a	NMR (ppm) ^{31}P	^{13}C	^{1}H	[η]^b	T_g (°C)
$NPR'_{0.95}(OCH_2CH_2OCH_2CH_2NHCH_2CH_2CH_2SO_3H)_{1.05}]_n$ (**28**)	−7.7	26.5, 41, 58, 67, 68, 71, 72.5	1.8, 2.65, 2.9, 3.3, 3.7, 4.1	0.70	−24
$[NPR'_{0.83}R''_{0.4}(OCH_2CH_2OCH_2CH_2NHCH_2CH_2CH_2SO_3H)_{0.77}]_n$ (**29**)	−8.3	26.5, 41, 58, 64, 67, 68, 71, 72.5, 124	1.8, 2.65, 2.9, 3.3, 3.7, 4.1, 4.4	0.58	−22
$[NPR'_{0.57}R''_{0.86}(OCH_2CH_2OCH_2CH_2NHCH_2CH_2CH_2SO_3H)_{0.57}]_n$ (**30**)	−8.4	26.5, 41, 58, 64, 67, 68, 71, 72.5, 124	1.8, 2.65, 2.9, 3.3, 3.7, 4.1, 4.4	0.54	−21
$[NPR'_{0.1}R''_{1.76}(OCH_2CH_2OCH_2CH_2NHCH_2CH_2CH_2SO_3H)_{0.14}]_n$ (**31**)	−8.6	26.5, 41, 58, 64, 67, 68, 71, 72.5, 124	1.8, 2.65, 2.9, 3.3, 3.7, 4.1, 4.4	0.52	−30

^{a} R′ = $OCH_2CH_2OCH_2CH_2NH_2$, R″ = OCH_2CF_3. ^{b} Viscosity measurements were carried out in methanol at 32 °C with the use of an Ubbelohde viscometer.

Chart II. General Structures for the Starting and Alkanesulfonated Polymers

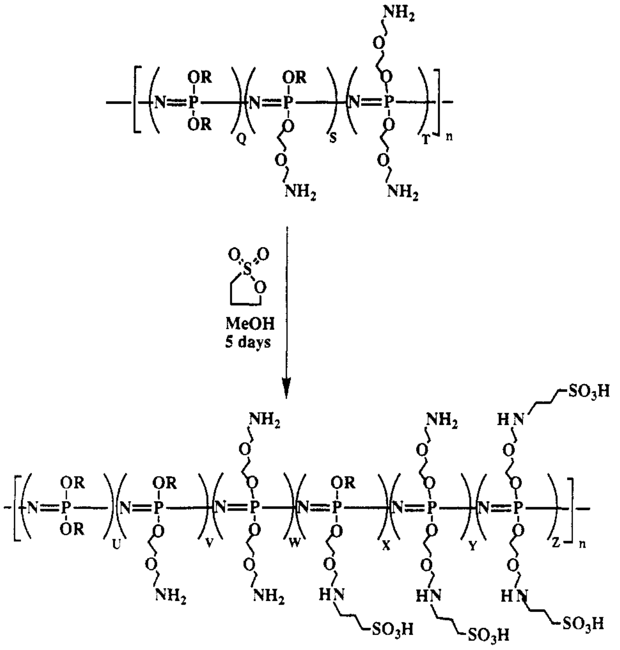
Starting Polymers
$[NP(OCH_2CF_3)_x(OCH_2CH_2OCH_2CH_2NH_2)_y]_n$

compd	x	y
23	0	2
24	0.4	1.6
25	0.86	1.14
26	1.76	0.24
27	2	0

Alkyl Sulfonated Polymers
$[NP(OCH_2CF_3)_x(OCH_2CH_2OCH_2CH_2NH_2)_y(OCH_2CH_2OCH_2CH_2NHCH_2CH_2CH_2SO_3H)_z]_n$

compd	x	y	z
28	0	0.95	1.05
29	0.4	0.83	0.77
30	0.86	0.57	0.57
31	1.76	0.10	0.14

Scheme VII



58, and 72.5 ppm). No polymer decomposition was evident, as indicated by the absence of both general peak broadening and a detectable phosphate peak in the ^{31}P NMR spectra.

(d) Solubility Changes. The solubility characteristics of the alkanesulfonated polymers **28**–**31** were not markedly different from those of the starting polymers. The most notable solubility change occurred following the alkanesulfonation of polymer **26**. Before the reaction, **26** was insoluble in water. However, after the polymer had reacted, it was readily soluble in water. Viscosity measurements of the starting polymers **23**–**26** in anhydrous methanol were carried out. It is interesting to note that the intrinsic viscosities of the polymers decrease with increasing trifluoroethoxy content. This is presumably due to the increased hydrophobic character of regions of the polymers. The same general trend can be seen with the alkanesulfonated polymers **28**–**31**. The most notable changes in polymer properties resulted from the ionomer characteristics of the alkanesulfonated polymers. Viscosity measurements in 1 M KOH/methanol solutions suggested that the alkanesulfonated polymers were ionic. Polymer **23** did not show an increase in reduced specific viscosity, η_{sp}/c, with dilution. However, the reduced specific viscosity of the corresponding alkanesulfonated polymer, **28**, increased with increasing dilution, as illustrated in Figure 1. This polyelectrolyte effect is ascribed to electrostatic repulsions between the sulfonic anion units. The relationship between concentration and viscosity was exponential, as expected for ionomers. However, solutions of the alkanesulfonated polymers in anhydrous methanol showed no increase in viscosity with dilution. This is

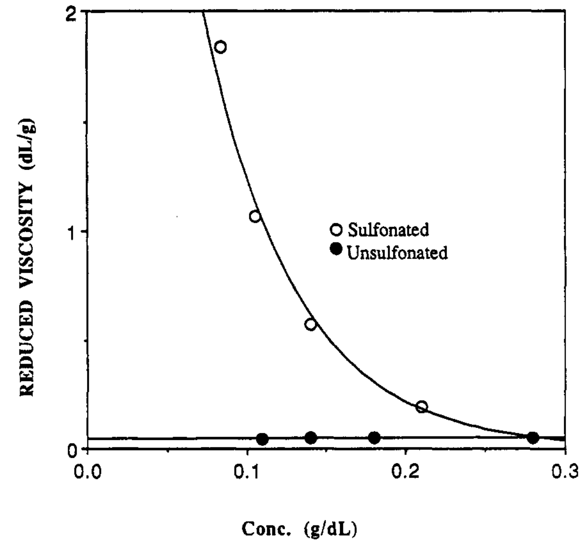


Figure 1. Reduced viscosity vs concentration curves for polymers **23** (●) and **28** (○) in 1 M KOH/methanol solutions. Measurements were made at 28 °C using an Ubbelohde viscometer.

consistent with the view that the sulfonic acid functionalities remained essentially un-ionized in anhydrous methanol.

(e) Glass Transition Temperatures. The glass transition temperatures (T_g) of the product polymers were very similar to those of their non-sulfonated precursors. This is probably a consequence of the separation between the alkanesulfonation sites and the polymer backbone and the relatively low degree of sulfonation, especially in the case of polymers **26** (T_g = −28 °C) and **31** (T_g = −30 °C). The largest decrease in T_g following sulfonation is seen in the comparison of **23** (T_g = −18 °C) with **28** (T_g = −24 °C), and this presumably reflects an increase in free volume associated with the alkanesulfonic acid units.

Conclusions

1,3-Propanesultone is a versatile alkanesulfonating reagent for both cyclic and high polymeric aminophosphazenes. Sulfonation can occur at the ring nitrogen atoms of cyclic trimers that bear electron donating side groups. The reaction of **5** with ring nitrogen atoms produces zwitterionic compounds **13** and **14**. Cyclotriphosphazenes with geminal NH_2 side groups also undergo ring nitrogen atom alkanesulfonation. However, in this case, alkanesulfonation proceeds rapidly to yield multiple sulfonation products, including species with pendent sulfonic acid groups. Aryloxycyclotriphosphazenes that bear only one exocyclic amino group attached directly to a ring phosphorus atom do not undergo ring nitrogen alkanesulfonation with **5**. However, these compounds react with **5** to produce mono- and disulfonated products when the sodium salts of the amino units are employed. The electron withdrawing influence of the phosphazene ring can be reduced by the interposition of a spacer group between the amino group and the ring phosphorus atoms. Cyclic trimers of this type react with **5** under mild conditions to produce only the monoalkanesulfonic acid products.

Alkanesulfonation reactions occur with high polymeric aminophosphazenes that bear amino groups linked directly to the backbone to yield polymers with low loadings of both zwitterion and sulfonic acid groups. Even these low loadings of the new groups dramatically changed the properties of the polymers, increasing the solubility in polar media and rendering the macromolecules susceptible to ionic cross-linking in the presence of divalent cations. Polymers with amino groups separated from the polymer chain by spacer groups react with **5** under milder conditions than do their counterparts with the amino groups linked directly to the backbone. These polymeric sulfonic acids show typical characteristics of ionomers.

Experimental Section

Equipment and Characterization Procedures. ^{31}P, ^{1}H, and ^{13}C NMR spectra were obtained with the use of a Bruker WM360 spectrometer. Chemical shifts are relative to external 85% H_3PO_4 (^{31}P) or tetramethylsilane (^{1}H and ^{13}C). All heteronuclear NMR spectra were proton decoupled. A Kratos MS90/50 spectrometer was used to obtain the +FAB mass spectra. Perkin-Elmer-7 thermal equipment was used to obtain the DSC thermograms. All viscosity measurements were carried out using a Cannon Ubbelhode capillary viscometer. Elemental microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Materials. Hexachlorocyclotriphosphazene (provided by Ethyl Corp.) was purified by vacuum sublimation, recrystallization from heptane, and a final sublimation before use. Poly(dichlorophosphazene) was obtained by the thermal polymerization of hexachlorocyclotriphosphazene at 250 °C in an evacuated sealed tube. Phenol (Aldrich) was purified by vacuum sublimation and was stored in a desiccator before use. 1,3-Propane sultone (Aldrich), 2-(dimethylamino)ethanol (Aldrich), and 2-(2-aminoethoxy)ethanol (Aldrich) were vacuum distilled and stored under argon. 2,2,2-Trifluoroethanol (Halocarbon) was dried and stored over molecular sieves. Sodium metal (Aldrich) was stored and used in a glovebox. *tert*-Butyldicarbamate (Aldrich) was used as received. Triethylamine was distilled from calcium hydride before use. Ammonia (Matheson), monomethylamine (Matheson), dimethylamine (Matheson), and hydrogen chloride gas (Matheson) were used as received. Solvents were dried and distilled under nitrogen by standard methods.

Synthesis of 2-[2-((*tert*-Butoxycarbonyl)amino)ethoxy]-ethanol. To a solution of 2-(2-aminoethoxy)ethanol (48.0 g, 0.456 mol) and triethylamine (48.49 g, 0.479 mol) in dioxane (600 mL) was added a solution of di-*tert*-butyldicarbamate (100 g, 0.458 mol) in dioxane (300 mL) over 3 h at room temperature (25 °C). The reaction was then stirred for 12 h at room temperature. The solvent was removed under reduced pressure, and the residual oil was vacuum distilled at 110 °C at 5 μmHg to yield the desired product in 34% yield.

Synthesis of Hexafluorocyclotriphosphazene.[29-33] Hexachlorocyclotriphosphazene (500 g, 1.44 mol) was dissolved in acetonitrile (1.5 L) in a 3-L round bottom flask equipped with a condenser. Sodium fluoride (600 g, 14.29 mol) was added slowly over 4 h in 100-g portions. The solution was then refluxed for 17 h. The product was distilled from the reaction mixture at 50–80 °C and was further purified by fractional distillation (300 g, 84% yield).

Synthesis of Aminopentafluorocyclotriphosphazene.[34,35] Hexafluorocyclotriphosphazene (25 g, 0.100 mol) was dissolved in THF (300 mL) in a 1-L round bottom flask equipped with a dry ice condenser. Excess ammonia was bubbled through the solution for 1 h. The product was extracted with diethyl ether (3 × 200 mL) and dried over $MgSO_4$. The ether was removed under reduced pressure, and the resulting oil was vacuum distilled to give the pure product in 86% yield.

Synthesis of *gem*-Diaminotetrachlorocyclotriphosphazene.[36-38] Hexachlorocyclotriphosphazene (130 g, 0.388 mol) was dissolved in diethyl ether (250 mL) in a round bottom flask equipped with a dry ice condenser. Excess ammonia was bubbled through the solution for 2 h. The ethereal solution was washed with deionized water (3 × 500 mL) and dried over $MgSO_4$. The ether was removed under reduced pressure to give the product in 55% yield.

Synthesis of Pentaphenoxychlorocyclotriphosphazene.[39-41] Sodium hydride (20 g of 60% dispersion, 0.5 mol) and hexachlorocyclotriphosphazene (29.99 g, 0.0863 mol) were dissolved in THF (600 mL) in a 1-L round bottomed flask. Phenol (42.98 g, 0.457 mol) was dissolved in THF (250 mL) and added dropwise into the flask containing the sodium hydride and hexachlorocyclotriphosphazene at 0 °C. The resulting solution was stirred at room temperature for 18 h. The solution was quenched with

5% HCl (600 mL) and the product extracted with methylene chloride (500 mL). The organic layer was washed with deionized water (3 × 250 mL), filtered through Fuller's earth, and dried with $MgSO_4$. The solvent was removed under reduced pressure to give a viscous oil which was further purified on a silica column (30% ethyl acetate/70% hexanes eluent). The white crystalline solid was obtained in a 40% yield.

Synthesis of Hexamethylcyclotriphosphazene (6). This compound was prepared following procedures described earlier.[42-50] The synthesis was carried out on a 5-g scale and resulted in a 57% overall yield.

Synthesis of Hexakis(trifluoroethoxy)cyclotriphosphazene (7). Compound 3 was prepared as reported previously.[51-53] The reaction was carried out on a 5-g scale and resulted in a 65% yield of the product.

Synthesis of Hexaphenoxycyclotriphosphazene (8). The synthesis of 4 was carried out as previously described.[54-61] The reaction was carried out on a 5-g scale, resulting in a 70% overall yield.

Synthesis of *gem*-Diaminotetraphenoxycyclotriphosphazene (9). Sodium metal (3.10 g, 129 mmol) was placed in a round bottom flask with dioxane (150 mL). Phenol (12.7 g, 135 mmol) in dioxane (100 mL) was added dropwise to the sodium metal in dioxane, and the mixture was stirred at room temperature for 12 h. *gem*-Diaminotetrachlorocyclotriphosphazene (5.24 g, 16.9 mmol) in dioxane (100 mL) was added dropwise, and the solution was heated to reflux for 14 h. The product was then extracted with methylene chloride (3 × 200 mL) and washed with deionized water (2 × 150 mL). The organic layer was removed under reduced pressure after drying with $MgSO_4$ and the white solid was recrystallized from methylene chloride and hexanes to give **9** in 50% yield.

Synthesis of Pentaphenoxyaminocyclotriphosphazene (10). This compound was synthesized in a similar manner to compound **9** except that pentafluoroaminocyclotriphosphazene was used in place of *gem*-diaminotetrachlorocyclotriphosphazene. The reaction was carried out on a 4-g scale, resulting in a 60% yield.

Synthesis of Pentaphenoxy [[[(*tert*-butoxycarbonyl)amino]ethoxy]ethoxy]cyclotriphosphazene.[62] Pentaphenoxychlorocyclotriphosphazene (3.6 g, 16 mmol) was dissolved in THF (100 mL), and the solution was added dropwise to a solution of NaH (1.8 g of 60% dispersion) in 100 mL of THF. The mixture was stirred at room temperature for 6 h and was added dropwise to a solution of **10** (10.0 g, 15.9 mmol) in THF (200 mL). The solution was heated to reflux for 4 h and was quenched with 300 mL of water. The product was extracted with methylene chloride (3 × 200 mL). The organic layer was then dried with $MgSO_4$ and the methylene chloride was evaporated under reduced pressure. The resultant oil was purified by column chromatography on silica gel (30% ethyl acetate/70% hexanes as the eluent). The yellow oil was obtained in 50% overall yield.

Synthesis of Pentaphenoxy[(aminoethoxy)ethoxy]cyclotriphosphazene (11). The Boc protected pentaphenoxy[(aminoethoxy)ethoxy] trimer $N_3P_3(OC_6H_5)_5(OCH_2CH_2OCH_2CH_2NHBoc)$ was dissolved in 80% trifluoroacetic acid and stirred at room temperature for 24 h. The solution was then made alkaline (pH 9) with a 1 M NaOH solution while being cooled in an ice bath. The product was extracted with chloroform (3 × 200 mL) and was washed twice with 200 mL of water. The organic layer was then dried with $MgSO_4$ and the solvent was removed under reduced pressure. The product was obtained as an oil, 70% yield.

Synthesis of Pentaphenoxy[(dimethylamino)ethoxy]cyclotriphosphazene (12). 2-Aminoethanol (1.69 g, 18.9 mmol) in THF (100 mL) was added to Na (0.4 g, 17.4 mmol) in THF (50 mL). The solution was warmed to 40 °C for 24 h. **10** (6.00 g, 9.54 mmol) in 200 mL of THF was then added to the sodium alkoxide solution. This solution was heated to reflux for 12 h. The reaction was quenched with 300 mL of water, and the product was extracted with diethyl ether (3 × 200 mL). The ethereal layer was dried with $MgSO_4$ and was filtered through a silica plug. The pure product was obtained as a white solid in 40% yield after the evaporation of the ether.

Synthesis of $[NP(OCH_2CF_3)_2]_n$ (27). Trifluoroethanol (11.00 g, 0.110 mol) was dissolved in 200 mL of THF and was added dropwise into a 1000-mL round bottom flask containing sodium metal (2.32 g, 0.1009 mol) immersed in 250 mL of THF. The solution was stirred for 12 h. Poly(dichlorophosphazene) (2.00 g, 0.0174 mol) was dissolved in 200 mL of THF in a Schlenk flask. The polymer solution was canulated into an addition funnel and was added dropwise to the alkoxide solution. The resulting solution was heated to reflux for 15 h. After cooling to room temperature, the solution was concentrated and reprecipitated into water twice and into hexanes twice. The polymer was obtained in a 40% yield.

Synthesis of $[NP(OCH_2CH_2OCH_2CH_2NHBoc)_2]_n$. A mixture of the Boc protected (aminoethoxy)ethanol (5.90 g, 26.08 mmol) and NaH (1.04 g of 60% dispersion, 26.09 mmol) in THF (250 mL) was stirred for 4 h at room temperature to give a pale yellow solution. This was added to a solution of poly(dichlorophosphazene) (1.00 g, 8.7 mmol), and the solution was stirred at room temperature for 12 h. The polymer was purified by dialysis against methanol (5 days), 90% yield.

Synthesis of $[NP(OCH_2CH_2OCH_2CH_2NH_2)_2]_n$ (23). The Boc protected polymer $[NP(OCH_2CH_2OCH_2CH_2NHBoc)_2]_n$ was dissolved in 80% trifluoroacetic acid and was stirred at room temperature for 24 h. The solution was then made alkaline (pH 9) with 1 M NaOH solution and was dialyzed against methanol for 5 days. Yield: 80%.

Synthesis of $[NP(NMe_2)(NHMe)]_n$ (21). To a solution of poly(dichlorophosphazene) (1.00 g, 8.7 mmol) in THF (150 mL) was added by condensation (dry ice condenser) 8.7 mmol of dimethylamine. This solution was stirred at room temperature for 12 h. Excess monomethylamine was then condensed into the solution, and the mixture was stirred for an additional 12 h. The resultant polymer was purified by reprecipitations into water (×3) and hexanes (×3) to give the pure polymer in 70% yield.

Typical Synthesis of $[NP(OCH_2CF_3)_x(OCH_2CH_2OCH_2CH_2NHBoc)_y]_n$. The sodium salt of trifluoroethanol was prepared from trifluoroethanol and NaH in THF. This suspension was added dropwise to a solution of poly(dichlorophosphazene) in THF. After the solution had been stirred for 24 h at room temperature, the sodium alkoxide of the Boc protected (aminoethoxy)ethanol in THF (prepared in a way similar to that of the sodium trifluoroethoxide) was added to the polymer solution. The mixture was stirred for 12 h, concentrated on a rotary evaporator, and dialyzed against methanol for 5 days.

Typical Synthesis of $[NP(OCH_2CF_3)_x(OCH_2CH_2OCH_2CH_2NH_2)_y]$ (24, 25, 26). The corresponding Boc protected polymers were dissolved in 80% trifluoroacetic acid and were stirred for 24 h. The solutions were made alkaline (pH 9) with 1 M NaOH solution at 0 °C. The polymers were then dialyzed against methanol for 5 days.

Typical Synthesis of Ring Sulfonated Phosphazene Trimers. The trimers were dissolved in 1,3-propanesultone (**5**) at 60 °C. The temperature was then raised to 100 °C, and the reactions were monitored by ^{31}P NMR spectroscopy.

Synthesis of Sulfonated *gem*-Diaminotetraphenoxycyclotriphosphazene. Compound **9** was dissolved in THF, and **5** was added via syringe. The solution was then heated to reflux and monitored by ^{31}P NMR spectroscopy.

Synthesis of $N_3P_3(OR)_5NHCH_2CH_2CH_2SO_3^{-+}Na$ via the Sodium Amide. The aminocyclotriphosphazenes were dissolved in dry THF in a Schlenk flask under argon. Sodium metal was then placed in the flask, and the mixture was stirred at room temperature (25 °C) for 12 h. The resulting sodium amide was then canulated into another Schlenk flask containing 1,3-propane sultone in dry THF. The solution was then refluxed for 2 days to yield both the mono- and dialkanesulfonated products.

Alkanesulfonation of 11. Compound **11** (2.00 g, 2.84 mmol) was dissolved in 50 mL of THF, and **5** (0.50 g, 4.10 mmol) was added as a THF solution (20 mL). The solution was stirred at room temperature (25 °C) for 5 days. The solution was poured into 70 mL of water and was extracted with chloroform (3 × 50 mL). The chloroform was removed under reduced pressure to give **19** in 60% yield. Characterization: ^1H NMR δ 1.8 (m, 2H), 2.6 (t, 2H), 3.0 (t, 2H), 3.4 (t, 2H), 3.7 (m, 4 H), 4.1 (t, 2H), 7.3 (m, 25H); ^{13}C NMR δ 26.5, 40.8, 58.0, 67.0, 67.9, 71.2, 72.5, 121.0, 125.0, 129.8, 150.0.

Alkanesulfonation of 12. Compound **8** (0.24 g, 0.0351 mol) was dissolved in THF (10 mL), and **5** (0.08 g, 0.0656 mol) in THF (5 mL) was added via syringe. The resulting solution was stirred at room temperature for 16 h. The solution was poured into 50 mL of water, and the product was extracted with diethyl ether (3 × 20 mL). The ethereal layer was filtered through a 2-cm silica plug and was dried over $MgSO_4$. Evaporation of the ether left yellow oil **20** in 50% yield. Characterization: ^1H NMR δ 2.2 (m, 2 H), 2.7 (t, 2H), 3.1 (t, 2H), 3.2 (t, 2H), 3.6 (s, 6H), 4.6 (t, 2H), 7.3 (m, 25H); ^{13}C NMR δ 26.0, 49.8, 52.2, 58.0, 69.1, 121.0, 125.0, 130.1, 150.0.

Synthesis of $[NP(NMe_2)_{0.85}(NHMe)_{0.85}(NMe_2{}^+CH_2CH_2CH_2SO_3{}^-)_{0.27}(NMeCH_2CH_2CH_2SO_3H)_{0.03}]_n$. $[NP(NMe_2)(NHMe)]_n$ (1 g) was dissolved in dry THF in a Schlenk flask, and 2 equiv of 1,3-propanesultone were added via syringe. The reaction was carried out under argon. The solution was then stirred in refluxing THF for 48 h, at which time the polymer precipitated from the solution. The alkanesulfonated polymer was then purified by dialysis against deionized water (3 days) and methanol (3 days). The product polymer was obtained in 95% yield.

Typical Synthesis of $[NP(OCH_2CF_3)_x(OCH_2CH_2OCH_2CH_2NH_2)_y(OCH_2CH_2OCH_2CH_2NHCH_2CH_2CH_2SO_3H)_z]_n$. Compound **5** (0.90 g, 7.4 mmol) was added to 6.15 mmol of the precursor polymer in 10 mL of ethanol. The solution was stirred at room temperature for 5 days and was then dialyzed against water for 3 days and methanol for 5 days. The solvent was then removed under reduced pressure to give a white polymeric product. The sulfonated polymer was obtained in quantitative yield.

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