compounds $[NP(OTFE)_2]$ and $[NP(OPr)_2]$ contain only a single oxygen atom in each side chain which is sterically restricted and reduced in basicity by bonding to phosphorus.

The conductivities of $MEEP_xI$ and $[NP(OPr)_2]_xI$ were examined well above the T_g and show a temperature dependence that is close to Arrhenius-type $\exp(1/T)$ response (Figure 2). The bulk conductivity data do not show a VTF-type correlation[24] with T_g, as both T_g and conductivities increase with increasing iodine content. For these reasons, effects other than local polymer dynamics (for example, carrier number or type) may dominate the conduction process. It is also interesting to note that despite an increase in T_g, the $MEEP_xI$ and $[NP(OPr)_2]_xI$ complexes become markedly less viscous with increased iodine loading; similar observations were made for $MEEP_xMI_n$ complexes.[3]

Bulk conductivities as a function of iodine content are given in Figure 3. $MEEP_xI$ and $[NP(OPr)_2]_xI$ show similar behavior, which involves a marked increase in conductivity even at low iodine loadings ($x = 16$) and a more gradual increase with higher iodine loading. The $[NPCl_2]_xI$ complexes show no enhancement in conductivity compared with the pristine polymer (approximately 10^{-8} S cm^{-1}). $[NP(OTFE)_2]_xI$ complexes show only a very slight increase in conductivity over that of the parent polymer. $[NPCl_2]_xI$ complexes do not contain polyiodides, and $[NP(OTFE)_2]_xI$ complexes are crystalline at ambient temperature. Therefore, neither exhibits high conductivity. Further illustrations of this behavior can be found in both PPO_xMI_n and $MEEP_xMI_n$ complexes, in which the amorphous complexes which contain I_n^- are highly conducting.

The mode of conduction within polymer–polyiodide complexes has been addressed previously.[3,4] Impedance measurements for all the polymer–polyiodide complexes studied in these laboratories consistently show that both interfacial and bulk conduction processes are present. In summary, the present research on the interaction of I_2 with a diverse set of polymers indicates that the conduction process involves the polyiodides rather than the polymer backbone, and that polyether side chains are conducive to polyiodide formation.

Acknowledgment. The research at Northwestern University was supported by DOE by Grant DE-FG02-85ER45220, and the facilities were provided by the Northwestern Materials Research Center sponsored by National Science Foundation Grant No. DMR 881571. The research at The Pennsylvania State University was supported by the Office of Naval Research. M.M.L. acknowledges support by the National Science Foundation under Grant CHE-8807987 awarded in 1988.

Registry No. I_2, 7553-56-2.

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Sulfonation of (Aryloxy)- and (Arylamino)phosphazenes: Small-Molecule Compounds, Polymers, and Surfaces

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Sulfonation reactions have been developed that convert aryloxy or arylamino groups linked to phosphazenes to the arylsulfonic acid derivatives. The reactions were developed at three levels—first, with small-molecule phosphazene cyclic trimers; second, with phosphazene high polymers in the solution state; third, at the surfaces of solid polyphosphazenes. The reagents employed included concentrated H_2SO_4, fuming H_2SO_4, and $ClSO_3H$. Molecular level products were studied by ^{31}P, ^{13}C, and ^1H NMR spectroscopy, while the surface-reacted materials were examined by XPS, SEM, ATR-IR, contact angle, and optical microscopy. This chemistry is of broad utility for the preparation of hydrophilic and hydrogel surfaces on polymers and for the development of biocompatible or antibacterial materials.

For the past 50 years polymer chemists have been involved in the design and synthesis of polymers that yield specific bulk properties such as elasticity, strength, or rigidity. However, in recent years it has become evident that the *surface* properties of solid polymers are equally important.[1-4] This is especially true when the polymers are to be used in biomedical devices, surface coatings, or composite materials. Adhesion is another property that depends critically on surface structure.

Occasionally the molecular structure of a polymer will yield an appropriate combination of bulk and surface properties, but more often the control of macromolecular

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[1] Wu, S. *Polymer Interfaces and Adhesion*; Marcel Dekker: New York, 1982.

[2] Andrade, J. D., Ed. *Surface and Interfacial Aspects of Biomedical Polymers*; Plenum: New York, 1985; Vols. 1 and 2.

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[4] Hastings, G. W., Ducheyne, P. Eds. *Macromolecular Biomaterials*; CRC Press: Boca Raton, FL, 1984.

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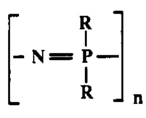
structure to generate specific bulk characteristics is at the expense of surface properties and vice versa. For this reason, the most promising approach to generating a balance of properties is to choose a polymer for its bulk characteristics and then carry out surface chemistry to generate the required surface character. This is the principle that underlies the work described in this paper.

One of the most useful properties that can be generated at the surface of a polymer is hydrophilicity. Among the various functional groups that give rise to this property, the sulfonic acid unit, $-SO_3H$, has many attributes. Sulfonated polymers are widely used in ion-exchange resins, reverse osmosis membranes, and non-thrombogenic biomedical materials.[5-8] The development of methods to incorporate sulfonic acid units into a particular class of polymers is the main objective of this present work.

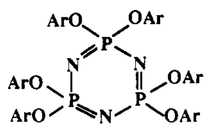
The polymers used in this investigation are polyphosphazenes (1).[9-11] These macromolecules are of synthetic and technological interest because of the way in which the side groups can be varied over an exceedingly wide range of structures, and this provides access to species with an almost unprecedented variety of tailored properties. They are also particularly suitable for side-group and surface modification chemistry because of the stability of the phosphorus–nitrogen backbone. The surface chemistry of specific polyphosphazenes has already been studied with respect to nitration and reduction,[12] hydrolysis of side units,[13] organic side-group exchange,[14] and formation of quaternary ammonium salts.[15] Here we extend these surface reactions to include sulfonation processes.



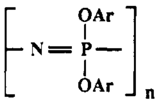
$$\left[-N=\overset{R}{\underset{R}{P}}-\right]_n$$

1

Because of the complexity of most surface chemistry, an attempt has been made to understand the processes involved at three levels. First, the target sulfonation reactions were developed initially with small-molecule cyclic trimeric phosphazenes of the type shown in structure 2 to allow careful molecular characterization using the normal range of small-molecule analysis techniques.[16]

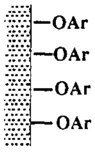


2



$$\left[-N=\overset{OAr}{\underset{OAr}{P}}-\right]_n$$

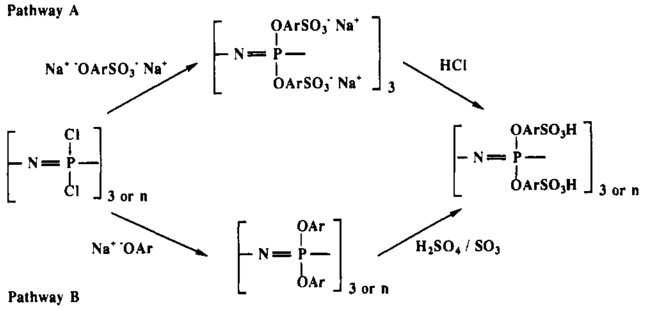
3



4

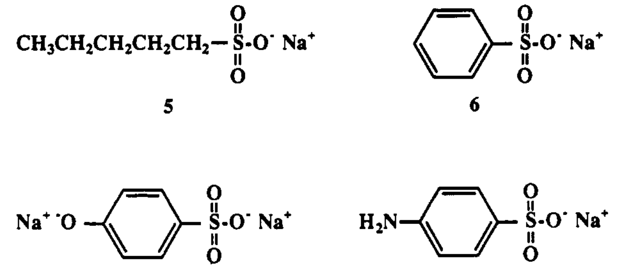
Second, the same reactions were carried out with the corresponding linear high polymers (3). Standard polymer solution and materials' characterization methods were applied to the product polymers in order to determine the molecular structures and materials' characteristics.[17] Both the small-molecule and polymer reactions can be considered as solution processes, since the starting materials were soluble in strong acids.

Scheme I



n = 5,000 to 15,000 or (for pathway B) units at the surface of polymer films

Chart I



5 6 7 8

Finally, the same reactions were applied to the surfaces of films (4) prepared from polymers 3. The modified surfaces were examined by a variety of surface analysis techniques.

Several questions formed the starting point for this research: Can aryloxy, arylamino, or phenyl side groups attached to a phosphazene ring, chain, or surface be sulfonated without degradative attack on the polymer backbone by the aggressive reagents required for these reactions? Which of the several available sulfonation processes is the most appropriate for this system? What degree of sulfonation can be achieved before side reactions (for example, skeletal or side-group cleavage) becomes serious? What physical, chemical, and biological changes to the polymers or their surfaces result from the introduction of sulfonic acid groups?

Results and Discussion

Alternative Synthesis Pathways. Two general approaches are available for the synthesis of polyphosphazenes with sulfonated aryloxy side groups, and these are shown in Scheme I. The first approach, and perhaps the simplest in theory, is shown in pathway A in which an aryl oxide, alkoxide, or arylamine that already bears a terminal sulfonic acid or sulfonate group (compounds 7 and 8, Chart I) is allowed to replace the chlorine atoms in poly(dichlorophosphazene). In essence, this approach attempts to achieve surface hydrophilicity via side groups that also exist within the bulk material. The second approach (Scheme I, pathway B) first involves the synthesis of phosphazenes with unsubstituted aryloxy (or arylamino) side groups, followed by sulfonation of those

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(14) Allcock, H. R.; Fitzpatrick, R. J. *Chem. Mater.*, in press.

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side groups. This approach is the main focus of this paper. However, pathway A was examined first for comparison purposes, and the following comments refer to this alternative.

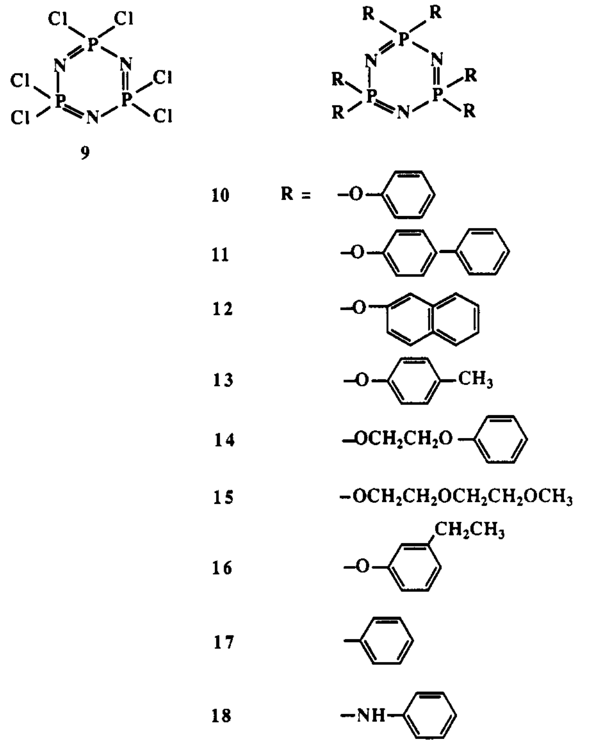
The use of a difunctional nucleophile such as **7** or **8** in pathway A raises the possibility that linkage to the phosphazene could take place through the aryloxide, alkoxide, or amino unit, through the sulfonic group, or through both. The last possibility would lead to cross-linking. A report in the literature[18] indicates that the interaction of poly(dichlorophosphazene) with $NaOCH_2CH_2SO_3Na$ leads to cross-linking of the chains. The cross-links could be broken by subsequent displacement of one linkage site by a different nucleophile.

Our small-molecule studies using cyclic trimer **9** and reagents **5–8** were designed to determine the ease of halogen replacement in **9** by sodium sulfonate groups (reagents **5** and **6**), the relative reactivity of sodium sulfonate units versus hydroxyl or amino functional sites (reagents **7** and **8**), and the likelihood of cross-linking (reagents **7** and **8**). Overall, the reactions were limited by the low solubility in etheric solvents of reagents **5–8** and the partly substituted cyclic trimers. For example, reagents **5** and **6** did not react with **9** in boiling THF (67 °C), while reactions in diglyme at 100 °C brought about replacement of only one chlorine atom per phosphazene ring. Reagent **7**, as its sodium aryloxide salt in THF, dioxane, or diglyme, replaced only one or two chlorine atoms per ring before the products precipitated from solution, probably as cross-linked species. The reaction of **9** with reagent **8** in the presence of triethylamine as a hydrohalide receptor again led to the precipitation of mono- and disubstituted products. Thus, the results from the small-molecule studies suggested that series difficulties would be encountered if these reactions were attempted at the high polymer level. Consequently, all the following discussion applies to pathway B only.

Small-Molecule Model Compound Sulfonation Reactions. The following discussion deals with the reaction conditions needed to bring about the sulfonation of phosphazene cyclic trimers **10–18** (Chart II), the pattern by which sulfonic acid groups are introduced around the aryl rings, and the changes in properties of the trimers that result from the presence of the sulfonic acid units.

Four sulfonating agents were examined. These are concentrated sulfuric acid, fuming sulfuric acid, sulfur trioxide, and chlorosulfonic acid. Of these, concentrated and fuming H_2SO_4 proved to be the most useful. Chlorosulfonic acid required the use of solvents such as chloroform or 1,1,2,2-tetrachloroethane and generated side reactions which (at the high polymer level) led to cross-linked, insoluble products. Sulfur trioxide proved to be a difficult reagent to use at both the small-molecule and macromolecular levels, since appropriate media for these reactions were nonsolvents for the phosphazenes, and heterogeneous reaction conditions pertained. Although concentrated and fuming H_2SO_4 could be used in the presence of solvents such as chlorinated organic media, the use of such solvents proved to be unnecessary. The phosphazene cyclic trimers (or the high polymers) were soluble in concentrated or fuming H_2SO_4, and these solutions provided satisfactory reaction conditions for the sulfonations. Use of concentrated H_2SO_4 as a solvent and reagent provided an additional advantage since reaction temperatures above 100 °C could be employed, and this assisted in the removal of water formed as a side product.

Chart II



The small-molecule model reactions with concentrated H_2SO_4 as a reagent were used first to identify those side groups that are most effective in protecting the molecule against phosphazene ring or side-group cleavage. It was found that species such as **15**, which lacked aromatic rings in the side-group structure, were decomposed (to phosphate) even under mild reaction conditions. Species **14**, with a phenyl ring separated from the phosphazene ring by an alkyleneoxy spacer group, underwent phenyl ring sulfonation without phosphazene ring cleavage at temperatures below 100 °C but was decomposed at 150 °C. The phosphazene cyclic trimers that could be sulfonated without significant inorganic ring cleavage were those with aryl rings linked to phosphorus through oxygen or nitrogen or through carbon–phosphorus bonds. Thus, trimers **10–13** and **16–18** were the main models used in this work. The reaction conditions employed are summarized in Table I.

The progress of each sulfonation reaction was followed by ^{13}C NMR analysis of the products. The extent of sulfonation under different reaction conditions is shown in Table I. In general the number of sulfonic acid groups introduced per molecule increased with increases in reaction time and temperature. The rate of sulfonation was higher when fuming H_2SO_4 was used in place of concentrated H_2SO_4, and the aryloxy rings were sulfonated faster than phenyl rings linked directly to phosphorus. Compounds **10**, **11**, **16**, and **18** underwent sulfonation at the 4-position of the aryl rings, with only one sulfonic acid group being introduced per aryl ring. However, when the 4-position was blocked, as in compound **13**, sulfonation took place at the 3-position. When a phenyl ring was bonded directly to phosphorus, as in **17**, substitution was at the 3-position, and this may reflect an electron-withdrawing effect by the phosphazene ring. The trimers with 2-naphthoxy side groups underwent sulfonation at several different sites on each naphthyl unit, with a corresponding increase in complexity of the ^{13}C NMR spectra. However, sulfonation at the 6-position predominated.

Sulfonation of the aryl groups changed the solubility properties of the cyclic trimers. Compounds **10–14** and

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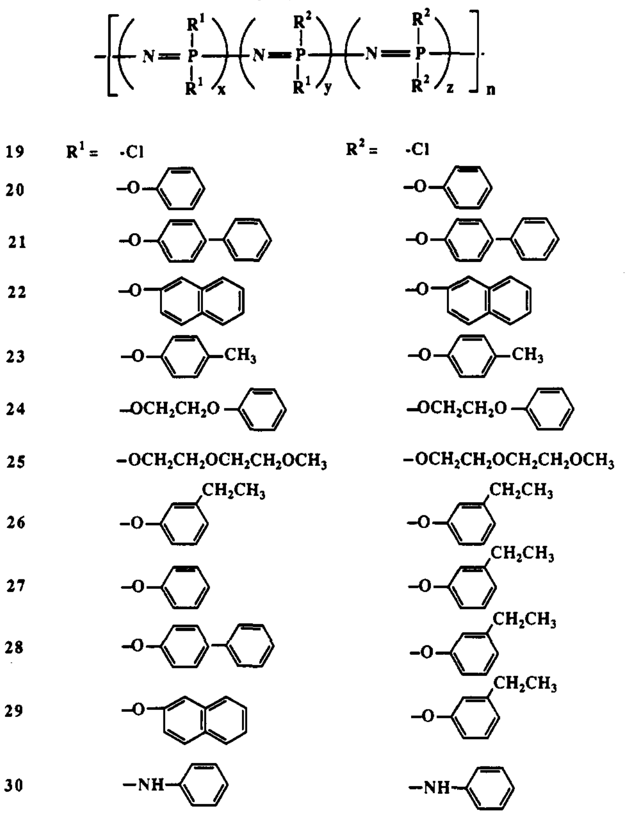
(18) Ganapathiappan, S.; Chen, K.; Shriver, D. F. *Macromolecules* 1988, *21*, 2301.

Chart III



16–18 are insoluble in water. Sulfonation dramatically increased the solubility in water when either the free acid form or the sodium salt was present.

Sulfonation of High Polymers 20–30. Chart III lists the high polymers used in this work. As with the cyclic trimers, the polymers were soluble in concentrated or fuming H_2SO_4, and these were the media used for these studies. In general, the reactivities and substitution patterns resembled those found for the cyclic trimers. These are summarized in Table II. However, the rate and degree of sulfonation decreased by roughly one-half when a cyclic trimer was replaced by its high polymeric counterpart. This was attributed partly to the lower solubility of the polymers in concentrated and fuming H_2SO_4. Thus, more forcing conditions were required to generate the same degree of substitution in the high polymers as in the cyclic trimers. Polymer **23** underwent sulfonation at a slower rate than **20**, presumably because the 4-position is blocked. The reaction of **21** was also slower than that of **20**, but this can be attributed partly to the slower dissolution of **21** in concentrated H_2SO_4 at 60 °C.

As in the case of the cyclic trimers, the progress of each sulfonation reaction was followed by ^{31}C NMR analysis of the products. Figure 1 illustrates the ^{13}C NMR spectrum of polymer **20** before and after sulfonation. The introduction of sulfonic acid groups results in a shift in the positions of all carbon atoms except "b", with the sulfonated products showing broadened and upfield shifted peaks. Similar spectral changes were found for **21–24**. The ^{13}C NMR spectra were used to estimate both the degree of substitution and the pattern of sulfonation.

The data in Table II and Figure 2 illustrate that, as with the cyclic trimers, the extent of polymer sulfonation increases as the temperature is raised and the reaction time extended. For example, the number of aryl units sulfonated in **20** increased from 28% to 59% when the reaction time was increased from 0.25 to 2 h in concentrated H_2SO_4 at 100 °C and from 59% to 100% when the temperature

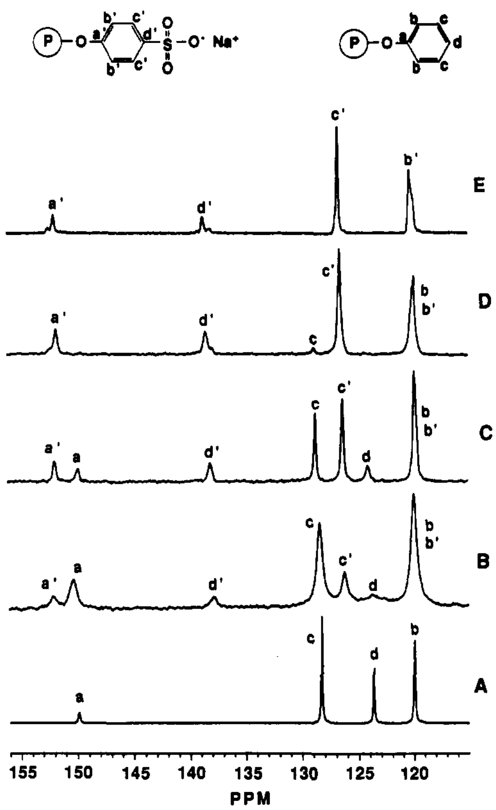


Figure 1. ^{13}C NMR spectra of polymer **20** sulfonated in concentrated H_2SO_4. (A), Unsulfonated control; (B) sulfonation at 100 °C for 15 min.; (C), 100 °C for 90 min.; (D), 100 °C for 240 min.; (E), 150 °C for 120 min.

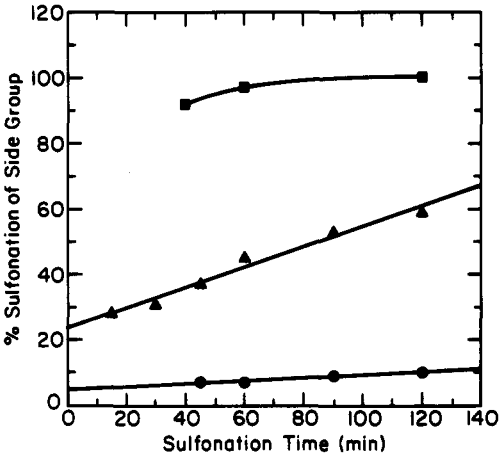


Figure 2. Percentage of side groups in polymer **20** sulfonated in concentrated H_2SO_4 as a function of time (min) at 150 °C (■), 100 °C (▲), and 60 °C (●).

was increased from 100 to 150 °C during 2 h of reaction. Again, only one sulfonic acid unit was introduced per aryl ring, except in the case of polymers **22** and **29** where the naphthyl units underwent multiple sulfonation. As in the cyclic trimers, polymers **24** and **25** proved to be less stable under these reaction conditions than those species that lacked aliphatic spacer groups. The site of sulfonation, again deduced from ^{13}C NMR spectra, was at the 4-position of the aryl groups in polymers **20**, **21**, **24**, **26**, and **30**, the 3-position in polymer **23**, and mainly at the 6-position in polymer **22**. The 4-position substitution in **20** is in contrast to a literature report[19,20] that this polymer un-

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Table I. Reaction Conditions for Sulfonation of Cyclic Trimers

trimer	sulfonation conditions in H_2SO_4[a] acid	temp, °C	time, min	side groups sulfonated,[b] %	site of sulfonation[c]	water solubility after sulfonation	notes
10	fum	25	120	100	4–	+	*d, j, l*
	conc	150	120	100	4–	+	*d, j, l*
	conc	100	15	34	4–	+	*d, j, l*
	conc	100	30	44	4–	+	*d, j, l*
	conc	100	45	54	4–	+	*d, j, l*
	conc	100	60	63	4–	+	*d, j, l*
	conc	100	90	80	4–	+	*d, j, l*
	conc	100	120	91	4–	+	*d, j, l*
	conc	60	15	11	4–	–	*d, j, k*
	conc	60	120	24	4–	–	*d, j, l*
	conc	25	120	5	4–	–	*d, j, k*
	conc	25	21	12	4–	–	*d, j, k*
11	fum	25	120	100	4′–	+	*d, g, l*
	conc	150	120	100	4′–	+	*d, g, l*
	conc	100	15	100	4′–	+	*d, g, l*
	conc	100	30	100	4′–	+	*d, g, l*
	conc	100	45	100	4′–	+	*d, g, l*
	conc	100	60	100	4′–	+	*d, g, l*
	conc	100	90	100	4′–	+	*d, g, l*
	conc	100	20	100	4′–	+	*d, g, l*
	conc	40	120	insol in H_2SO_4		–	*f*
	conc	25	120	insol in H_2SO_4		–	*f*
12	fum	25	120		multiple sulfonation sites	+	*d, h, l*
	conc	150	120		multiple sulfonation sites	+	*d, h, l*
	conc	100	120		multiple sulfonation sites	+	*d, h, l*
	conc	25	120	insol in H_2SO_4		–	*f*
13	fum	25	120	75	3–	+	*d, i, l*
	conc	150	120	58	3–	+	*d, i, l*
	conc	100	120	12	3–	–	*d, i, k*
	conc	25	120	~0	–	–	*d, j, k*
16	fum	25	120	90	4–	+	*d, i, l*
	conc	150	120	75	4–	+	*d, i, l*
	conc	100	120	32	4–	–	*i*
	conc	25	120	5	4–	–	*i, k*
17	conc	100	60	11	3–	–	*d, j, k*
18	conc	100	120	90	4–	+	*d, j, l*

[a] 1.4×10^{-3} mol of trimer per 20 mL of (fum) fuming H_2SO_4 or (conc) concentrated H_2SO_4. [b] Determined by peak ratios from ^{13}C NMR spectra. [c] Determined from ^{13}C and ^1H NMR spectra. [d] Homogeneous reaction mixture. [e] Trimer did not completely dissolve. [f] Little or no trimer dissolved. [g] Scarlet reaction mixture. [h] Yellow reaction mixture. [i] Brown reaction mixture. [j] Colorless reaction mixture. [k] Insoluble material or solid trimer was evident after neutralization. [l] Neutralized reaction mixture was homogeneous.

dergoes 3-position substitution by SO_3 in 1,2-dichloroethane.

The molecular weight of a soluble polymer after reaction provides a sensitive measure of skeletal cleavage processes. As shown in Table II, the molecular weights of the sulfonated polymers were still high ($M_w = 3 \times 10^4$–5×10^5). However, these values reflect some skeletal cleavage during sulfonation since the starting polymers **19–30** had M_w values of 2×10^6 or higher. The chain cleavage reaction was enhanced at higher temperatures (150 rather than 100 °C) and by the use of fuming H_2SO_4 rather than the concentrated acid. The most significant molecular weight decreases occurred during the first 10 min of sulfonation. Some evidence was obtained that chain cleavage was retarded by the presence of the bulkiest aryloxy side groups.

The most obvious change in polymer properties following sulfonation was a markedly enhanced affinity toward water. In general, those polymers with less than 30% of the side groups sulfonated formed hydrogels or emulsions in water. Those with more than 30% sulfonation were readily soluble in water. Sulfonated **21** and **22** formed hydrogels or viscous solutions in water. In solution, the sulfonated polymers behaved as polyelectrolytes. In addition, aqueous solutions of the sulfonated polymers precipitated in the presence of divalent cations, such as Mg^{2+}, as dicoordination brought about ionic cross-linking of the chains.[21,22] These results provided strong encouragement for the view that surface sulfonation of solids derived from **20–30** should generate hydrophilic surface properties.

Surface Sulfonation Reactions. The initial experimental approach for the surface chemistry involved the solvent casting of films of the poly(organophosphazenes) such as **20–31**, followed by exposure of the film surfaces to the various sulfonation agents. However, the solubility of polymers **20–30** in concentrated and fuming H_2SO_4 severely complicated these experiments. Even short exposure times to the acids or the use of chlorosulfonic acid in 1,2-dichloroethane resulted in severe distortion of the films, accompanied by swelling and reaction of the total material.

For this reason, films for surface reaction experiments were prepared via a different technique. Specifically, polymers were designed and synthesized that could be γ-radiation cross-linked to prevent their dissolution in the reagents and to stabilize the surface structure. Ethylphenoxy groups are particularly appropriate for γ-radiation cross-linking because of the high tendency of aliphatic C–H bonds to undergo free-radical cleavage under irradiation conditions.[23,24] Thus, mixed substituent polyphosphazenes

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(22) Cohen, S.; Bano, M. C.; Visscher, K. B.; Chow, M.; Allcock, H. R.; Langer, R. *J. Am. Chem. Soc.* **1990**, *112*, 7832.

(23) Allcock, H. R.; Gebura, M.; Kwon, S.; Neenan, T. X. *Biomaterials* **1988**, *9*, 498.

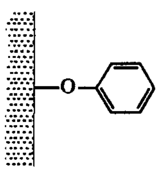
Table II. Reaction Conditions for Polymer Sulfonations

	sulfonation conditions in H_2SO_4[a]						
polymer	acid	temp, °C	time, min	percentage of side groups sulfonated[b,c]	site of sulfonation	10^{-4}mol wt/polydispersity	notes
20	conc	150	120	100	4–	2.8/9	*e, l, n*
	conc	150	60	97	4–		*e, l, n*
	conc	150	40	92	4–	5.0/5	*e, l, n*
	conc	100	15	28	4–		*e, l, n*
	conc	100	30	31	4–	14/43	*e, l, n*
	conc	100	45	37	4–	39/29	*e, l, n*
	conc	100	60	45	4–	47/40	*e, l, n*
	conc	100	90	53	4–	30/18	*e, l, n*
	conc	100	120	59	4–	31/17	*e, l, n*
	conc	100	240	97	4–		*e, l, n*
	conc	60	45	7	4–		*e, l, n*
	conc	100	60	7	4–		*e, l, n*
	conc	100	90	9	4–		*e, l, n*
	conc	100	120	10	4–		*e, l, n*
	conc	25	120	~0			*e, l, n*
	conc	25	1440	<5	4–	52/6	*e, l, n*
	fum	25	120	100	4–	3.7/8	*e, l, n*
21	conc	150	120	100	4′–		*e, h, i, n*
	conc	100	120	88	4′–		*e, h, i, n*
	conc	60	120	insol in H_2SO_4			*g*
	fum	25	120	100	4′–		*f, h, i, n, o*
22	conc	150	120	100		3.1/6	*e, h, k, n*
	conc	100	120	100		35/33	*e, h, j, n*
	conc	60	120	38			*e, h, j, m*
	conc	25	120	insol in H_2SO_4			*g*
	fum	25	120	100		8.6/7	*e, h, k, n*
23	conc	100	120	21	3–		*e, j, m*
	fum	25	120	58	3–	4.3/7	*e, j, n*
24	conc	150	120	100	4–	2.1/6	*e, k, n*
	conc	100	120	62	4–	5.1/9	*e, j, n*
	fum	25	120	100	4–	3.2/7	*f, j, m, o*
25	conc	150	120	dec			*e, k*
	conc	100	120	dec			*e, k*
26	conc	150	120	dec			*e, k*
	conc	100	120	78	4–	8.4/5	*e, k, n*
	fum	25	120	78	4–		*f, k, n, o*
30	conc	100	120	66	4–	3.1/9	*e, l, n*

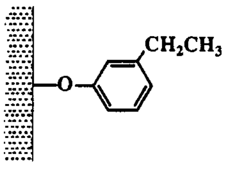
[a] Polymer reactions were carried out at a concentration of 1 × 10^{-3} mol of polymer repeating unit per 20 mL of the sulfonating agent. [b] Recovered yields were typically 70–100%. [c] The degree of sulfonation was determined by ratio of peak height in both the ^{13}C and ^1H NMR spectra. [d] The position of sulfonation was determined by the ^{13}C NMR spectra. [e] A homogeneous reaction mixture. [f] The polymers did not completely dissolve. [g] Little of no polymer dissolved. [h] The dissolved polymer formed a very viscous solution. [i] Scarlet reaction mixture. [j] Yellow reaction mixture. [k] Brown reaction mixture. [l] Colorless reaction mixture. [m] Solid polymer was present when the reaction was neutralized. [n] The neutralized reaction mixture was homogeneous. [o] Most of the original polymer did not dissolve in the medium, and the data refer to the polymer that did not dissolve.

27–29 were solvent-cast as films **32–35** (Chart IV) and were cross-linked by ^{60}Co γ-radiation. Although irradiation did not alter the surface morphology (as determined by optical or scanning electron microscopy), films prepared in this way did not dissolve in organic solvents or in concentrated or fuming H_2SO_4, although slight swelling did take place after extended exposure to these media. Moreover, the cross-linked films suffered less physical surface damage during sulfonation than their un-cross-linked counterparts. Scanning electron microscopy indicated that the initially smooth film surface underwent microscopic roughening during sulfonation (Figure 3), but catastrophic surface damage was absent. The cross-links presumably prevent dissolution of the polymer chains in the acid and slow the penetration of acid into the bulk material. After sulfonation of the surfaces of **32–35** using fuming H_2SO_4, the films were immersed sequentially in cold, concentrated H_2SO_4 (to prevent deformation by heat of mixing), water, and aqueous Na_2CO_3. The surface functional groups were $-SO_3H$ or SO_3Na units, depending on the final treatment. A summary of the reaction conditions is given in Table III.

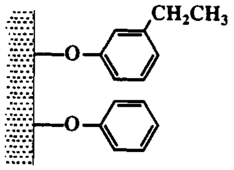
Chart IV



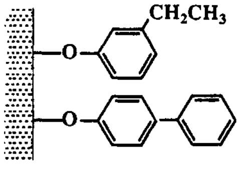
31



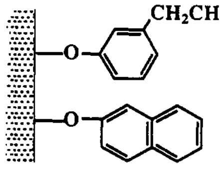
32



33



34



35

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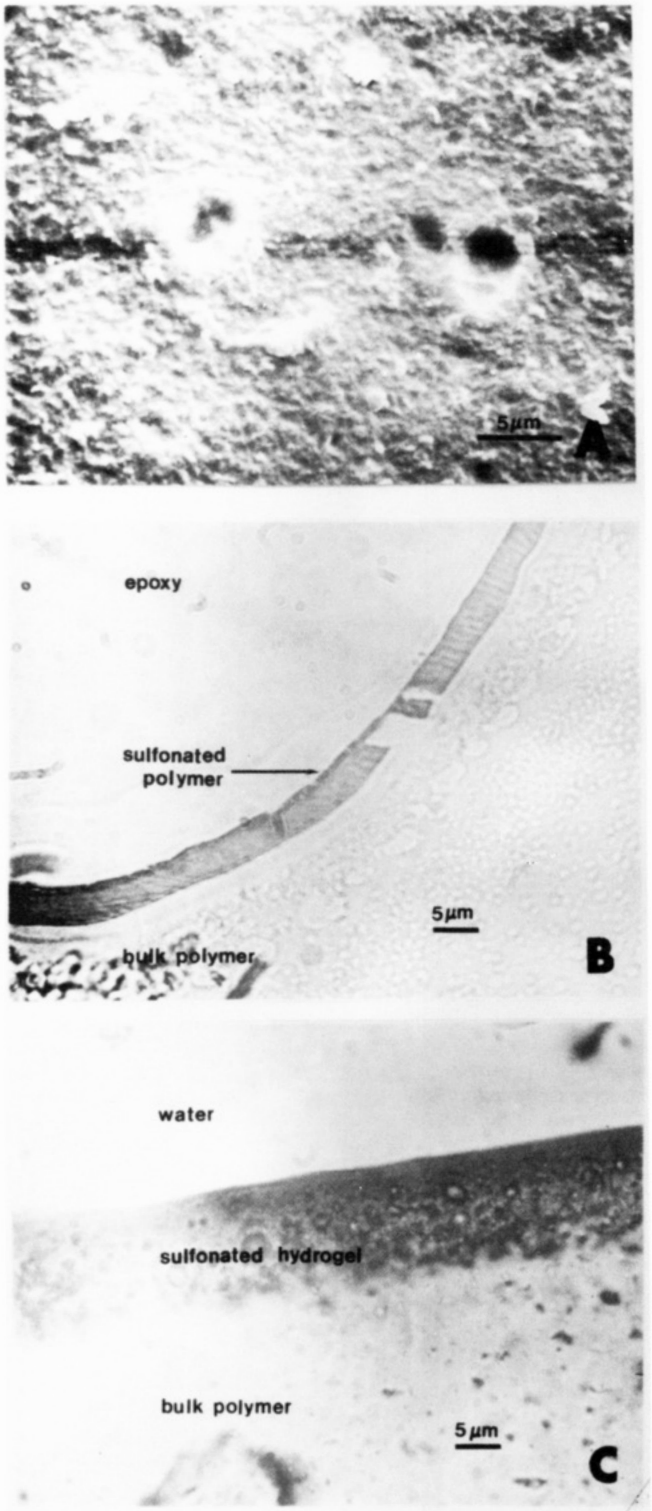

Figure 3. Surface **34** sulfonated with 20% fuming H_2SO_4 for 60 s at 25 °C. (A), Scanning electron micrograph of the reacted surface; (B), cross-section of the dried, reacted film as seen by light microscopy; (C), the same as B, but with the surface swelled to a hydrogel in water.

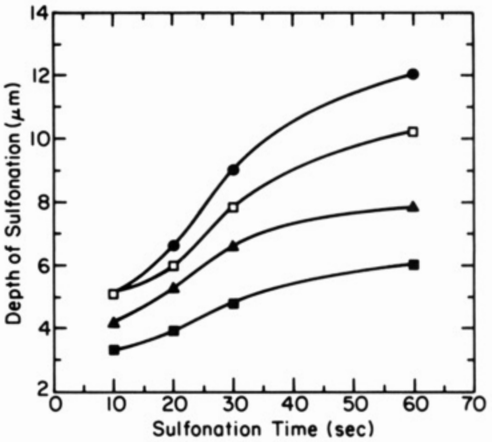

Figure 4. Depth of sulfonation for surfaces **32** (●), **33** (□), **34** (■), and **35** (▲), following treatment with 20% fuming H_2SO_4 at 25 °C as a function of time.

The sulfonated surfaces were analyzed by ATR-IR[25] and XPS[26,27] techniques. The depth of reaction was estimated from basic dye absorption experiments followed by sectioning and optical microscopy. The surface analyses were focused on two questions—the degree of sulfonation of the aryloxy groups, and the association of the reagent or protons with polymer backbone. First, it has been reported that SO_3 in solution is capable of coordination to the backbone nitrogen atoms of phosphazenes and that subsequent exposure to water yields protonated skeletal nitrogen atoms and bisulfate counter ions.[19,20] In the present work, it was found that the surfaces of **32–35** after treatment with concentrated or fuming H_2SO_4, but before neutralization, showed ATR-IR peaks in the 3400–3000-cm^{-1} region that were assigned to N–H stretching modes. XPS spectra of the same materials contained a shoulder (400.2 eV) on the N(1s) peak (397.6 eV) that was attributed to the presence of $N-H^+$ units. An S(2p) peak at 168.4 eV is consistent with the presence of a highly oxidized (sulfate) group. The S/P ratio (and, by implication, the S/N ratio) was found by XPS spectroscopy to correspond to a structure in which as many as 40% of the nitrogen atoms in the surface regions were in the form of $N-H^+$ units. The peaks associated with the $N-H^+$ units disappeared from the ATR-IR and XPS spectra or were appreciably diminished when the films were soaked in aqueous Na_2CO_3.

Sulfonation of the aryloxy groups was monitored from the ATR-IR spectra. Thus, changes in intensity of the aromatic C–C peaks at 1600 and 1450 cm^{-1} were detected, together with the appearance of S=O peaks at 1160 and 1040 cm^{-1} ($-SO_3Na$ groups). The XPS data allowed the concentration of $-SO_3H$ or $-SO_3Na$ units in the outer 100 Å of the films to be estimated on the basis of the S/P atomic ratios. For example, surfaces **34** and **35** were sulfonated to the highest degrees (S/P = 0.6 and 1.75, respectively), presumably because of the larger number of sites available for sulfonation and the greater susceptibility of biphenyl and naphthyl groups to electrophilic substitution. Surfaces **32** and **33** had S/P ratios of 0.25–0.3. The increase in sulfur concentration was minimal after the first 10 s of reaction.

The depth of sulfonation was estimated by an optical microscopic examination of the cross sections of films dyed with methylene blue. Under the reaction conditions employed, sulfonation was restricted to the outer ~3 to ~12 μm of the surfaces (Figure 3). The depth of sulfonation increased with reaction time (Figure 4), but the rate of penetration decreased at longer times. For the different polymers, the depth of sulfonation in a given time decreased in the order **32 > 33 > 35 > 34**, which parallels the decreasing solubility of the un-cross-linked polymers in fuming H_2SO_4. For comparison purposes, similar depths

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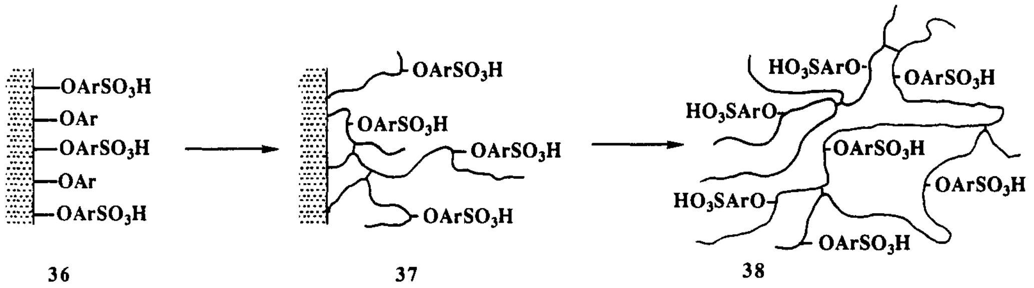
Table III. Reaction Conditions for Sulfonation of Films[a]

film	sulfonation time in H_2SO_4,[a] s	contact angle, deg ~10 min	contact angle, deg ~60 min	depth of sulfonation, μm	hydrogel layer thickness, μm
31[b]	0	99	99		
	60	*c*	*c*	*c*	*c*
32	0	67	67		
	10	50	44	5.1	12
	20	48	42	6.6	16
	30	48	40	9.0	22
	60	50	42	12.0	32
33	0	90	90		
	5	63	53		
	10	50	40	5.1	22
	20	52	42	6.0	28
	30	49	41	7.8	31
	60	49	40	10.2	44
34	0	94	94		
	1	52	41		
	5	28	21		
	10	12	5	3.3	12
	20	11	5	3.9	15
	30	10	7	4.8	19
	60	10	5	6.0	24
35	0	70	70		
	1	51	44		
	5	39	31		
	10	24	8	4.2	15
	20	24	7	5.3	20
	30	24	5	6.6	26
glass		75	75		
silylated glass		94	94		
Teflon		107	107		
mylar		74	74		

[a] γ-irradiation dose = 13 Mrad, except for *b* where dose = 0 Mrad. [b] In fuming H_2SO_4 at 25 °C. [c] Films deformed and agglomerated, preventing characterization.

Scheme II



of surface sulfonation can be achieved with polystyrene,[28] but reaction times of an hour or more are needed compared to the order of seconds required in the present work.

Hydrogel Formation via Sulfonation. The progress of surface sulfonation can be visualized as a process in which sulfonation proceeds from the surface, and at longer reaction times progresses to deeper and deeper regions of the material. Prolonged reaction will eventually bring about sulfonation of all the bulk material in the film. Because the polymer chains are cross-linked, the resultant sulfonated regions are unable to dissolve in water, but will absorb water to form hydrogel regions. This is illustrated by the three stages shown in Scheme II, in which the sulfonation is at the outer surface (**36**), at a greater depth below the surface (**37**), and throughout the material (**38**). Exposure of the three species to water causes the formation of a surface hydrogel bonded to a solid polymer (**37**) or a complete hydrogel (**38**). Hydrogels are important materials in biomedical science,[29] ion-exchange technology, and in biochemistry and molecular biology. The ability to tailor the depth of a hydrogel attached to a solid polymer provides an almost unprecedented advantage in the design of new materials.

The depth of a hydrogel layer can be estimated by staining and optical microscopy of wet sectioned samples. Hydrogel layer thickness can be controlled not only by sulfonation time but also by chemical composition (Table III). For example, for identical sulfonation conditions, the hydrogel thickness increased in the order of sulfonated **32** < **33** < **34** < **35**, with swelling ratios of 2.4, 2.9, 3.8, and 3.8, respectively. Species **32** yields a hydrogel more slowly because the rate of sulfonation is the lowest in the series.

If 10% fuming H_2SO_4 is allowed to penetrate the complete thickness of the film (roughly 1 h of reaction), the product will absorb water to form a stable, uniform hydrogel (**38**). This method provides a marked advantage over the conventional method for the preparation of sulfonated hydrogels, in which a sulfonated molecular level polymer is cross-linked by irradiation. The existence of $-SO_3H$ groups *before* radiation cross-linking limits the degree of cross-linking that can be obtained. Thus, the system described here offers advantages for the preparation of biomedical and biochemical devices, as well as for ion transport applications.

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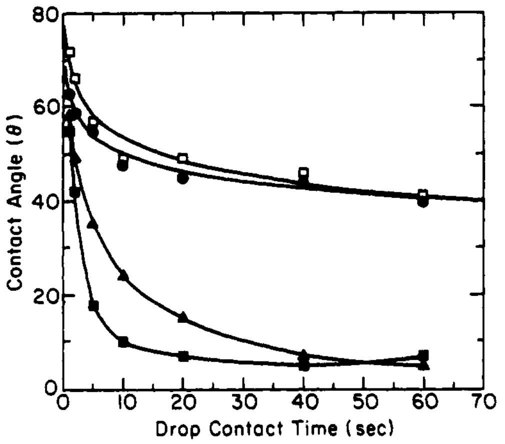

Figure 5. Contact angles of water droplets on the surface of **32** (●), **33** (□), **34** (■), and **35** (▲) after sulfonation with 20% fuming H_2SO_4 for 30 sec. at 25 °C as a function of the time (min) after the initial application of the water drop.

Surface Hydrophilicity by Contact Angle Measurements. The contact angle of a water droplet on the surface of a film provides a sensitive measure of the surface energy and, in this case, of the presence of polar or ionic $-SO_3H$ or $-SO_3Na$ sites. The contact angles of the unsulfonated polymers **20–23** and **26–29** are in the region of 70–90°, which reflects the hydrophobicity of aromatic rings and aliphatic substituents on those rings. Sulfonation of surfaces **32–35**, followed by conversion to the sodium sulfonate salt, resulted in a dramatic decrease in contact angle (to 5–40°) as the water droplets interacted strongly with the surfaces (Table III). Short sulfonation times (1–5 s) yielded materials with heterogeneous surfaces and a wide scatter (20°) in contact angles for the same surface. The heterogeneity was reduced at longer reaction times (10 s) as the overall contact angle was reduced. However, longer sulfonation times did not decrease the contact angle further, and this probably reflects a uniform coverage of the surface. XPS data indicate that, after 10 s of reaction, the concentration of sulfonate groups in the outer 100 Å does not increase. Thus, we visualize the initial stages of sulfonation to involve an initial, wetting process in which the fuming H_2SO_4 generates an intimate contact with the surface. This may take as long as 10 s. After this stage, sulfonation proceeds rapidly both at the surface and as the reagent penetrates into the film, with the reaction slowing as the byproduct, water, formed in the interior dilutes the reagent. These reactions below the outer ~10 Å of the surface do not alter the contact angle significantly.

Changes in the contact angle as the water droplet remains on the surface can also provide valuable information about the structure of that surface. Values of contact angles as a function of droplet interaction time are shown in Figures 5 and 6. For example, surface **34** undergoes little or no sulfonation in concentrated H_2SO_4 at 25 °C. Yet the contact angle was reduced from 94° to 52° with the angle decreasing slowly over a 1-h period. No staining of the surface by methylene blue was detected. Treatment with base caused the angle to rise to 75°. These changes can be ascribed to coordination of sulfuric acid to the polymer backbone nitrogen atoms rather than to sulfonation of the side groups and perhaps also to roughening of the surface. By contrast, films of **34** exposed to fuming H_2SO_4 and then neutralized to the $-SO_3Na$ form showed contact angles that fell rapidly from the time of droplet contact, with values of <10° being evident within 20 s. If $-SO_3H$ functional sites are present, the contact angle fell slowly over 1 h to ~28°. Moreover, the contact angles varied with the pH of the applied droplet, with low pH values generating higher angles than high pH solutions. The major changes occurred between pH 3 and 6.

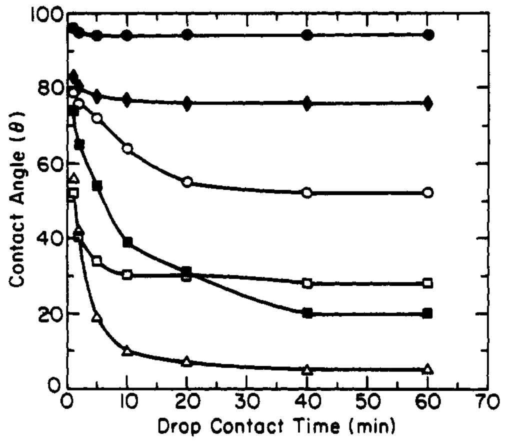

Figure 6. Contact angle of a sessile water droplet on surface **34**; unsulfonated (●), treated with concentrated H_2SO_4 for 60 sec at 25 °C (○), the same reacted surface as in (○) but neutralized with $NaHCO_3$ solution (◆), treated with 20% fuming H_2SO_4 for 60 s at 25 °C and then neutralized with aqueous $NaHCO_3$ (△), the same surface as in (△) but after treatment with aqueous HCl (pH = 1), surface (△) treated with aqueous 1 M $BaCl_2$ solution (■), as a function of time that the droplet was in contact with the surface.

Overall, water droplet contact angles indicated that increases in surface energy result when (a) the sulfonic group content increases to a value of ~25% of the side groups present (but the surface energy does not increase beyond this percentage), (b) the sulfonation proceeds to the point of hydrogel formation at the surface, and (c) when the $-SO_3H$ groups are converted to $-SO_3Na$ units.

Reactions of Surface Sulfonic Acid Groups. Sulfonic acid groups at the surfaces of systems **32–35** underwent reactions that could be followed by ATR-IR and XPS methods, as well as by contact angle changes. For example, replacement of Na^+ by Mg^{2+} ions occurred in the presence of $MgCl_2$, an exchange that was detected by the appearance of an XPS Mg(2s) peak at 90.0 eV and the absence of an Na(1s) peak. Replacement of Na^+ by K^+ from aqueous KCl solution yielded materials with both Na(1s) (1071.5 eV) and K($2p_{3/2}$) (293.0 eV) peaks. Thus, the sulfonated surfaces participate in cation-exchange reactions.

Ionic immobilization of a polypeptide to the surface was also accomplished. Aqueous solutions of protamine chloride, a polypeptide with many basic amino acid residues, formed an insoluble, coordinatively cross-linked matrix when mixed with aqueous solutions of the sulfonated phosphazene macromolecules. Surface-sulfonated films of **32–35** were exposed to aqueous solutions of protamine chloride for 48 h at 25 °C, and the resultant surfaces were rinsed with and soaked for 96 h in deionized water. The amount of surface-immobilized protamine was determined gravimetrically and was found to be in the range 190–280 $\mu g/cm^2$. ATR-IR spectra of these films contained resonances at 3500–3000 and 1675 cm^{-1}. These resonances are due to N—H and C═O stretches from the protein. XPS spectra of these films contained new C(1s) (286.5 eV), N(1s) (399.7, 401.0, and 401.8 eV), and O(1s) (532.5 eV) peaks. The new C(1s) peak is due to the amide carbonyl group in the protein. The N(1s) peaks were due to the amide, quaternized, and pendent nitrogen atoms present in the protamine. The O(1s) peak was derived from the amido carbonyl unit. Immobilization of this material at the surface of polyphosphazene films is significant since protamines are strong blood anticoagulants. Thus, these complexes may have potential as biocompatible materials.

Cross-linked films with surface **34** were also allowed to react with 20% chlorosulfonic acid in 1,2-dichloroethane at 25 °C for 60 s. This resulted in a surface on which roughly 50% of the side groups (mainly *m*-ethylphenoxy) were unreacted, typically 32% bore $-SO_3Cl$ groups, and 18% bore $-SO_3H$ groups. These values were based on ATR-IR and XPS analysis. Subsequent treatment of these functionalized surfaces with ammonia converted the $-SO_3Cl$ sites to $-SO_3NH_2$ units. Treatment with butylamine-generated $-SO_3NHBu$ units. These transformations were followed via the ATR-IR spectra, which contained peaks attributed to N–H units (3400–3000 cm^{-1}), aliphatic C–H groups (from butyl groups) (3000–2850 cm^{-1}), and sulfonamide S=O units (1325 cm^{-1}). Unreacted sulfonic groups were also present based on the presence of other S=O peaks in the same region. XPS spectra revealed the presence of sulfonamide nitrogen and protonated skeletal nitrogen from the new N(1s) peaks at 399.1 and 401.6 eV. Reduction of the $-SO_3Cl$ groups by $LiAlH_4$ converted them to –SH units, which were detected by the appearance of an S(2p) peak at 164.1 eV. The XPS data suggested that roughly 7% of the side groups at the surface bore –SH units, 43% bore $-SO_3Na$ sites, and 50% contained no sulfur. Again, these are assumed to be the less reactive *m*-ethylphenoxy side groups.

Antibacterial, Anticoagulent, and Cell Adhesion Properties.[30] The fully and partially sulfonated soluble polymers derived from **20**, both as the free acid and the sodium salt, showed antibiotic activity against *Salmonella typhimurium* (TA 100) and *Bacillus subtilis* but not against *Salmonella pullorum*, *Escherichia coli*, or *Streptococcus faecalis*. The activity may be due to the fact that *Salmonella typhimurium* is a genetically engineered strain that has no cell coating and an inferior DNA repair mechanism. Most likely, the polymers disrupt the bacterial cell membrane, and this inhibits the cell's ability to control diffusion through the membrane. There appears to be no inherent antibiotic character associated with the phosphazene structure itself, but only with side-group structure. Other experiments on phosphazene toxicology are underway.

The Lindholm test[31,32] is a simple preliminary test for the blood compatibility of polymer films. The interaction between blood and synthetic polymer surfaces is very complex as is the process of thrombus formation. Sulfonated compounds and surfaces are reported to inhibit the clotting process.[33] The unsulfonated, sulfonated, and protamine-immobilized films were tested in a Lindholm cell with EDTA-treated human blood. The unsulfonated films had an average clotting time of 12 min. The sulfonated and protamine immobilized films both had average clotting times of >60 min. Thus, these materials exhibited enhanced blood compatibility with respect to the untreated films.

The immobilization of mammalian cells on synthetic polymer substrates is of great interest. Such systems are being investigated for the purpose of enhancing the compatability of biomaterials, assembling artificial organs, and improving bioreactors. Most untreated polymer surfaces are unsuitable for cell culture because they do not allow attachment and spreading of the cells. Rubin[34] reported in 1966 that sulfonated polystyrene surfaces are an excellent substrate for cell attachment. The introduction of polar, especially ionic, groups to a polymer surface will enhance its capability for cell attachment. Both the unsulfonated and sulfonated films from **33** were first sterilized and then placed in a culture of African Green Monkey kidney cells (CV-1). All the sulfonated films had a complete monolayer coverage of cells after 3 days of incubation. By contrast, the unsulfonated polymer surfaces were colonized only in small regions of the surface. The ionic and hydrogel character of the sulfonated films appears to enhance their suitability for cell attachment and growth. Unlike sulfonated polystyrene, these films are flexible after sulfonation and cell attachment. The potential of these polymers and surfaces for use as biomedical materials is being investigated further.

Experimental Section

Equipment and Characterization Procedures. ^{31}P NMR spectra were obtained with the use of a JEOL FX-90Q spectrometer, and ^{13}C and ^1H NMR spectra with a Bruker 200-MHz spectrometer. A Perkin-Elmer Model 1710 infrared Fourier transform spectrometer was used to obtain infrared spectra, with a Harrick variable-angle twin parallel mirror reflection attachment equipped with a 45° Ge crystal (50 × 10 × 3 mm) for ATR-IR spectra. ^{60}Co γ-irradiation experiments were carried out at the Breazeale Nuclear Reactor at The Pennsylvania State University. SEM analyses were obtained with the use of an ISI SX-40A instrument.

Gel permeation chromatography molecular weight estimates were obtained by the use of a Hewlett-Packard HP 1090 liquid chromatograph equipped with a refractive index detector. Polymer Laboratories gel columns were used for the analysis of polymers that were soluble in THF, with samples being injected as 1% solutions in THF. A solution of Bu_4NBr (0.1%) in THF was the eluent. The instrument was calibrated against secondary polystyrene standards. Columns packed with Corning Controlled-Pore Glass were used for water-soluble polymers, in which case the elution solvent was aqueous 0.5 M Na_2SO_4. For these systems the instrument was calibrated with secondary sodium poly(styrenesulfonate) standards.

X-ray photoelectron spectra were obtained at the Perkin-Elmer Physical Electronics Laboratory (Edison, NJ) using a Perkin-Elmer Physical Electronics 5000 LS spectrometer. A monochromatic X-ray source using an Mg anode (Mg Kα, 1486.6 eV) operated at 600 W (15 kJ, 40 mA) was employed as the primary excitation source. Charge compensation was accomplished by flooding the sample surface with low-energy (<2 eV) electrons. Spectra were recorded with a 62° takeoff angle. Atomic composition data were determined by using the instrument's computer and programmed sensitivity factors.

Contact-angle measurements were made using a Ramé-Hart Model 100 contact angle goniometer equipped with an environmental chamber. Contact angles were determined at various times after the application of a 1-μL distilled water drop. Troughs in the chamber were filled with distilled water in order to maintain 100% relative humidity. The temperature varied between 20 and 25 °C. All reported values are the average of at least 10 measurements taken at different locations on the film surface.

All phosphazene syntheses were carried out under an inert atmosphere of dry nitrogen (Matheson). A Büchi BEP 280 stirred autoclave was used for higher temperature (160 °C) reactions.

Starting Materials. Hexachlorocyclotriphosphazene (**9**; Ethyl Corp.) was purified by vacuum sublimation, recrystallization from hexane, and a final sublimation. Poly(dichlorophosphazene) (**19**) was obtained by the thermal polymerization at 250 °C of **9** in evacuated sealed tubes. Phenol (Aldrich), 2-naphthol (Aldrich),

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(30) The procedures used for the bacterial response tests made use of standard zone of inhibition and solution turbidity methods at concentrations of 50000, 10000, and 1000 μg/mL. The details are to be published—Allcock, H. R.; Pucher, S. R.; Fitzpatrick, R. J.; Rashid, R. *Biomaterials*, submitted.

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Table IV. Characterization Data for Cyclic Trimeric Starting Materials

trimer	melting point, °C	NMR spectra, ppm ^{31}P	^{1}H	^{13}C	mass spec obs	calc
10	114–115[a]	8.8 (s) 6.9 (d)	7.3 (m)	150.6 129.3 124.8 120.9	693	693
11	201–202[a]	9.3 (s)	7.3 (m)	150.0, 128.0 139.8, 127.2 137.8, 126.8 128.8, 121.4	1149	1149
12	160–162[b]	9.2 (s)	7.2 (m)	148.5, 127.6 134.2, 126.8 131.3, 125.8 129.7, 121.3 127.9, 117.9	993	993
13	116–117[b]	9.2 (s)	7.0 (d) 6.8 (d) 2.1 (s)	148.5 134.0 129.7 120.9 20.7	777	777
14	75–76[a]	17.8 (s)	7.3 (m) 6.9 (m) 4.4 (t) 4.2 (t)	158.5, 66.6 129.4, 64.4 121.0 114.6	957	957
16	*d*	8.8 (s)	7.2–7.7 (m) 2.5 (q) 1.1 (t)	150.9, 120.7 145.7, 118.5 129.5, 29.0 124.3, 15.5	861	861
17	230–231[a]	15.1 (s)	7.3–7.8 (m)	131.0 130.5 128.2 127.6	597	597
18	270–272[a]	3.1 (s)	6.9–7.4 (m)	141.8 129.2 121.0 118.3	687	687

[a] White crystals. [b] White powder. [c] Green oil. [d] Yellow oil.

and 4-phenylphenol (Aldrich) were purified by sublimation and were stored in a desiccator. Sodium metal (Aldrich) was stored and used in a glovebox. Concentrated sulfuric acid (Fisher), fuming sulfuric acid (Fisher), chlorosulfonic acid (Aldrich), and protamine chloride (Sigma) were used as received. Aniline (Aldrich) was distilled from $Ca(OH)_2$ immediately before use. 3-Ethylphenol (Aldrich), 2-phenoxyethanol (Aldrich), and 2-(2-methoxyethoxy)ethanol (Aldrich) were vacuum distilled and then stored over molecular sieves.

Preparation of $[NP(OPh)_2]_3$ (10). Sodium metal (12.05 g, 0.524 mol) was placed in a dried 3-L flask equipped with a condenser. Into the flask was distilled dry THF (600 mL). Phenol (62.0 g, 0.659 mol) was dissolved in dry THF (400 mL) in a separate flask and then added dropwise to the sodium. The salt solution was stirred for 12 h at room temperature and then heated for 12 h until all the sodium had reacted. At that time, **9** (15.0 g, 0.129 mol) was dissolved in dry THF (500 mL) and then added to the salt solution. The reaction mixture was refluxed for 48 h, then cooled and filtered through silica gel. The filtrate was concentrated, redissolved (diethyl ether), and extracted (2 × 150 mL of 0.05 M NaOH, 3 × 150 mL of distilled H_2O). The ether layer was concentrated and the oily residue crystallized from hexane. The characterization data for **10** and the other cyclic trimers are listed in Table IV.

Preparation of $[NP(OC_{12}H_9\text{-}p)_2]_3$ (11), $[NP(OC_{10}H_7\text{-}2)_2]_3$ (12), and $[NP(OC_6H_4CH_3\text{-}p)_2]_3$ (13). These compounds were prepared in the same way as **10**, except that for **11** the solid was recrystallized from CH_2Cl_2, $R_f = 0.65$ (CH_2Cl_2, 100%), and for **12**, $R_f = 0.46$ (CH_2Cl_2, 100%).

Preparation of $[NP(OCH_2CH_2OPh)_2]_3$ (14). A solution of 2-phenoxyethanol (55.0 g, 0.398 mol) was added to a suspension of sodium (5.4 g, 0.235 mol) in dioxane (200 mL). The reaction mixture was stirred and heated for 24 h until all the sodium had reacted. A solution of **9** (7.0 g, 6.03×10^{-2} mol) in dioxane (40 mL) was added to the salt solution. The mixture was stirred and heated for 24 h, allowed to cool, and then filtered through silica gel. The filtrate was concentrated, dissolved in toluene and extracted with 1 M NaOH (3 × 100 mL) and deionized water (2 × 100 mL). The collected fractions were concentrated on the rotary evaporator. The resulting oil was dissolved in hot hexane/ethanol (1:1) and the solution was cooled to 25 °C. The crystals that formed were collected by suction filtration and were then recrystallized from MeOH/hexane (1:1). Yield 11.70 g (61%) of white, needle-shaped crystals.

Preparation of $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_3$ (15). This compound was prepared by the method described for **14**, except that the product was not purified by liquid–liquid extraction because it is water soluble. The compound did not crystallize. It was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent.

Preparation of $[NP(OC_6H_4Et\text{-}3)_2]_3$ (16). The synthesis method described for **10** was used, except that the product did not crystallize. The ethereal layer was concentrated and the oil further purified by column chromatography on silica gel with elution by hexane. The product was a viscous, yellow oil.

Preparation of $[NP(Ph)_2]_3$ (17). This compound was prepared by the reaction of sodium azide with chlorodiphenylphosphine.[34]

Preparation of $[NP(HNPh)_2]_3$ (18). Aniline (100 mL) was distilled from $Ca(OH)_2$ and added to dry dioxane (50 mL). A solution of **9** (5.0 g) in dioxane (50 mL) was prepared. The solution of **9** was added to the aniline solution. The mixture was stirred and refluxed for 48 h. The reaction mixture was allowed to cool and then filtered through silica gel. The silica gel was washed with diethyl ether. The collected filtrates were concentrated on the rotary evaporator and then redissolved in CH_2Cl_2. The CH_2Cl_2 solution was extracted with 0.1 M HCl (5 × 50 mL) and then with deionized water (3 × 50 mL). The CH_2Cl_2 solution was evaporated to dryness and the resultant powder recrystallized from methanol.

Preparation of $[NP(OPh)_2]_n$ (20). A 10.0-g (8.62×10^{-2} mol) sample of **19** was dissolved in warm dioxane (500 mL). In separate flasks, phenol (55.2 g, 0.587 mmol) was dissolved in dioxane and added to an ice-bath cooled suspension of sodium (11.10 g, 0.483 mol) in dioxane (200 mL). The salt solution was warmed for 24 h until all the sodium had reacted. At that time, the polymer and salt solutions were added separately to an autoclave reactor. The mixture was stirred and heated at 160 °C and 60 psi in the autoclave for 24 h. The suspension was then concentrated and precipitated into deionized water. The polymer was reprecipitated from THF into deionized water (3×), hexane (3×), and ethanol (1×). A tough white polymer (14.4 g, 72%) was recovered. The characterization data for this polymer and polymers **21–30** are summarized in Table V.

Preparation of $[NP(OC_6H_4C_6H_5\text{-}p)_2]_n$ (21). This polymer was prepared in the same way as **20**, except for the purification method. The reaction mixture gelled when cooled to room temperature. Hence, the mixture was suspended in deionized water for 24 h, and the polymer was then isolated by suction filtration. The isolated polymer was Soxhlet extracted with ethanol for 5 days. The final product was a white, powdery, intractable solid.

Preparation of $[NP(OC_{10}H_7\text{-}2)_2]_n$ (22) and $[NP(OC_6H_4CH_3\text{-}p)_2]_n$ (23). Both polymers were prepared in the same way as **21**, except that the reaction mixture was stirred and heated in an autoclave for 55 h. Polymer **22** was obtained as an off-white powdery material (6.97 g, 30%). Polymer **23** was a tough, white material.

Preparation of $[NP(OC_6H_4CH_3\text{-}p)_2]_n$ (23). This compound was prepared in the same way as **21**. Yield 17.2 g (77%).

Preparation of $[NP(OCH_2CH_2OPh)_2]_n$ (24). A sample of **19** (5.0 g, 4.31×10^{-2} mol) was dissolved in warm dioxane (250 mL). To a suspension of sodium (6.05 g, 0.263 mol) in dioxane (250 mL) was added 2-(phenoxy)ethanol (46 g, 0.333 mol), and the mixture was stirred and heated for 24 h until all the sodium had reacted. The salt solution was then added via double-tipped syringe to the polymer solution. The reaction mixture was stirred and heated for 72 h, although it was evident that the reaction was complete after 24 h. The mixture was cooled and was concentrated on a rotary evaporator. The viscous solution was then poured into deionized water, and the polymer was isolated as a tough white solid. The product was purified by further reprecipitations from THF into deionized water (3×) and hexane (3×). Yield 10.76 g (78%).

Table V. Characterization Data for Starting Polymers 20–30

polymer	mol wt (M_w)[a]	NMR spectra, ppm			T_g, °C	elem anal.		
		^{31}P	^{1}H	^{13}C			obs	calcd
20	2.1 × 10^6	−7.8 (s)	6.5–7.2	148.5	−8	C	68.28	62.34
				127.2		H	4.57	4.36
				122.5		N	6.13	6.06
				118.7		Cl	0.11	0.0
21					93	C	75.92	74.79
						H	4.12	5.23
						N	3.60	3.64
						Cl	0.05	0.0
22	1.1 × 10^6	−18.8 (s)	7.0–7.9	149.7, 127.6	41	C	71.52	72.50
				134.2, 125.8		H	4.52	4.26
				130.9, 124.6		N	4.21	4.23
				129.2, 121.7		Cl	0.01	0.0
				127.9, 117.6				
23	3.6 × 10^6	−19.6 (s)	7.0–7.5	149.6	−2	C	64.78	64.86
			2.3	132.1		H	5.24	5.44
				129.1		N	5.71	5.40
				121.0		Cl	0.03	0.0
				20.6				
24	4.6 × 10^6	−7.8 (s)	6.9–7.4	158.6	−7	C	59.99	60.18
			3.5	129.40		H	5.82	5.68
				120.6		N	4.19	4.39
				114.5		Cl	0.66	0.0
				67.0				
				64.6				
25	1.7 × 10^6	−7.4 (s)	3.0–4.0	70.8	−67	C	42.04	42.40
				69.5		H	7.73	7.83
				69.3		N	5.07	4.95
				64.9		Cl	0.00	0.0
				57.7				
26	3.3 × 10^6	−20.2 (s)	6.6 (m)	151.7, 118.4	−47	C	66.93	66.88
			2.1 (q)	144.6, 28.3		H	6.58	6.63
			0.8 (t)	128.5, 15.1		N	4.91	4.88
				122.6		Cl	0.03	0.0
				120.6				
27	2.2 × 10^6	−20.2 (s)	6.8 (m)	152.7, 122.2	−34	C	65.08	64.86
			2.1 (q)	145.8, 121.5		H	5.19	5.44
			0.8 (t)	129.6, 119.4		N	5.33	5.40
				124.2, 29.2		Cl	0.01	0.0
				123.8, 15.8				
28	3.0 × 10^6	−19.0 (s)	6.9 (m)	152.8, 127.4	21	C	71.53	71.63
			2.2	152.2, 124.0		H	5.03	5.41
			0.8	146.0, 122.5		N	4.12	4.18
				141.2, 121.5		Cl	0.00	0.0
				137.2, 119.4				
				129.7, 29.2				
				129.3, 15.6				
				128.2				
29	4.7 × 10^5	−19.6 (s)	7.0	152.7, 126.2	−4	C	69.45	69.90
			2.0	150.3, 125.0		H	4.99	5.21
			0.7	145.8, 123.9		N	4.48	4.53
				134.7, 121.4		Cl	0.05	0.0
				131.4, 119.2				
				129.6, 118.2				
				128.5, 29.0				
				128.0, 15.6				
30	3.3 × 10^5	−15.1 (s)	7.4	141.8	91	C	61.92	61.92
				129.5		H	5.25	5.28
				121.2		N	18.80	18.34
				118.6		Cl	0.08	0.0

[a] By gel permeation chromatography.

Preparation of $[NP((OCH_2CH_2)_2OCH_3)_2]_n$ (25). This polymer was prepared in the same way as 24 except that purification was achieved by concentration of the reaction mixture on the rotory evaporator, followed by dialysis against deionized water and then against methanol.

Preparation of $[NP(OC_6H_4Et)_2]_n$ (26). Polymer 26 was prepared by the method described for 20.

Preparation of $[NP(OC_6H_5)_x(OC_6H_4Et\text{-}3)_y]_n$ (27). Phenol (9.3 g) was dissolved in dioxane (50 mL) and was then added dropwise to an icebath-cooled suspension of sodium (2.89 g) and dioxane (100 mL). The mixture was stirred at room temperature for 24 h. 3-Ethylphenol (65 mL) was added dropwise to a cooled suspension of sodium (14.25 g) in dioxane (450 mL), and this mixture was stirred at room temperature for 14 h. Polymer 19 (10.09 g) was dissolved in warm dioxane (450 mL), and the solution was transferred to a cooled autoclave. The sodium phenoxide solution was separated from excess sodium and was added with stirring to the polymer solution. The mixture was then stirred and heated for 2 h at 150 °C. The sodium 3-ethylphenoxide solution was separated from excess sodium and was added to the main reaction mixture, which was stirred for 15 h at 150 °C. The product mixture was concentrated on the rotary evaporator and the polymer was precipitated into deionized water. The polymer was purified further by reprecipitations from THF into deionized water (4×) and ethanol (4×). The composition of the polymer indicated that the side groups were present in proportions con-

1132 *Chem. Mater.* **1991**, *3*, 1132-1137

sistent with $x = 1.04$ and $y = 0.96$.

Preparation of $[NP(OC_6H_4C_6H_5\text{-}p)_x(OC_6H_4Et\text{-}3)_y]_n$ (28). This polymer was prepared with use of the technique described for **27**. The side groups were present in the proportions $x = 1.06$ and $y = 0.94$.

Preparation of $[NP(OC_{10}H_7\text{-}2)_x(OC_6H_4Et\text{-}3)_y]_n$ (29). Polymer **29** was prepared in the same way as **27**. The side groups were present in the proportions $x = 1.10$ and $y = 0.90$.

Preparation of $[NP(HNPh)_2]_n$ (30). Aniline (150 mL) was distilled from $Ca(OH)_2$ and was added to dry dioxane (50 mL). A solution of **19** (5.0 g) in warm dry dioxane (200 mL) was prepared and was added to the aniline solution. The reaction mixture was stirred and refluxed for 96 h. The mixture was concentrated by means of a rotary evaporator and was then precipitated into deionized water. The particulate solids were isolated by suction filtration and were vacuum dried. The polymer was reprecipitated from THF into deionized water (4×), methanol (3×), and then hexane (3×) to give the white powdery product.

Procedure for Solution Sulfonation of Polymers with Concentrated or Fuming H_2SO_4. All sulfonation reactions were carried out under a dry nitrogen atmosphere in order to exclude moisture. Glassware was dried in an oven. The acid was heated in an oil bath to the specified temperature before the addition of the phosphazene. If the material to be sulfonated was added as a solid, it was first crushed into a powder and then added to the acid over a 5-min period. The volume of acid used varied from polymer to polymer, depending mainly on the ease of stirring. In all instances, the acid was present in a large excess. When a solvent was used, a 2% (g/mL) concentration of the polymer was employed. Solvent was also added to the acid, and the mixture was heated to the appropriate temperature. Each mixture was stirred and heated for a specific time and was then neutralized by pouring into a large excess of aqueous Na_2CO_3. The resulting solution was concentrated on a rotary evaporator. All polymer solutions, even if solid polymer was present, were placed in dialysis tubing (12000–14000 MW cutoff) and were dialyzed against deionized water for 5 days. The polymer was then isolated by evaporation of water from the contents of the dialysis tubing. The progress of a typical macromolecular sulfonation is illustrated by Figure 2.

Procedure for Solution Sulfonation of Cyclic Trimers with Concentrated or Fuming H_2SO_4. The trimers were treated in the same way as the polymers. Sulfonated trimeric compounds were isolated by dialysis. The neutralized solutions were placed in flasks, and the mouths of the flasks were covered with several layers of dialysis tubing (1000 MW cutoff). The solutions were then dialyzed against deionized water for 7 days. The contents of the flask were then evaporated to dryness and the residues analyzed.

Preparation of Films 31–35. The polymers were dissolved in dry distilled solvents (THF, dioxane, and or toluene). The solutions were filtered and films were then cast in a dust-free inert-atmosphere glovebox on a clean, level, glass surface. The samples were covered with small loose fitting covers to slow the evaporation rate. After at least 1 week, the films were removed from the casting chamber and were placed in the vacuum oven for 48 h at 80 °C. Films were then peeled from the glass plate.

Radiation Cross-Linking of 32–35. Films were dried under vacuum for 24 h and then sealed in an evacuated glass container. The samples were then exposed to ^{60}Co γ-rays at a dose rate of 0.3 Mrad/h.

Procedure for Sulfonation of Films with Fuming H_2SO_4. Films were rinsed in water, ethanol, and hexane and then dried before sulfonation. The film samples were held by Teflon forceps and immersed in the sulfonating agent for a limited period of time (typically 10–60 s), before being rinsed quickly in cold concentrated H_2SO_4 and then in cold deionized water. The sodium salt form of the active sites was generated by placing the films in deionized water and then gradually neutralizing with aqueous Na_2CO_3. The protonated variant was obtained by immersion of the neutralized films in 0.1 M HCl. All the films were rinsed with deionized water and were then stored in the same medium.

Procedure for Sulfonation of Films with $ClSO_3H$. A 20% solution of $ClSO_3H$ in 1,2-dichloroethane was used. The films were immersed in the solution for 60 s and were then rinsed quickly with fresh 1,2-dichloroethane under an atmosphere of argon. The films were subsequently exposed to condensed NH_3 (0 °C), *n*-butylamine in Et_2O (50%, 0 °C), or $LiAlH_4$ in Et_2O (0.5 M, 0 °C) for 12 h. Each film was then rinsed and soaked in deionized water and in ethanol.

Ion-Exchange Reactions. Sulfonated films were soaked in 1 M salt solutions for 24 h at room temperature and were then rinsed and soaked for 48 h in deionized water.

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Preparation of TiN and TiC from a Polymeric Precursor

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Hydrolysis of the $Ti(O\text{-}n\text{-}Bu)_4$/furfuryl alcohol mixture resulted in the formation of a polymeric solid. Pyrolysis of the polymer at 1150 °C under argon yielded metallic, gray TiC. When the pyrolysis was carried out in an atmosphere of anhydrous ammonia, pure TiN containing less than 0.8 wt % carbon was obtained at 1000 °C. The structure and pyrolysis chemistry of the precursor were studied by Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA), gas chromatography (GC), elemental analyses, and X-ray diffraction (XRD).

Introduction

Titanium nitride and titanium carbide have many desirable properties such as high melting point, extreme hardness, and strength at high temperatures.[1,2] At present, both TiN and TiC are used predominantly as cutting materials, although TiN layers also can be used as conductors for electronic applications. Previous studies indicated the addition of TiC to SiC[3,4] and TiN to BN[5]

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