known to react with organometallic reagents, and the synthetic chemical literature abounds with examples of removable protecting groups.

Acknowledgment. We thank J. T. Hucko for editorial assistance with this paper.

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Surface Reaction of Poly[bis(trifluoroethoxy)phosphazene] Films by Basic Hydrolysis

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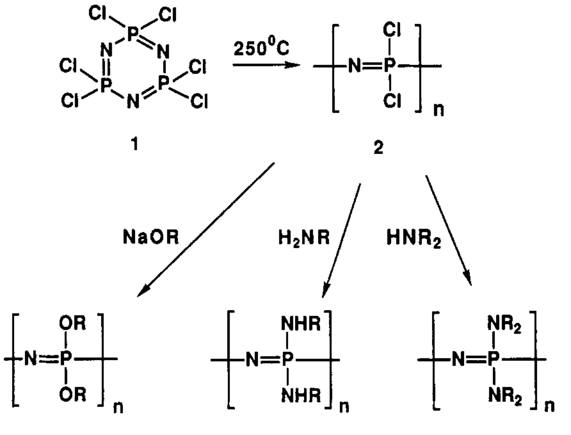
A novel surface reaction of a fluoroalkoxyphosphazene polymer is reported. Films of poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$, underwent surface hydrolysis when treated for 0–15 min with 8 M aqueous sodium hydroxide in the presence of 0.05 M tetra-*n*-butylammonium bromide as a phase-transfer agent. This reaction converted a hydrophobic surface to one with hydrophilic and adhesive character. No surface reaction by NaOH solutions was detected in the absence of Bu_4NBr. On the basis of a series of surface analytical data, the principle chemical reaction was found to be a replacement of $P-OCH_2CF_3$ side groups at the polymer surface by $P-O^-NBu_4^+$ units. The modified surfaces were found to possess anionic sites, since an exchange reaction with the cationic dye methylene blue took place readily at the surface. No exchange occurred with the anionic dye Biebrich scarlet. Microscopic examination of the dyed films allowed the depth of the surface reaction to be measured. Contact-angle analysis showed that the surface of the polymer became progressively more hydrophilic as the reaction progressed. No significant changes in surface texture were detected. Surface reactions were also carried out with a commercial mixed-substituent fluoroalkoxyphosphazene elastomer. After extensive surface hydrolysis, films of $[NP(OCH_2CF_3)_2]_n$ retained their solubility in organic solvents, in which they were analyzed by ^{31}P, ^{13}C, ^1H, and ^{19}F NMR spectroscopy. The NMR analysis also suggested the presence of $-O^-NBu_4^+$ units. GPC analysis of an extensively modified material indicated that some cleavage of the phosphazene backbone may have occurred. The hydrolysis process was monitored by the reaction of solutions of $[NP(OCH_2CF_3)_2]_n$ with NaOH in the presence of Bu_4NBr in refluxing THF. The mechanism of adhesion is discussed.

Introduction

A need exists to understand more fully the physical and chemical processes that are responsible for polymer adhesion and biocompatibility.[1,2] It is known that fluorinated polymers such as poly(tetrafluoroethylene) or poly(chlorotrifluoroethylene) are difficult to bond to other materials because of their hydrophobic surfaces. Surface reactions of fluoropolymers to enhance adhesion have been studied extensively.[3,4] In most cases, it is critical that the surface reaction should not affect the bulk properties of the polymer and that the depth of the reaction zone can be controlled easily.

Poly(organophosphazenes)[5-8] are a relatively new class of polymers that are of increasing scientific and technological interest. A typical two-step synthesis of a poly(organophosphazene) is illustrated in Scheme I. It involves a ring-opening polymerization of hexachlorocyclotriphosphazene (1) at 250 °C to form poly(dichlorophosphazene) (2). Polymer 2 functions as a macromolecular intermediate. The high reactivity of the P–Cl bonds allows the polymer to undergo facile nucleophilic substitution reactions with sodium aryl oxides or alkoxides or with primary or secondary amines. The resultant poly(organophosphazenes) are usually stable to air and moisture. A wide variety of different types of side groups can be incorporated into the polymer structure, with the bulk and surface properties being dependent on the side groups present. The reactions and structures of *cyclic* phosphazene molecules such as 1 are useful models for the reactions and structures of the analogous macromolecules.[9] Despite their technological utility, the surface chemistry

Scheme I



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[1] Fowkes, F. M.; Ed. *Contact Angle, Wettability, and Adhesion*; Advances in Chemistry Series, 43; American Chemical Society: Washington, D.C., 1964.

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[7] Neilson, R. H.; Wissian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.

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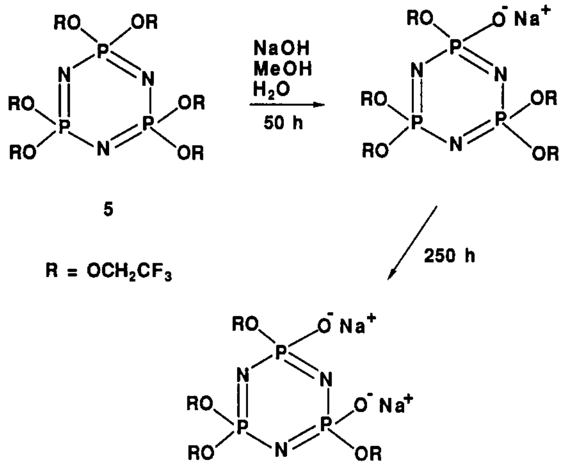
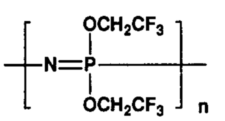
Scheme II



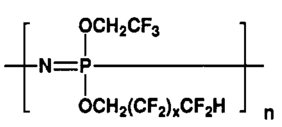
of poly(organophosphazenes) has not yet been investigated in detail.[10]

Poly[bis(trifluoroethoxy)phosphazene] (**3**) is prepared by the reaction of **2** with sodium trifluoroethoxide. Polymer **3** is a semicrystalline thermoplastic that is soluble in common organic solvents such as tetrahydrofuran (THF) or acetone. The surfaces of films of **3** are hydrophobic and show no adhesive character. Commercial fluoroalkoxyphosphazene elastomers (**4**) possess a chemical structure similar to that of **3** but contain both trifluoroethoxy and longer chain fluoroalkoxy side groups.[11] Many current or potential applications of **4** involve its contact with metals, ceramics, polymers, or fabrics. Hence, the surface character of **4** plays an important role in its use in a variety of applications. The surface modification of **3** and **4** to enhance its adhesion is also relevant to potential biomedical applications of phosphazene polymers.



$$\left[-\mathrm{N{=}P}(\mathrm{OCH_2CF_3})_2-\right]_n$$

3



$$\left[-\mathrm{N{=}P}(\mathrm{OCH_2CF_3})(\mathrm{OCH_2(CF_2)_xCF_2H})-\right]_n$$

4

Here we report that the hydrophobic surfaces of **3** and **4** can be modified by treatment with hot aqueous solutions of sodium hydroxide in the presence of tetra-*n*-butylammonium bromide as a phase-transfer agent to form hydrophilic and adhesive surfaces. This surface reaction is simple and rapid. Furthermore, the rate of the reaction can be controlled by several experimental parameters.

Previous research has shown that the cyclic analogue of **3**, $[NP(OCH_2CF_3)_2]_3$ (**5**), is hydrolyzed in aqueous organic sodium hydroxide solutions (Scheme II).[12] The hydrolysis reaction of **5** involves a nongeminal replacement of the trifluoroethoxy side groups by hydroxyl side groups. The first replacement is more facile than the second. Similar hydrolysis reactions were reported for the cyclic tetrameric analogue, $[NP(OCH_2CF_3)_2]_4$. However, films of polymer **3** are stable to hydrolysis when treated with aqueous sodium hydroxide, even at high temperatures and after prolonged reaction times.

It has recently been reported that the physical properties of **3** are slightly dependent on the exact experimental procedure used to prepare the polymer.[13,14] Some evidence exists that these differences in properties are due to the presence of small amounts of hydroxyl side groups generated during the reaction of **2** with sodium trifluoroethoxide or during the purification of the polymer.

The following questions were addressed in this investigation: (1) What types of reactions occur at the surface of **3** following its immersion in solutions of NaOH/Bu_4NBr? For example, does a replacement of trifluoroethoxy side groups by hydroxyl groups occur at the surface of **3** in a manner similar to the reactions of the model compound **5**? (2) Can the reactions be monitored by surface analytical methods such as depth profile, XPS, contact-angle, or ATR-IR analyses? (3) Can the modified polymer surfaces undergo surface reconstruction when exposed to solvent environments of different polarity or when heated? (4) If the surface reaction is allowed to proceed long enough, will the modified polymer still remain soluble in organic media to allow analysis by solution methods such as NMR spectroscopy or gel permeation chromatography (GPC)? (5) Does the *solution* hydrolysis of **3** by NaOH in the presence of Bu_4NBr in THF model the surface reactions of **3**? (6) Do mixed-substituent fluoroalkoxyphosphazene elastomers (**4**) and other poly(organophosphazenes) undergo similar surface reactions when treated with aqueous NaOH/Bu_4NBr solutions? (7) What is the mechanism of adhesion for these modified polymer surfaces?

Results and Discussion

Qualitative Aspects of the Surface Reaction of 3 with Base. Polymer **3** was prepared by a method reported earlier[5] (Scheme I) with the use of a recent modification.[13] Smooth opalescent films of **3**, 140 μm thick, were prepared on glass plates by solution-casting methods. The films possessed no adhesive character before the surface reaction, and scanning electron microscope (SEM) analyses showed that the films were smooth on both the glass and air sides. Although **3** is a microcrystalline polymer, SEM analyses did not distinguish the crystalline regions from the amorphous regions at the polymer surface.[15] Gentle scraping of the films did not remove any of the polymeric material from the surface. The films were washed with hexane before use to remove any contaminants (e.g., organosiloxanes from stopcock grease) that may have migrated to the surface.

Films of **3** were immersed in 8 M NaOH/0.05 M Bu_4NBr solutions at 80 °C. After several minutes of immersion, the treated films were removed from the hot base solution and were rinsed with distilled–deionized water for several minutes to remove loosely adsorbed species. Finally, the films were dried under vacuum.

The surface-reacted films of **3** were pressed onto glass, stainless steel, aluminum foil, ceramic, polymer, or human skin substrates and were found to adhere to each of these materials. Attempts were made to peel the films from these substrates with forceps, but both visual and SEM analyses indicated that some of the polymer remained on the substrates (cohesive failure). The peel strength of surface-modified **3** pressed onto aluminum foil by hand at room temperature was 20 N/m. As a comparison, the peel strength of a typical consumer-grade Scotch tape pressed onto aluminum foil by hand at room temperature was 80 N/m, measured under the same conditions as for modified **3**.

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(10) For example, see: Allcock, H. R.; Kwon, S. *Macromolecules* **1986**, *19*, 1502.

(11) See: *EYPEL-F, Performance Elastomers, Technical Data*; Ethyl Corp., Baton Rouge, LA, 70801, 1987.

(12) Allcock, H. R.; Walsh, E. J. *J. Am. Chem. Soc.* **1972**, *94*, 119.

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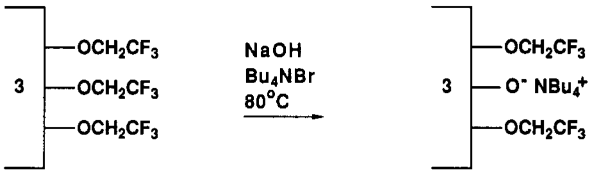
(15) Blais, P.; Carlsson, D. J.; Csullog, G. W.; Wiles, D. M. *J. Colloid Interface Sci.* **1974**, *47*, 637.

Scheme III



The films were still opalescent after the surface reaction, and gentle scraping of the surface revealed the presence of a gellike adhesive material at the surface. When films of 3 were floated on the 8 M NaOH/0.05 M Bu_4NBr solution at 80 °C for several minutes, only the treated side showed the adhesive property. In control experiments, films of 3 did not become adhesive after they were immersed in aqueous 8 M NaOH solution alone or in 0.05 M Bu_4NBr solution at 80 °C for several days. Thus, Bu_4NBr appears to increase the effectiveness of the reaction, probably by enhancing the nucleophilicity of the hydroxide anion. However, the surfactant properties of Bu_4NBr may also contribute to the catalysis.

Finally, it should be noted that the surface reaction of 3 could also be carried out in 8 M NaOH/0.05 M Bu_4NBr solutions at room temperature but that the rate of the surface reaction was noticeably slower than at 80 °C. Adhesive surfaces of 3 similar to those detected in the 80 °C experiments were apparent after 9 days at room temperature. Polymer 3 undergoes a softening transition at about 80 °C, the temperature employed for the surface reactions. However, the reaction at room temperature shows that 3 need not be heated to the softening transition to induce the surface reaction. But softening of the polymer probably increases the rate of the surface reaction. Although the effect of temperature on the rate of surface hydrolysis was not quantified, it seems clear that temperature variations can be used to control the rate of the reaction. Similarly, it appears that the rate of surface modification can be controlled by variations in the concentration of NaOH and/or Bu_4NBr. Reactions to generate adhesive surfaces were also carried out with KOH/Bu_4NBr or Bu_4NOH solutions.

Surface Analysis of the Modified Films. On the basis of the solution reactions of the model compound 5 (Scheme II), it was suspected that Bu_4NBr facilitates a nucleophilic replacement of trifluoroethoxy side groups by $-O^-NBu_4^+$ groups at the film surface (Scheme III). If the reaction illustrated in Scheme III does occur, then the modified films should undergo exchange reactions with cationic dyes but not with anionic dyes. This was found to be the case.

Surface-treated films of 3 that were immersed in aqueous solutions of the cationic dye methylene blue instantly adopted the dye's blue color and retained the color after extended immersion in pure water to remove loosely adsorbed dye. However, immersion of the treated films of 3 in aqueous solutions of the anionic dye Biebrich scarlet resulted in no permanent color change. Control experiments showed that both untreated films of 3 and films of 3 that had been treated with 8 M NaOH alone or in 0.05 M Bu_4NBr solutions at 80 °C did not become colored when immersed in the cationic or anionic dyes.

The staining by methylene blue allowed the approximate depth of the surface reaction to be measured by optical microscopic examination of a cross section of the dyed film.[16] The depth of reaction was estimated by means of a calibrated eye piece. The data are illustrated in Figure 1 and show a nonlinear increase in the depth of modification as a function of reaction time. The reduction in penetration rate can be attributed to a decrease in the concentration of the active species, Bu_4NOH, at increasing distances from the surface due to diffusion effects. In addition, replacement of trifluoroethoxy side groups by tetra-*n*-butylammonium hydroxyl side groups probably becomes more difficult as the reaction progresses (see Schemes II and III and later comments).

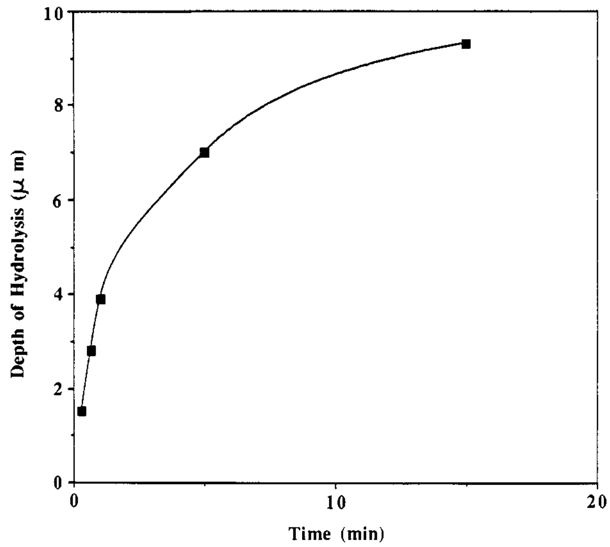


Figure 1. Depth of surface hydrolysis of $[NP(OCH_2CF_3)_2]_n$ as a function of reaction time.

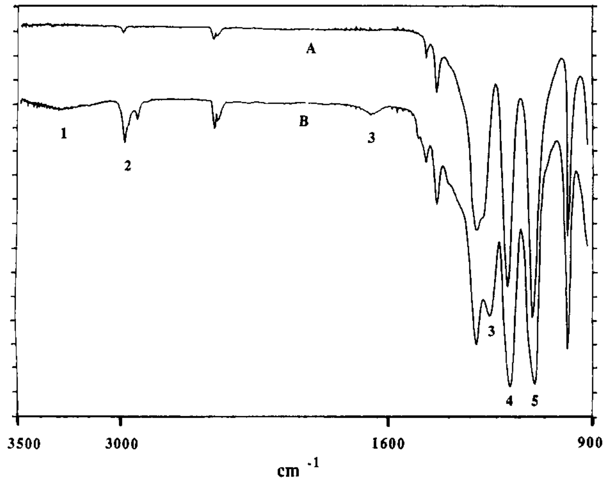


Figure 2. Attenuated total internal reflectance infrared spectra of the surface of $[NP(OCH_2CF_3)_2]_n$ (A) before surface hydrolysis and (B) after treatment for 1 min with an aqueous 8 M NaOH/0.05 M Bu_4NBr solution at 80 °C. The assignments for absorption peaks of interest are (1) OH or H_2O, (2) aliphatic C–H stretching mode from CH_2 units in OCH_2CF_3 and butyl units, (3) Bu_4N^+ units, (4) the phosphazene skeleton, and (5) CF_3 groups.

The ATR-IR spectra of films of 3 before reaction and after 1 min of reaction in 8 M NaOH/0.05 M Bu_4NBr solutions at 80 °C are shown in Figure 2. The ATR-IR spectra are sensitive to the composition of *approximately* the top 1 μm of the polymer surface.[17] On the basis of the depth profiling data in Figure 2, the surface reaction should be detectable by this method. Spectrum A of the pristine film showed aliphatic C–H stretches at 2950 cm^{-1} for the methylene unit of the trifluoroethoxy groups. Enhanced absorptions at 2850–3000, 1647, and 1300–1600

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[17] Harrick, N. J. *Internal Reflection Spectroscopy*; Interscience: New York, 1967.

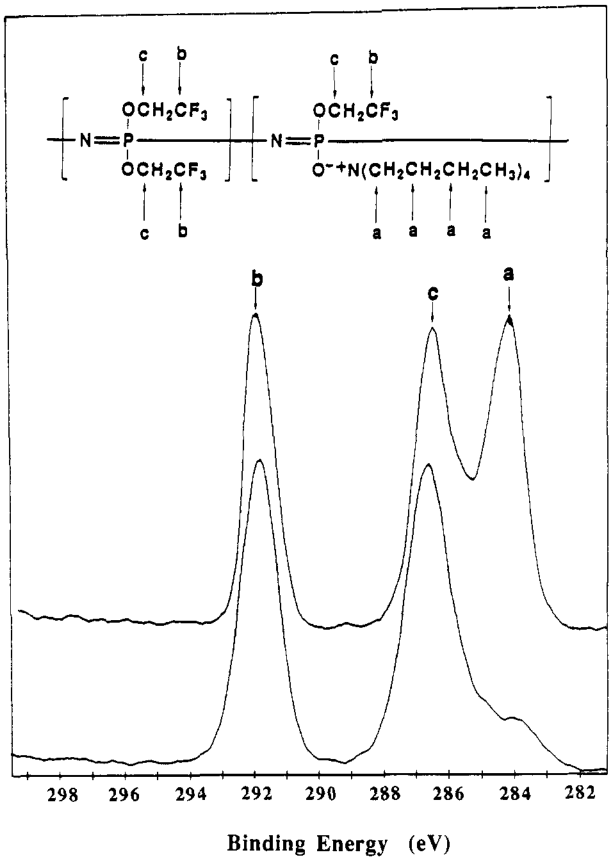

Figure 3. X-ray photoelectron spectrum of the surface of $[NP(OCH_2CF_3)_2]_n$ before (lower spectrum) and after surface hydrolysis, showing the C 1s binding energies.

cm^{-1} were detected in the ATR-IR spectrum of the treated film (spectrum B), and on the basis of the transmission IR spectrum of Bu_4NBr, these were assigned to tetra-*n*-butylammonium hydroxyl groups present on the film surface. It is noteworthy that large amounts of surface hydroxyl groups (3500–3200 cm^{-1}) or P–OH groups (2700 cm^{-1}) were not detected in the ATR-IR spectrum B. The broad, low-intensity absorption at 3200–3400 cm^{-1} in spectrum B was tentatively assigned to adsorbed water associated with the hygroscopic tetra-*n*-butylammonium sites on the film surface. Little change in the ATR-IR spectra was detected with longer reaction times. No significant changes in the ATR-IR spectra below 1300 cm^{-1} were detected following the surface reaction.

X-ray photoelectron spectroscopic (XPS) analysis was also carried out. In contrast to the ATR-IR measurements, the XPS measurements are sensitive to the composition of the outer 50–100 Å of the film surface.[18] XPS spectra of untreated 3 and the fluoroalkoxyphosphazene elastomer 4 have been reported in the literature.[2,19] In the present work, the untreated polymer yielded one O 1s peak (535 eV), one N 1s peak (400 eV), one P 2p peak (136 eV), one F 1s peak (689 eV), and two C 1s peaks (294, 289 eV), and this is consistent with the bulk structure of 3. It was necessary to wash films of 3 in hexane to remove traces of silicon-containing contaminants (probably organosiloxanes from stopcock grease) that had migrated to the surface.

After the surface treatment, films of 3 were immersed in distilled–deionized water for several minutes to remove loosely adsorbed species, and the films were dried under vacuum. The surface elemental analysis of the modified films after 1 min of treatment with the 8 M NaOH/0.05 M Bu_4NBr solution at 80 °C indicated an 8% increase in carbon and a 7% decrease in fluorine concentrations at the surface. This is consistent with the reaction shown in Scheme III. The XPS analysis suggested an approximate surface formula of $[NP(OCH_2CF_3)_{1.80}(OBu_4N)_{0.20}]_n$.

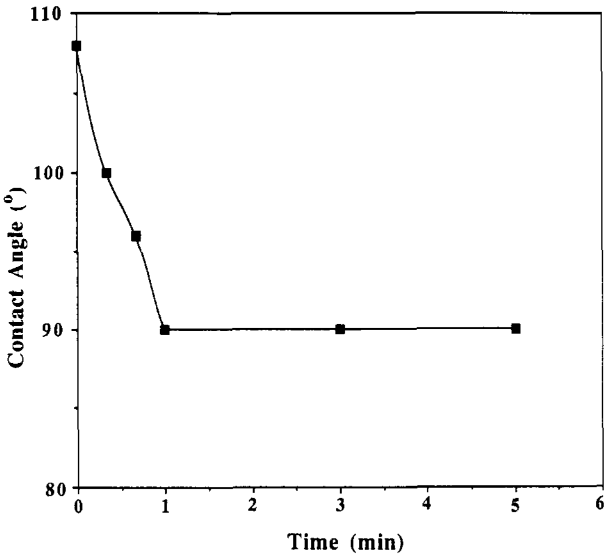

Figure 4. Hydrophobicity of the surface of $[NP(OCH_2CF_3)_2]_n$, as measured by water droplet contact angle, as a function of reaction time when films of the polymer were treated with aqueous 8 M NaOH/0.05 M Bu_4NBr at 80 °C.

In addition to the change in elemental composition at the surface, a new C 1s peak at 285 eV and a new N 1s peak at 405 eV were detected after the reaction. These new peaks were assigned to the tetra-*n*-butylammonium cation. The C 1s spectra before and after the surface reaction are shown in Figure 3. No new O 1s, P 2p, or F 1s peaks were detected in the XPS spectra after the reaction. In control experiments, no major changes in the XPS spectra were detected when films of 3 were immersed in 8 M NaOH alone or in 0.05 M Bu_4NBr solutions at 80 °C for 1 min.

It is important to note that the XPS spectra of the films after the reaction showed that significant amounts of sodium (from NaOH) or bromine (from Bu_4NBr) were not present in the film surface. In addition, elemental analysis for sodium and bromine of bulk films of 3 that had been hydrolyzed in 8 M NaOH/0.05 M Bu_4NBr at 80 °C for 24 h and washed with water also suggested that sodium and bromine were not incorporated into the modified films.

Changes in the surface hydrophilicity of 3 as a function of immersion time in the 8 M NaOH/0.05 M Bu_4NBr reagent at 80 °C were measured by contact-angle analysis (using drops of unbuffered, distilled–deionized water, pH = 5.6).[20] Contact-angle measurements are sensitive to the composition of the outer 5–10 Å of a surface. Untreated films of 3 are hydrophobic, with a water contact angle of 108°. Replacement of trifluoroethoxy side groups by ionic tetra-*n*-butylammonium hydroxyl side groups (Scheme III) would be expected to increase the hydrophilicity. This was found to be the case (Figure 4).

The variation of contact angle as a function of immersion time in the 8 M NaOH/0.05 M Bu_4NBr solution at 80 °C is shown in Figure 4. Although the surface became more hydrophilic following the initial treatment, exposure to the reagent solution for more than 1 min did not bring about

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(18) Gardella, J. A. *Appl. Surf. Sci.* **1988**, *31*, 72.

(19) Hiraoka, H.; Lee, W. Y.; Welsh, L. W.; Allen, R. W. *Macromolecules* **1979**, *12*, 753.

(20) Yasuda, H.; Sharma, A. K. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1285.

a further increase in the surface hydrophilicity. It is perhaps surprising that the minimum contact angle was 90°, and this indicated that appreciable hydrophobic character remained. This residual surface hydrophobicity can be explained by the presence of *n*-butyl and/or trifluoromethyl groups in the top 5–10 Å of the surface or by the fact that the extent of the surface reaction is quite low. Although water does not progressively wet the surface of untreated **3** over a period of time, the surface of modified **3** was progressively wetted over a period of 15 min. This suggested that water interacts with and perhaps reacts with the modified surface. Although surface roughness can affect contact angle measurements, SEM analyses of the modified surfaces showed that the surface texture did not change.

The contact angles of water on the modified surfaces were found to be insensitive to the acidity or basicity of the water drop (pH of 3 or 10, buffered). This suggests that, although an anionic hydroxyl surface is formed by the reaction, instantaneous acid–base reactions do not occur at the solid–liquid interface. This contrasts with the behavior of carboxylic acid groups generated by surface oxidation of polyethylene[21] or sulfonic acid groups in surface-sulfonated polystyrene.

Attempted Reconstruction of the Modified Surface. It is known that polymer surfaces may reorganize in different environments or at different temperatures.[2,22] Typically, if a polymer is exposed to a polar environment, polar functional groups may migrate to the surface. In a nonpolar environment, nonpolar functional groups in the polymer will migrate to the surface. These reorganizations may or may not be reversible, and the thermodynamic and kinetic factors that govern the reversibility of surface reconstruction are only poorly understood. A characteristic feature of phosphazene polymers is the facile torsional mobility of the polymer backbone. For example, the T_g of **3** is −66 °C. Thus, a room temperature, **3** is well above its T_g, and the polymer backbone can undergo torsional motions that should facilitate a surface reconstruction. Reconstruction should also be facilitated by heating the polymer to the phase transitions at 80 °C.

The reacted polymer surface shown in Scheme III is potentially amphiphilic, since both the ionic tetra-*n*-butylammonium hydroxyl side groups and the hydrophobic trifluoroethoxy side groups are present. In the experiments described in the previous sections, the reacted films of **3** were removed from the aqueous NaOH/Bu_4NBr reagent, rinsed with distilled–deionized water for several minutes, and dried under vacuum. No change in adhesion (as defined previously) was apparent when modified films of **3** were exposed to the air or water over extended periods of time.

It was anticipated that the surface free energy of the film would perhaps be minimized if low surface energy trifluoroethoxy groups were induced to replace tetra-*n*-butylammonium groups at the film surface by heat treatment or by placement in a nonpolar environment (see Experimental Section). However, surface-treated films of **3** retained their adhesive character after being heated to 80 °C under vacuum. Similarly, when the reacted films of **3** were immersed in boiling hexane, the adhesive surface properties remained. In these experiments, surface reconstruction to form a hydrophobic surface composed principally of trifluoroethoxy side groups could not be detected by ATR-IR analysis, by contact-angle analysis, or by exchange reactions with cationic dyes.

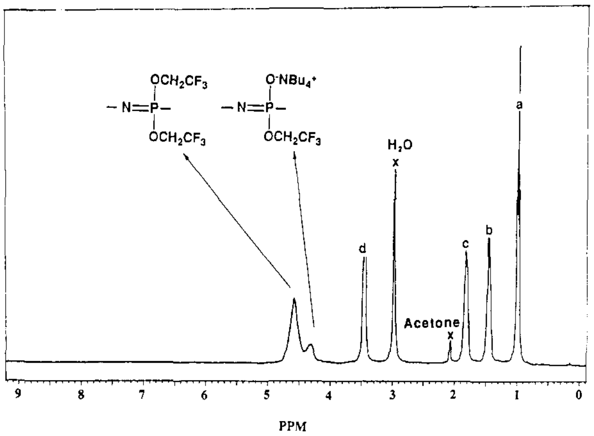

Figure 5. ^{1}H NMR spectrum of an acetone solution made from a film of $[NP(OCH_2CF_3)_2]_n$ treated for 24 h with aqueous 8 M NaOH/0.5 M Bu_4NBr at 80 °C.

Surface-treated films of **3** immersed in ethanol lost their capacity to adhere to metals polymers or ceramics. However, it was clear that ethanol slowly *dissolved* the surface material from the bulk of the film and that the loss of adhesive character was not due to reconstruction. Despite these changes, it should be noted that ATR-IR analysis, contact-angle analysis, and exchange reactions with cationic dyes indicated that some tetra-*n*-butylammonium hydroxyl groups were still present on the film surface after immersion in ethanol.

Several reasons for the apparent lack of reconstruction of the modified surfaces can be given. The process may not be thermodynamically favored despite the ionic character of the surface, due to the hydrophobic character of butyl groups or the relatively small differences in surface energies. The ionic character of the hydroxyl side groups may become sufficiently important to drive a reorganization only when the ions are dissociated. Also, even if the reconstruction process is favored thermodynamically, the process may be blocked kinetically. For example, the stronger mechanical integrity of the bulk of the polymer relative to the surface could, in principle, slow a reconstruction process.

NMR and GPC Analysis of the Surface-Modified Films. It seemed likely that a prolonged surface reaction might be sufficiently pervasive to allow classical *solution* methods of analysis, such as NMR, to be applied to the system. Thus, the surface reaction of **3** in 8 M NaOH/0.05 M Bu_4NBr solution at 80 °C was allowed to proceed for 24 h, and the modified films were then immersed in water for several hours and were dried under vacuum. The films were gellike and retained little mechanical strength. This prevented an accurate measurement of the depth of reaction by dye exchange. However, the films were still completely soluble in THF or acetone. The ^{1}H NMR spectrum of the modified film dissolved in acetone-d_6 is shown in Figure 5.

The ^{1}H NMR spectrum of unreacted **3** consists of a methylene resonance for the trifluoroethoxy groups at δ 4.6. The ^{1}H NMR spectrum for the hydrolyzed film (Figure 5) consisted of two sets of trifluoroethoxy resonances (δ 4.6, 4.2), four resonances for the *n*-butyl protons (δ 1.0, 1.5, 1.9, and 3.4), and a resonance for residual water (δ 3.3). This water could not be removed completely under vacuum, and its presence was attributed to the hygroscopic nature of tetra-*n*-butylammonium salt units. As mentioned previously, water was also detected from the

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(21) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921.

(22) Gagnon, D. R.; McCarthy, T. J. *J. Appl. Polym. Sci.* **1984**, *29*, 4335.

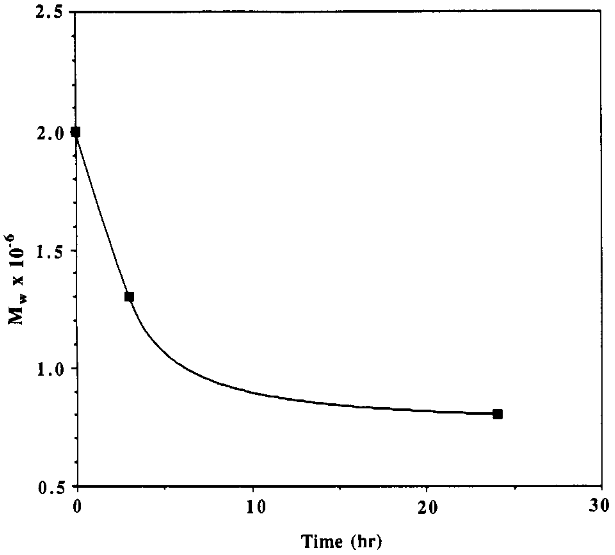


Figure 6. Plot of molecular weight versus time for the polymer obtained by the heterophase treatment of a film of $[NP(OCH_2CF_3)_2]_n$ with an aqueous solution of 8 M NaOH/0.05 M Bu_4NBr at 80 °C. The molecular weight values were obtained by gel permeation chromatography with the system calibrated by polystyrene standards.

ATR-IR spectra of the modified film surfaces.

The δ 4.6 resonance was assigned to trifluoroethoxy side groups geminal to another trifluoroethoxy structure, while the δ 4.2 peak was assigned to trifluoroethoxy side groups that were adjacent to geminal tetra-*n*-butylammonium hydroxyl side groups.[14] The degree of replacement of trifluoroethoxy side groups by tetra-*n*-butylammonium hydroxyl side groups could be estimated by integration of the trifluoroethoxy and the *n*-butyl resonances. Approximately 34% of the side groups were tetra-*n*-butylammonium hydroxyl units after 24 h of hydrolysis.

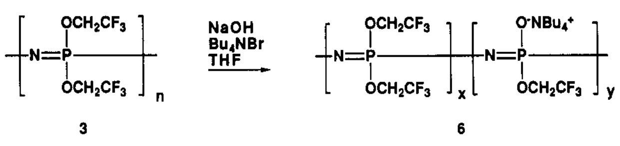
The ^{13}C NMR spectrum of unreacted **3** consisted of a quartet centered at δ 63 for the methylene carbon of the trifluoroethoxy group and a quartet centered at δ 120 from the CF_3 carbon of the trifluoroethoxy group. The ^{13}C NMR spectrum of the modified polymer consisted of the four *n*-butyl carbon resonances (δ 12, 19, 23, and 57) and the two trifluoroethoxy quartets.

The ^{31}P NMR spectrum of **3** in acetone before reaction consists of a singlet at δ −4. However, the ^{31}P NMR spectrum of the modified polymer consisted of a singlet at δ −4 plus two minor broad resonances at δ −1 and −6. The sharp singlet was attributed to unreacted $P(OCH_2CF_3)_2$ units, and the broad resonances were assigned to hydrolyzed units. The trifluoroethoxy fluorine atoms (δ 39.3) were detected in the ^{19}F NMR spectra of both the unmodified and modified films. Thus, the NMR spectra were consistent with the belief that tetra-*n*-butylammonium hydroxyl side groups had replaced some of the trifluoroethoxy side groups at the surface (Scheme III).

The solubility of the grossly modified films also allowed analysis by gel permeation chromatography (GPC). In Figure 6, the GPC average molecular weight of the modified polymer is shown as a function of immersion time in 8 M NaOH/0.05 M Bu_4NBr solution at 80 °C. A slight but statistically significant decrease in molecular weight was detected with increasing reaction time.

Although some change in hydrodynamic volume may occur with the hydrolysis reaction and this may affect the GPC measurements, changes were also found in the molecular weight distribution of the polymer. A bimodal molecular weight distribution was present before and after the reaction. However, after the reaction, the proportion of the higher molecular weight fraction was reduced relative to that of the lower molecular weight component. Replacement of the trifluoroethoxy side groups (99 g/mol) by tetra-*n*-butylammonium hydroxyl side groups (258 g/mol) would increase the M_w slightly. In control experiments, no change in molecular weight was detected by GPC analysis when films of **3** were immersed in 8 M NaOH only or in 0.05 M Bu_4NBr solutions at 80 °C for 24 h.

Scheme IV



Hydrolysis of Solutions of 3 by NaOH/Bu_4NBr in THF. The hydrolysis reaction of solutions of **3** by NaOH in the presence of Bu_4NBr in refluxing THF (66 °C) was also investigated in order to provide further information about possible reactions that may occur during the surface reaction. Polymer **3** was dissolved in THF, NaOH and Bu_4NBr were added, and the reaction mixture was heated to reflux and monitored by ^{31}P NMR spectroscopy.

The ^{31}P NMR spectrum of **3** in THF solution consists of a singlet at δ −8. A new resonance appeared at δ −6 as hydrolysis progressed. This resonance was also detected in the surface modified films and was assigned to $P(OCH_2CF_3)(O^-Bu_4N^+)$ phosphorus atoms. Consistent with the model-compound studies (Scheme II), the spectra showed that the hydrolysis reaction proceeded by a nongeminal mechanism. After 90 min of hydrolysis, the ^{31}P NMR spectrum still consisted only of the δ −6 and −8 resonances. Hydrolysis of **3** by NaOH/Bu_4NBr for 9 h in refluxing THF generated broad peaks in the ^{31}P NMR spectrum over a range δ 4 to −8.

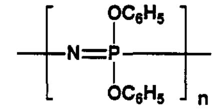
After 90 min of hydrolysis, analysis of the ^{31}P NMR spectrum indicated that approximately 20% of the trifluoroethoxy side groups had been replaced by tetra-*n*-butylammonium hydroxyl side groups (Scheme IV). This polymer is designated as structure **6**. Polymer **6**, when isolated from solution, was gellike, adhesive, and stable to the atmosphere over extended periods of time. It did not cross-link, despite the presence of the hydroxyl side groups.

The ^1H NMR spectrum of **6** matched that of the surface modified films. According to the ^1H NMR analysis, water was present in **6** despite drying, which indicated that **6** was hygroscopic (as were the surfaces of the modified films). In addition, the ^{13}C and ^{19}F NMR spectra of **6** were identical with the spectra of the surface-reacted films. The transmission IR spectrum of **6** was also very similar to that of the surface-modified material and showed the characteristic absorptions of the tetra-*n*-butylammonium hydroxyl side groups.

GPC analysis of **3** before the solution hydrolysis reaction indicated an M_w of 3.9×10^5. After hydrolysis for 90 min, a GPC analysis of **6** indicated a slightly lower M_w of 2.4×10^5. Although the change was small, the result suggests that a limited amount of chain cleavage may occur in the solution hydrolysis as well as during the surface hydrolysis. From these data, it appears that the reactions at the surface of **3** resemble closely those of **3** in solution.

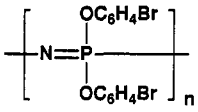
Surface Treatment of Fluoroalkoxyphosphazene Elastomers and Other Phosphazene Polymers. The surface reactions of a commercial fluoroalkoxyphosphazene elastomer (**4**) was examined briefly. This elastomer is composed of approximately 65% trifluoroethoxy side groups and 35% mixed, longer chain fluoroalkoxy side groups. The commercial product is also cross-linked and contains additive materials. Hence, differences in the rates of surface reaction for 3 and 4 might be expected. When samples of 4 were immersed in 8 M NaOH/0.05 M Bu_4NBr solution at 80 °C for 6 h, the surfaces became adhesive, although the changes were much slower than for polymer 3.

Films of the phosphazene polymers poly(diphenoxyphosphazene) (7), poly[bis(*p*-bromophenoxy)phosphazene] (8), and poly[bis(2-phenoxyethoxy)phosphazene] (9) were immersed in 8 M NaOH/0.05 M Bu_4NBr solutions at 80 °C for six hours. No surface reactions were detected visually or by ATR-IR analysis, and the surfaces did not adhere to metals, ceramics, or other materials. In addition, polymers 7–9 did not react with NaOH/Bu_4NBr in *solution* in refluxing THF after 3 h. The phenoxy analogue of 3, $[NP(OC_6H_5)_2]_n$, has been reported to be resistant to hydrolysis by NaOH under conditions that will induce the hydrolysis of 5.[23] Thus, the trifluoroethoxy side group appears to provide a special opportunity for surface reactions with polyphosphazenes. This is a consequence of its high reactivity as a leaving group.



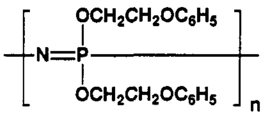
$$\left[-N{=}\overset{OC_6H_5}{\underset{OC_6H_5}{P}}-\right]_n$$

7



$$\left[-N{=}\overset{OC_6H_4Br}{\underset{OC_6H_4Br}{P}}-\right]_n$$

8



$$\left[-N{=}\overset{OCH_2CH_2OC_6H_5}{\underset{OCH_2CH_2OC_6H_5}{P}}-\right]_n$$

9

Mechanism of Adhesion. In the past 50 years, many theories have been proposed to explain adhesion, and numerous interrelated physical, chemical, mechanical, and rheological factors have been identified that appear to influence the adhesion of materials.[24-26] Much disagreement still exists about the relative importance of each factor for specific systems, since it is difficult to analyze an adhesive joint nondestructively or to isolate the influence of one factor from others. A survey of the literature indicates that the adhesive properties of phosphazene polymers is an area that has not yet been explored extensively.

Several processes occur at the polymer surface when films of 3 are immersed in hot, aqueous NaOH/Bu_4NBr solutions. These include the generation of ionic, hygroscopic tetra-*n*-butylammonium hydroxyl side groups, formation of a gellike surface, an increase in surface hydrophilicity, and limited chain cleavage. All of these changes can, in principle, contribute to adhesion of the reacted films to the surfaces of common substrates such as metals, glasses, polymers, ceramics, or living tissue.

The gellike character of the surface could allow the polymer chains to penetrate into the microcrevices of the substrate surface. Ionic groups at the surface increase the hydrophilicity and allow the polymer to wet the surface of a polar substrate. In addition, the ionic hydroxyl side groups can hydrogen-bond to hydroxyl groups on the substrate surface and can generate ion–dipole/ion–ion forces at the interface. Thus, at a qualitative level, the adhesive properties of the surface-hydrolyzed phosphazene polymer can be rationalized in terms of molecular structure and current views concerning adhesion.

Experiments indicated that the cation associated with the hydroxyl side group at the surface of the reacted films plays a role in determining the adhesive behavior. For example, when the surface modified films were soaked in aqueous solutions of sodium, potassium, calcium, magnesium, copper(II), or iron(III) chloride for 24 h at 50 °C, the films lost their adhesive character. Furthermore, films soaked in solutions of the divalent cations were clearly more brittle than those exposed to solutions of the monovalent cations. This presumably reflects an ionic cross-linking by the divalent or trivalent metal cation at the surface. ATR-IR experiment analysis after this treatment suggested that the tetra-*n*-butylammonium groups were no longer present. Adhesive films could also be generated by the surface modification of 3 in aqueous potassium hydroxide solutions with 18-crown-6 ether present as phase transfer agent.

Conclusions

The linkage of tetra-*n*-butylammonium hydroxyl groups to the surface of other polymers may generate adhesive character for these species as well. Polymers that possess quaternary ammonium salt side groups have shown enhanced antibacterial activity,[27] and anionic sites at polymer surfaces typically improve the blood compatibility of a polymer.[2] Further experiments to modify the surfaces of 3 with other nucleophiles and to test effects of surface reactions on the biological properties of 3 are in progress.[28]

In general, a need exists to develop the surface chemistry of phosphazene polymers, and it is significant that the reactions that take place at the surface of 3 are very similar to those that occur in solution. Thus, the solution reactions of phosphazene polymers appear to "model" the surface reactions of the same material. The generation of hydroxyl side groups also offers opportunities for further functionalization of the polymer surfaces.

Experimental Section

Materials. Compound 1 was provided by Ethyl Corp. (Baton Rouge, LA) and was recrystallized from hexane before use. Polymer 2 was obtained by the thermal ring-opening polymerization of 1 at 250 °C. Tetra-*n*-butylammonium bromide (Aldrich) and 18-crown-6 ether (Aldrich) were used as received. Tetra-*n*-butylammonium hydroxide (Aldrich) was obtained as a 40% aqueous solution. Biebrich scarlet (Aldrich) and methylene blue (Aldrich) were used as received. Distilled water was passed through a Millipore ion-exchange resin before use. Commercial fluoroalkoxyphosphazene O-rings 4 were provided by Ethyl Corp. THF and toluene were distilled from sodium benzophenone under a nitrogen atmosphere. The syntheses of 3,[5] 7,[5] and 8[29] are described elsewhere.

Instrumentation and Methods. NMR spectra were obtained with the use of either a JEOL FX90Q or a Bruker WP-360 NMR spectrometer, with ^{31}P chemical shifts referenced to aqueous 85% phosphoric acid and ^1H spectra to acetone-d_6. IR spectra were obtained with use of a Perkin-Elmer 1710 FT-IR spectrometer. GPC data were obtained by means of a Hewlett-Packard HP1090 liquid chromatograph equipped with Polymer Lab PLGel columns

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(10^6, 10^6, 10^3 Å) and a refractive index detector. The mobile phase was a 0.1% solution of tetra-*n*-butylammonium bromide in THF. The GPC columns were calibrated with narrow molecular weight polystyrene standards.

ATR-IR spectra were obtained with the Perkin-Elmer 1710 FT-IR spectrometer equipped with an ATR attachment (Harrick Scientific Corp., Ossining, NY). A germanium (Ge) internal reflection element (45°) was positioned at a 45° angle with respect to the incident IR beam. Both faces of the Ge crystal were covered with polymer film. The intensity of the IR beam at the detector was maximized by adjusting the positions of the Ge crystal and the reflecting mirrors. One hundred scans were averaged. A resolution of 2 cm^{-1} was employed. The Ge crystal was cleaned with carbon tetrachloride before and after use.

Contact-angle measurements were obtained with a Rame-Hart contact angle goniometer equipped with a telescope, an environmental chamber, and a Gilmont syringe fitted with a 24-gauge flat-tipped needle. The polymer films were mounted on microscope slides by means of double-sided adhesive tape. Polymer films were placed in the environmental chamber, the atmosphere of which was saturated with water vapor. A 1-μL drop of unbuffered, distilled–deionized water was suspended from the syringe needle above the film surface, and the needle was lowered carefully until the water drop was placed onto the polymer surface. The needle was raised carefully, and the contact angle measurement was made on both sides of the drop (within 30 s). The contact angle values reported are averages of five measurements made on different areas of the film surface. Scatter in the data was 5° or less.

X-ray photoelectron spectra (XPS) were recorded at the Perkin-Elmer Physical Electronics Laboratory (Edison, NJ) on a Perkin-Elmer-Physical Electronics 5000 LS spectrometer. A monochromatic X-ray source using an Al anode (Al Kα = 1486.6 eV) operated at 600 W (15kJ, 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 65° takeoff angle. Atomic composition data were determined by using the instrument's computer and programmed sensitivity factors. Scanning electron microscopic analysis was performed with the use of an ISI SX-40A instrument.

Adhesion Testing. A film of **3** was immersed in 8 M NaOH/0.05 M Bu$_4$NBr solution at 80 °C for 5 min. The film was rinsed with distilled–deionized water for 5 min and dried under vacuum for 1 h. The adhesive film was pressed with Teflon forceps onto degreased aluminum foil. The remaining side of the adhesive film was attached to a glass plate via double-sided adhesive tape. Strips of aluminum foil 3.2 cm wide were cut with a razor blade, and a tab was carefully initiated. Tabs were pulled with an Instron 4201. The peel angle was 90°, and data were collected when the films were between 85 and 95°. Tabs were pulled at a crosshead speed of 10.00 mm/min. Four runs were averaged, and values of 14.1, 23.2, 19.1, and 22.6 mN/mm were obtained.

Surface Reaction Experiments. The aqueous NaOH/Bu$_4$NBr solutions (typically 30 mL) were prepared in a clean glass jars, and the solutions were heated to 80 °C with an oil bath. Polymer films were handled at the edges with Teflon-coated forceps. It should be noted that at an 8 M concentration of NaOH, much of the Bu$_4$NBr is insoluble in the aqueous solution, and the insoluble material floats to the surface of the solution. The films were immersed below the surface of the NaOH/Bu$_4$NBr solutions for the required period of time. They were then quickly removed, gently rinsed with and immersed in distilled–deionized water for several minutes, and dried under vacuum for at least an hour.

Depth Profiling Data. Modified films of **3** were immersed in a 2×10^{-2} M aqueous solution of methylene blue for 48 h at room temperature. The dyed films were then immersed in distilled–deionized water for 48 h until no additional free dye was removed from the films. Cross sections of the films were examined with a light microscope (1500×) equipped with a calibrated eye piece.

Reaction of 3 with NaOH/Bu$_4$NBr in THF. Polymer **3** (1.0 g, 0.17 mmol P–Cl) was dissolved in 15 mL of THF, and Bu$_4$NBr (1.0 g, 3.1 mmol) and NaOH (1.0 g, 25 mmol) were added. The heterogeneous mixture was heated to reflux with an oil bath, and aliquots of the solution were removed for ^{31}P NMR analysis. The isolation of **6** consisted of decanting the THF solution from excess NaOH, concentration of the solution by rotary evaporation, and precipitation of the polymer into distilled-deionized water (four times) to remove salts. Polymer **6** was dried under vacuum.

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Registry No. **8** (SRU), 52734-85-7; **9** (SRU), 133294-79-8; [NP(OCH$_2$CF$_3$)$_2$]$_n$ (SRU), 28212-50-2; BuN$^+$Br$^-$, 1643-19-2; [Np(Ph)$_2$]$_n$ (SRU), 28212-48-8; methylene blue, 61-73-4; Biebrich scarlet, 4196-99-0.