

into deionized water (3×), hexane (3×), and ethanol (1×). A tough, white polymer was recovered. Characterization data:  $^1\text{H}$  NMR 7.0-7.5 (m), 2.3 (s);  $^{13}\text{C}$  NMR 149.6, 132.1, 129.1, 121.0, and 20.6 ppm;  $^{31}\text{P}$  NMR 19.6 ppm (s);  $T_g = -2^\circ\text{C}$ ;  $M_w = 3.6 \times 10^6$ . Elemental analysis: Calcd C, 64.86; H, 5.44; N, 5.40; Cl, 0.0. Found: C, 64.78; H, 5.24; N, 5.71; Cl, 0.3.

**Preparation of Polymer Films.** The polymer was dissolved in dry, distilled THF. The solutions were filtered and then cast in a dust-free drybox 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 samples were removed from the drybox and were placed in a vacuum oven at  $80^\circ\text{C}$  for 48 h. Films were then peeled from the glass plate.

**Radiation Cross-Linking of Films.** Samples were dried under vacuum for 24 h and were sealed in an evacuated glass container. The films were then exposed to  $^{60}\text{Co}$   $\gamma$  rays at a dose rate of 0.23 Mrad/h.

**Model Reactions.** Powdered cyclic trimer 2 was stirred as a suspension in an aqueous solution of  $\text{KMnO}_4$  (0.04 M) and  $\text{NaOH}$  (0.02 M) for 24 h at  $80^\circ\text{C}$ . The excess  $\text{KMnO}_4$  was deactivated with ethanol, and the  $\text{MnO}_2$  precipitate was removed by reduction with  $\text{NaHSO}_3$ . The solution was acidified and the products were then isolated by liquid-liquid extraction.

**Procedure for Surface Oxidation of Polymer Films.** Films of polymer 1 were immersed in an aqueous solution containing  $\text{KMnO}_4$  (0.04 M) and  $\text{NaOH}$  (0.02 M) for various times and temperatures. The films were then removed from the reaction solution and were soaked in an aqueous  $\text{NaHSO}_3$  solution for 5 h in order to remove the  $\text{MnO}_2$ . Finally, the films were soaked in and stored in deionized water.

**Protonation of the Oxidized Surfaces.** Oxidized film samples were soaked in dilute  $\text{HCl}$  solutions ( $\text{pH} = 3$ ) for 24 h at room temperature. The films were then rinsed and stored in deionized water.

**Reduction of the Oxidized Surfaces with  $\text{LiAlH}_4$ .** Oxidized film samples that had been protonated were vacuum-dried over-

night and then placed in a 0.5 M solution of  $\text{LiAlH}_4$  in diethyl ether at room temperature. The films were allowed to react for 4 h, during which time vigorous bubble formation occurred at the polymer surface. The surfaces were deactivated by immersion in cold ethanol. The films were then soaked and sonicated in deionized water before storage in deionized water.

**Immobilization of 4-Nitrofuroic Ester.** The reduced film samples were vacuum-dried for at least 24 h. A solution of 4-nitrofuroyl chloride (0.5 g) in dry DMF (300 mL) was prepared. The film sample was immersed in the solution, and triethylamine (1 mL) was then added. The reaction was allowed to proceed for 6 h at  $40^\circ\text{C}$ . The film was removed from the reaction medium and was rinsed with and soaked in DMF for 12 h. The film was then vacuum-dried and stored under nitrogen.

**Formation of the Active Ester.** Oxidized film samples were vacuum-dried for at least 24 h. A solution of *N*-hydroxysuccinimide (0.4 g) was prepared in dry DMF (30 mL). The film samples were immersed in the solution, and DCC (1.0 g) was added. The reaction was allowed to proceed for 12 h at  $40^\circ\text{C}$ . The films were then removed from the reaction solution and were rinsed with and soaked in DMF for 12 h.

**Immobilization of Oligopeptides.** The tetrapeptide Arg-Gly-Asp-Ser (0.4 g) was dissolved in dry DMF (30 mL). Films with the activated ester surface groups were immersed in this solution for 24 h at  $40^\circ\text{C}$ . The films were then rinsed extensively and soaked in both DMF and deionized water.

**Ion-Exchange Reactions.** Previously oxidized films were immersed 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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## Thin-Layer Grafts of Poly[bis((methoxyethoxy)ethoxy)phosphazene] on Organic Polymer Surfaces

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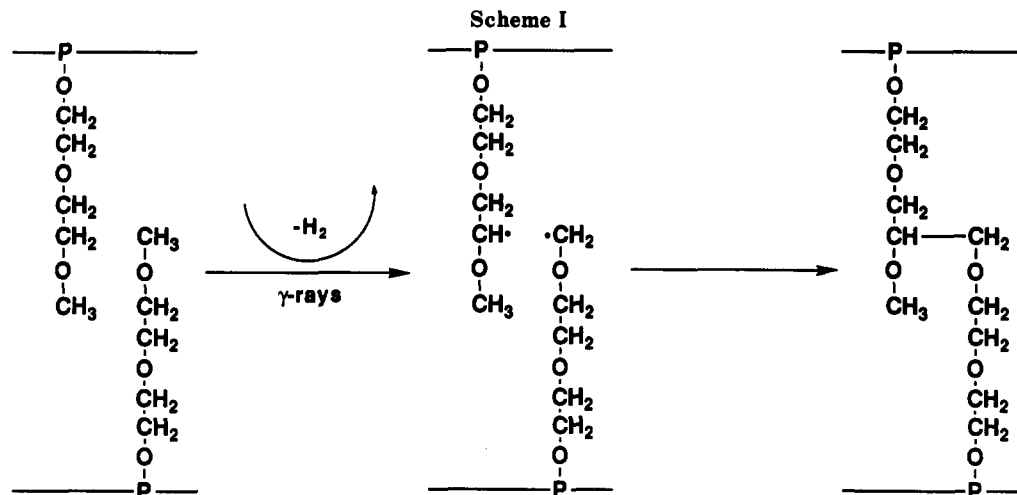
Poly[bis((methoxyethoxy)ethoxy)phosphazene] (1) was covalently bonded and cross-linked to the surfaces of several organic polymers. Polypropylene, poly(vinyl chloride), poly(ethylene terephthalate), poly(bisphenol A carbonate), and poly(methyl methacrylate) were coated with polymer 1, and the coated materials were then exposed to 5 Mrad of  $^{60}\text{Co}$   $\gamma$ -rays. The resultant surfaces were studied by ATR-IR, XPS, SEM, and contact angle techniques. The modified surfaces showed marked increases in hydrophilicity or hydrogel character and are excellent candidates for a number of biochemical, biomedical, and electrochemical uses.

### Introduction

The conversion of a hydrophobic polymer surface to a hydrophilic or hydrogel variant is a challenge that has far-reaching implications in both surface science and technology. For example, polymers of interest as biomedical materials could have appropriate bulk properties but be biomedically incompatible because of their surface characteristics. Tailoring of the surface to generate a bioinert hydrogel layer may be a starting point for ob-

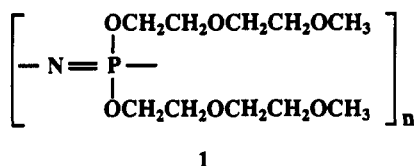
taining a combination of useful properties. In a second example, the development of ionically conducting thin films on the surfaces of hydrophobic polymers offers opportunities for the development of memory devices and display panels. The synthesis and materials processing of such laminate systems is a considerable challenge.

Surface chemistry carried out on polymeric materials provides one approach to solving these and other problems. Polyethylene and polypropylene<sup>1-4</sup> surface oxidations have



been studied in detail. We have used members of a new class of polymers, known as polyphosphazenes, for surface reaction studies that involve hydrolysis,<sup>5-7</sup> sulfonation,<sup>8</sup> nitration,<sup>9</sup> and oxidation,<sup>10</sup> together with the use of the functionalized units for the linkage of bioactive agents to the surfaces.<sup>11</sup>

Here we describe an alternative to these processes, which involves the radiation grafting of an unusual polymer to the surfaces of conventional organic polymers to form molecular-level laminates. The polymer is poly[bis((methoxyethoxy)ethoxy)phosphazene] (1), also known as



MEEP. In the anhydrous state this polymer is an excellent medium for solid ionic conduction.<sup>12-16</sup> The polymer is also soluble in water. Moreover, the solid polymer can be cross-linked by exposure to  $\gamma$ -radiation to yield materials that serve as solid ionic conduction matrices or that absorb water to form hydrogels.<sup>17-21</sup>

Hydrogels are materials which swell in but do not dissolve in aqueous media. A water-soluble polymer cross-linked by covalent or ionic bonding will behave in this way, with the limits to water absorption being controlled by the density of cross-linking. Polymers such as agar, gelatin, poly(vinyl alcohol), poly(acrylic acid), or poly(hydroxyethyl methacrylate) are commonly used to prepare hydrogels. Hydrogels grafted onto the surface of hydrophobic polymers are reported to increase both the hydrophilicity and biocompatibility of the material<sup>22</sup> and to modify the permeability of membranes.<sup>23</sup>

The choice of MEEP for the present studies was made on the basis of its unusual combination of solid state and hydrogel properties and its ease of radiation cross-linking by  $\gamma$ -rays or ultraviolet light.<sup>24</sup> In the radiation cross-linking of 1, an increase in cross-link density eliminates viscous flow and increases the structural stability but decreases the amount of water that can be imbibed. The amount of cross-linking can be controlled easily by variations in the irradiation dose. The rate of cross-link formation is approximately 1 cross-link/1000 repeat units/Mrad. Hydrogels derived from polymer 1 provide a facile pathway for small molecule diffusion,<sup>17,18</sup> an effect that can be attributed to the ease of main-chain and side-group reorientation in this polymer, and the high ratio of water to polymer in the hydrogels, even when the degree of cross-linking is as high as 1 cross-link/25 repeating units. It was considered possible that a thin coating of 1 may impart some of these characteristics to the surfaces of other materials such as widely used classical organic polymers.

The proposed mechanism for the cross-linking of 1 is shown in Scheme I.  $\gamma$ -ray-induced cleavage of the C-H bonds can generate free radicals at any of the five carbon atoms in each side group. Subsequent intermolecular radical combination leads to cross-linking. In most radiation-induced cross-linking reactions the side-group coupling processes are accompanied by backbone cleavage. The inorganic backbone structure in polymer 1 is less

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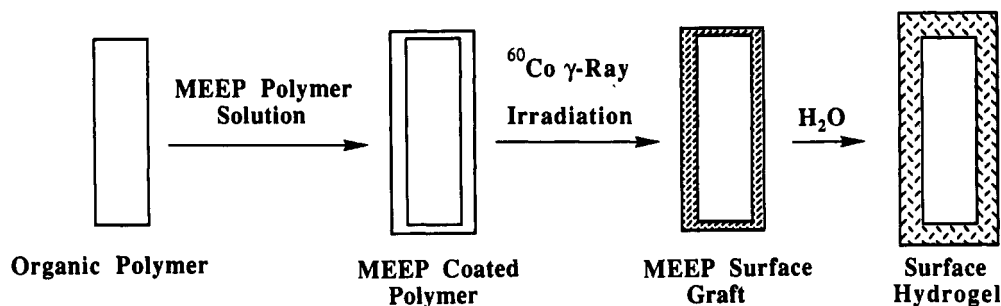
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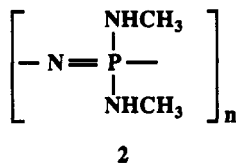
Scheme II. Surface Grafted MEEP Hydrogels on Organic Polymers



sensitive to radiation damage and cleavage than are the backbones in classical organic polymers, even at high radiation doses. This free radical cross-linking mechanism also offers the opportunity for covalent binding of the polymer chains to any substrate that bears surface carbon-hydrogen or carbon-chlorine bonds and especially to those that have aliphatic residues at the surface.

In addition to the biomedical utility of such systems we foresee possible uses for these laminates in the fields of adhesion, gel separation methodology, and the immobilization of living cell, enzymes, and antigens. Access to thin film ionic conductors also opens up many possibilities in electrooptical device design.

The three objectives of this study were (a) to investigate the interaction and adsorption of poly[bis((methoxyethoxy)ethoxy)phosphazene] (1) on the surfaces of solid polymers, (b) to determine if 1 can be covalently grafted onto the surfaces of organic polymers, and (c) to investigate how such grafts might affect the surface properties of the supporting polymers. As part of the attempt to probe the mechanism of grafting, the behavior of MEEP was compared with that of poly[bis(methylamino)phosphazene] (2), a polymer that also undergoes radiation crosslinking but has fewer carbon-hydrogen bonds per repeating unit, and has a lower molecular flexibility that becomes manifest in a higher glass transition temperature (14 °C).



## Results and Discussion

**Synthesis and Characterization of Polymer 1.** Un-cross-linked poly[bis((methoxyethoxy)ethoxy)phosphazene] (1) was prepared by a method described previously.<sup>12,13</sup> The synthesis is based on the replacement of chlorine atoms in poly(dichlorophosphazene) by treatment with the sodium salt of (methoxyethoxy)ethanol in tetrahydrofuran solution. The structure and composition of un-cross-linked polymer 1 were confirmed by a combination of <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy, infrared spectroscopy, thermal analysis, and gel permeation chromatography (GPC). The <sup>31</sup>P NMR spectrum consisted of a singlet at -6.7 ppm. The <sup>1</sup>H NMR spectrum contained two peaks at +3.4 and +3.6 ppm. The glass transition temperature (*T<sub>g</sub>*) was -84 °C, and the weight average molecular weight, as determined by gel permeation chromatography, was 1 × 10<sup>6</sup>. These data, together with the elemental microanalysis, were similar to those obtained for examples of the same polymer prepared previously for other studies.<sup>12,13</sup>

**Method of Grafting of 1 onto Organic Polymer Surfaces.** The grafting method is shown in Scheme II. Films of organic polymers 3-8 were multiple dip-coated

Table I. Contact Angle Measurements (deg) for Water on Control Surfaces and Grafted Polymer 1

substrate polym	original surface		surface plus 1	
	0 Mrad	10 Mrad	0 Mrad	5 Mrad
3	94	96	88	27
4	78	79	77	34
5	65	62	57	54/35
6	110	106	105	106
7	65	65	59	65/43
8	63	65	64	31

with solutions of 1, dried, and then irradiated with 5 Mrad of  $\gamma$ -rays. Two sets of control organic polymer samples were also prepared; one set was coated with 1 but not irradiated, and the other was irradiated but not coated. Before analysis, all the samples were soaked in water and ethanol for an extended period of time in order to remove ungrafted or loosely adsorbed 1.

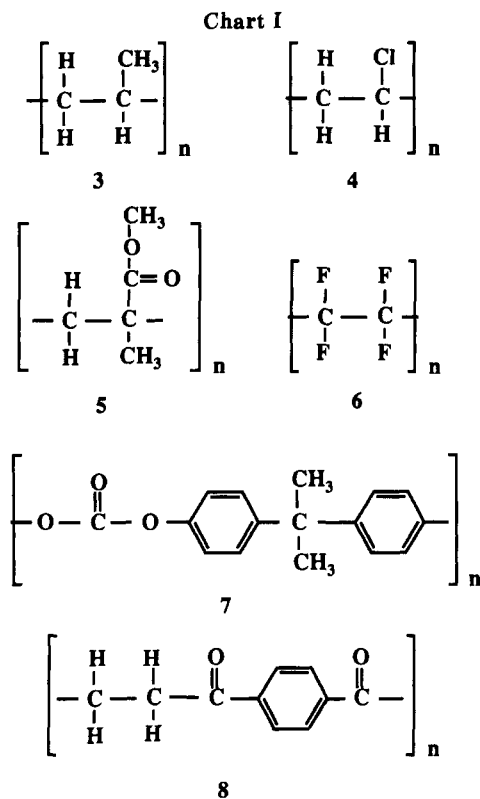
**Surface Characterization of Grafted Materials.** The grafted samples and controls were studied by contact angle measurements, ATR-IR spectroscopy, SEM, and XPS methods.

(a) *Contact Angle Measurements.* The measurement of contact angles provides a sensitive measure of changes to a polymer surface. The results of contact angle measurements with water droplets are summarized in Table I. The contact angle values for the uncoated but irradiated controls were not significantly different from those of the unirradiated starting polymers.

The controls of polypropylene (3, Chart I) poly(methyl methacrylate) (5), and polycarbonate (7) that were coated with 1 but *not* irradiated had slightly reduced contact angles compared to the untreated samples. This probably results from adsorption of 1 on the polymer surfaces. Samples of poly(vinyl chloride) (4), poly(ethylene terephthalate) (8), and poly(tetrafluoroethylene) (6) showed no change in contact angle under the same circumstances.

The polypropylene, poly(vinyl chloride), poly(methyl methacrylate), polycarbonate, and poly(ethylene terephthalate) films that were coated with 1 and irradiated with 5 Mrad of  $\gamma$ -rays showed a noticeable decrease in contact angle. The applied water droplets continued to spread steadily over a period of several minutes to give contact angle values in the range from 27 to 43°. Contact angles of similar samples irradiated for only 1 Mrad were not as low as those irradiated for 5 Mrad. They resembled the values of the controls following adsorption only. Apparently, 1 Mrad is not sufficient to bring about significant grafting of 1 to these surfaces.

The contact angles of samples of poly(methyl methacrylate), polycarbonate, or poly(ethylene terephthalate) that were coated with 1 and irradiated for 5 Mrad varied from region to region across the polymer film surface, with values that corresponded either to the presence of grafted hydrogel (35-43°) or to adsorbed polymer (57-64°). This suggests a nonuniform grafting of 1 to these polymer



surfaces. However, this was not the case for the grafts on poly(vinyl chloride) or polypropylene which had uniform surface characteristics.

Samples of poly(tetrafluoroethylene) that had been coated with 1 and irradiated showed no significant change in contact angle compared to that of the starting polymer. Polymer 1 appears to be unable to wet the hydrophobic surface of poly(tetrafluoroethylene) and this may explain the poor grafting behavior. In addition, this polymer lacks the surface C-H or C-Cl bonds needed for facile radiation grafting.

Most previously reported grafted hydrogels contain an ionic functionality. As a result, the contact angles at their surfaces depend on the pH of the applied solution. However, polymer 1 is non-ionic, and the contact angles of these surface grafts were independent of pH.

(b) *Infrared Spectroscopy.* The ATR-IR spectra generally confirmed the information obtained from the contact angle work. ATR-IR spectra of samples of poly(ethylene terephthalate) that were treated under different conditions are shown in Figure 1. Overall, the ATR-IR spectra of the controls that were irradiated but uncoated, and those that were coated with 1 but not irradiated and extracted with water were indistinguishable from those of the starting polymers. The spectra of the polypropylene, poly(vinyl chloride), poly(methyl methacrylate), polycarbonate, and poly(ethylene terephthalate) surfaces that had been coated with 1 and irradiated for 5 Mrad had new absorbances at 1455, 1245 (P=N), 1110 (C-O-C), and 1055  $\text{cm}^{-1}$  (P-O-C).

(c) *X-ray Photoelectron Spectroscopy.* The XPS spectra of the irradiated but uncoated samples were not significantly different from those of the starting polymers. The spectra of poly(vinyl chloride), poly(tetrafluoroethylene), and poly(ethylene terephthalate) that were coated with 1 but not irradiated (followed by extraction with water) were also identical to the spectra of the starting polymers, which suggests that little or no adsorption occurred. However, the XPS spectra of samples of poly-

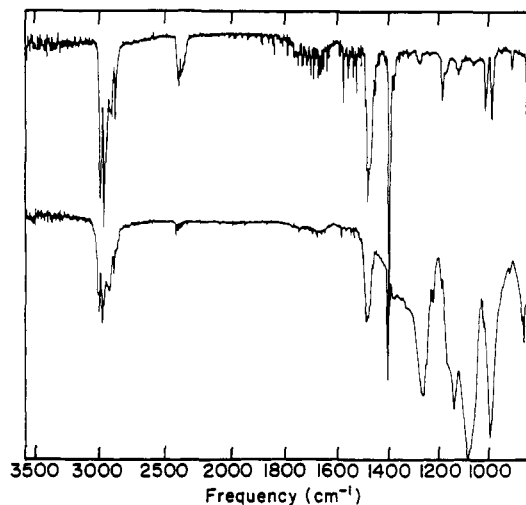


Figure 1. ATR-IR spectrum of a polypropylene film surface (upper), and of the same material coated with polymer 1 and irradiated with 5 Mrad of  $\gamma$ -rays (lower).

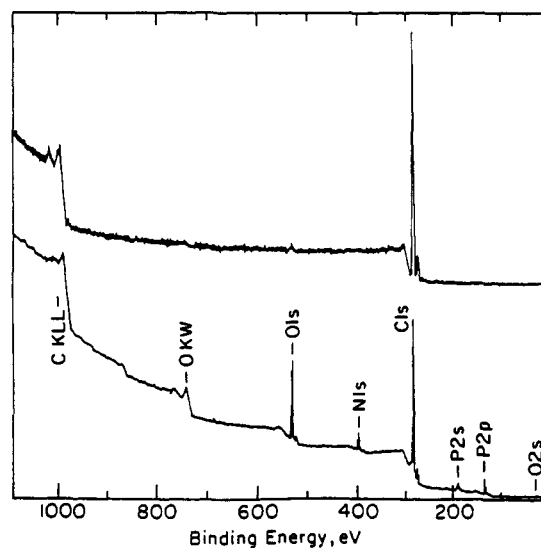


Figure 2. XPS spectrum of a polypropylene film surface (upper) and of the same surface coated with polymer 1 and then irradiated with 5 Mrad of  $\gamma$ -rays (lower).

propylene, poly(methyl methacrylate), and polycarbonate that were coated with 1 but not irradiated contained a small P(2p) peak at 134.3 eV and a N(1s) peak at 398.0 eV which were not present in the spectra of the starting polymers, and this provided additional evidence for the strong adsorption of 1 on these polymer surfaces. The XPS spectra of the samples of polypropylene, poly(vinyl chloride), poly(methyl methacrylate), polycarbonate, and poly(ethylene terephthalate) that were coated with 1 and irradiated with 5 Mrad contained large new P(2p) peaks at 134.3 eV and a N(1s) peak at 398.0 eV (Figure 2). New C(1s) (285.8 eV) and O(1s) (532.8 eV) peaks were also apparent in the spectra of polypropylene and poly(vinyl chloride) that were coated with 1 and irradiated for 5 Mrad. The new P(2p) and N(1s) peaks correspond to the phosphazene backbone of 1 and the new C(1s) and O(1s) to the side group of 1.

**Factors Affecting the Grafting of 1 onto Polymer Surfaces.** (a) *Adsorption and Adhesion of 1.* From the overall characterization data, it was possible to identify those surfaces on which 1 was strongly adsorbed before grafting occurred. Examination of the data for the samples coated with 1 but not irradiated suggests that polymer 1 was adsorbed on to polypropylene, poly(methyl meth-

acrylate), and polycarbonate but not on poly(vinyl chloride), poly(tetrafluoroethylene), or poly(ethylene terephthalate) and that the adsorbed layer survived the subsequent extraction with water and/or ethanol. SEM analysis of all the polymer film surfaces indicated that they were very smooth, and hence the differences could not be attributed to different surface topologies.

An important factor in surface grafting is adhesion between the two components before  $\gamma$ -irradiation, and this in turn depends on the close interactions between the two surfaces. Before an adhesive interface can be reinforced by covalent bond formation the materials must come within a van der Waals's interaction distance ( $\sim 2$  Å) of each other. The amphiphilic/surfactant nature of 1 allows it to interact well with a number of polymer surfaces. Un-cross-linked polymer 1 also undergoes viscous flow. Thus, the polymer may flow into surface imperfections and improve the mechanical adhesion of the uncrosslinked polymer to the surfaces.

By contrast, polymer 2 does not flow as a bulk material (its glass transition temperature is  $14$  °C).<sup>25</sup> No grafting of polymer 2 to any of the organic polymer surfaces was detected.

(b) *Covalent Grafting.* The polymers to which 1 became covalently grafted during 5 Mrad of  $\gamma$ -irradiation were polypropylene, poly(vinyl chloride), poly(methyl methacrylate), poly(ethylene terephthalate), and polycarbonate. Poly(tetrafluoroethylene) formed no grafted surfaces with either polymer 1 or polymer 2. As mentioned previously, polymer 1 has more aliphatic C-H bonds than does polymer 2. Surface grafting, like cross-linking, results from radical formation and combination at the carbon atoms of the side chains. Thus, polymer 1 has a greater probability of being grafted than polymer 2. By the same logic, substrate polymers that have a high concentration of aliphatic C-H bonds will be especially suitable for the grafting process. Presumably, this is why polypropylene, poly(methyl methacrylate), and poly(vinyl chloride) are excellent substrates for the grafting of 1. Moreover, the greater radiation-capture cross section and the ease of radical formation of chlorine probably enhance the grafting of polymer 1 to the surface of poly(vinyl chloride).

**Conclusions.** It is possible to modify organic polymer surfaces with covalently grafted thin films of polymer 1 by treatment with  $\gamma$ -rays. Polymer 1 has several physical and chemical properties which can be imparted to the surfaces of common organic polymers. The grafted surfaces are more hydrophilic than the starting surfaces and, in the presence of aqueous media, form hydrogels with high water content. All these features suggest that surfaces grafted with 1 may have enhanced biocompatibility with soft tissues and may be excellent substrates for cell adhesion and growth. In another publication<sup>26</sup> we have shown that hydrogels derived from polymer 1 have the ability to retard the growth of bacteria such as *Pseudomonas aeruginosa*, *Bacillus subtilis*, or *Salmonella typhimurium* (TA 100). Hence, this may provide a method for the generation of antibacterial surfaces for many materials used in biomedical devices. Small molecules readily diffuse through these gels, while macromolecules do not. Thus, the surface bound hydrogels are also attractive candidates for the immobilization of enzymes or antigens and for the development of a wide range of biomedical materials.

In addition, because cross-linked polymer 1 is known to

be an excellent medium for solid-state ionic conductivity,<sup>13-16,27</sup> the possibility exists that this polymer can be radiation grafted on to the surface of electronically conductive polymers, such as polyacetylene, poly(phenylenevinylene), polythiophene, or polypyrrole to form interfaces that may be useful in lightweight energy storage devices or sensors. Even when grafted onto the surfaces of non-conducting polymers, polymer 1 could provide access to thin-film ionic conducting devices. The cross-linking of this polymer by ultraviolet light<sup>28</sup> opens up possibilities for microlithography.

## Experimental Section

**Materials.** Most of the compounds were obtained and purified as described previously.<sup>5,6</sup> 2-(2-Methoxyethoxy)ethanol was obtained from Aldrich and was distilled under vacuum before storage over molecular sieves (40 nm). Sodium metal stick (Aldrich) was stored and used in a glovebox. All phosphazene syntheses were carried out under an atmosphere of dry nitrogen (Matheson). Hexachlorocyclotriphosphazene (supplied by Ethyl Corp.) was purified by vacuum sublimation, recrystallization (from hexane), and a final sublimation. Poly(dichlorophosphazene) was obtained by the thermal polymerization (250 °C) of hexachlorocyclotriphosphazene in an evacuated sealed glass tube. Films of polypropylene, poly(vinyl chloride), poly(methyl methacrylate), poly(tetrafluoroethylene), poly(bisphenol A carbonate), and poly(ethylene terephthalate) were provided by Dow Chemical Co., Midland, MI. The polymer films were rinsed, soaked, and sonicated in deionized water, ethanol, and hexane for several days.

**Equipment.** <sup>31</sup>P NMR spectra were recorded on a JEOL FX 90Q FT NMR spectrometer. <sup>13</sup>C and <sup>1</sup>H NMR spectra were obtained with a Bruker 200-MHz NMR spectrometer. Infrared (NaCl plate) spectra were recorded using a Perkin-Elmer FTIR 1700 instrument. A Harrick variable-angle twin parallel mirror reflection attachment equipped with a 45° Ge crystal (50 × 10 × 3 mm) was used to obtain all ATR-IR spectra. Thermomechanical analysis data were obtained using Perkin-Elmer Series 7 thermal analysis equipment. <sup>60</sup>Co  $\gamma$ -irradiation experiments were carried out at the Breazeale Nuclear Reactor at The Pennsylvania State University. SEM analyses were performed on an ISI SX-40A instrument.

**XPS Methodology.** X-ray photoelectron spectra were obtained 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 Mg anode (Mg K $\alpha$  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 25° takeoff angle. Atomic composition data were determined by using the instrument's computer and programmed sensitivity factors.

**Contact Angle Measurements.** Measurements were made using a Ramé-Hart Model 100 contact angle goniometer equipped with an environmental chamber. Contact angles were recorded 1 min after the application of a 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. The volume of the applied drop was 1  $\mu$ L. All reported values are the average of at least five measurements taken at different locations on the film surface.

**Preparation of [NP(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (1).** Sodium (15 g) was dispersed in THF (300 mL), and 2-(2-methoxyethoxy)ethanol (106.9 g, 0.891 M) was added. The reaction was allowed to proceed for 24 h at 25 °C. A solution of (NPCL<sub>2</sub>)<sub>n</sub> (30 g) in THF (300 mL) was added to the solution of sodium 2-(2-methoxyethoxy)ethoxide, and the mixture was stirred for 24 h at reflux. The solution was concentrated and then dialyzed against deionized water (4 days) and then methanol (3 days). The polymer was isolated by evaporation of the contents of the dialysis tube. IR: 2938, 2881, 2823 (m, CH), 1054 (vs, PN) cm<sup>-1</sup>. <sup>31</sup>P NMR:

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-8.4 ppm. Elem. Anal. Calcd C, 42.40% H, 7.83%; N, 4.94%. Found: C, 41.28%; H, 7.85%; N, 4.96%.  $M_w = 2 \times 10^6$ .

**Preparation of [NP(HNCH<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (2).** Polymer 2 was prepared by previously described methods.<sup>25</sup> The characterization data were consistent with previous preparations of this polymer: <sup>31</sup>P NMR +6.1 ppm(s);  $M_w = 1 \times 10^6$ .

**Coating and Irradiation of Samples.** Clean polymer film samples were dipped into 10% aqueous or methanolic solutions of 1 for 1 min and were then removed and allowed to dry. Each film was dipped a minimum of five times. The multicoated films were dried for 24 h and were then sealed in an evacuated container. Samples were degassed and sealed under vacuum in freeze-dryer bottles. The samples were then irradiated with <sup>60</sup>Co  $\gamma$ -radiation at a dose rate of 0.222 Mrad/h for 0, 1, 5, or 10 Mrad. After irradiation, the films were soaked in and regularly shaken in deionized water for 5 days and were then soaked and shaken in ethanol for 1 day.

Three sets of controls were prepared. The first set was the pure

polymer films that were simply soaked and shaken in water, as above. The second set were not coated with 1 but were exposed to 10 Mrad of  $\gamma$ -rays and then treated with water. The last control set was coated with 1 before exposure to water.

**Stability of Hydrogel Grafts.** Grafts of 1 were treated with 80% acetic acid, 0.1 N NaOH, THF, methanol, ethanol, hexane, and deionized water. During each treatment the samples were sonicated and agitated. The solutions were inspected visually to check for suspended hydrogel. In addition, the solutions were monitored by <sup>31</sup>P NMR spectroscopy to monitor for the presence of any dissolved polymer 1.

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## Polyphosphazenes Bearing Polymerizable Pyrrole, Thiophene, and Furan Side Groups: Synthesis and Chemical Oxidation

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The synthesis and chemical oxidation of linear poly(organophosphazenes) that bear polymerizable, heterocyclic side groups are described. The polymers were prepared for use as precursors to electronically conductive materials. The polymers have the general structure [NP(OR)<sub>2</sub>]<sub>n</sub>, where R is  $-\text{CH}_2\text{CCHSCHCH}$ ,  $-\text{CH}_2\text{CH}_2\text{CCHSCHCH}$ ,  $-\text{CH}_2\text{CH}_2\text{CSCHCHCH}$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NCHCHCHCH}$ ,  $-\text{CH}_2\text{CCHOCHCH}$ ,  $-(\text{CH}_2)_{11}\text{NCHCHCHCH}$ , or  $-(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\text{NCHCHCHCH}$ , and [NP(NHR)<sub>2</sub>]<sub>n</sub>, where R is  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NCHCHCHCH}$  or  $-\text{CH}_2\text{CH}_2\text{CCHSCHCH}$ . The cyclic trimer [NP(OCH<sub>2</sub>CCHSCHCH)<sub>2</sub>]<sub>3</sub> was synthesized as a model compound and as a possible precursor to cyclomatrix conductive materials. Molecular structural characterization for the linear high polymers was achieved by the use of <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy, gel permeation chromatography, and elemental microanalysis. The glass transition temperatures of the polymers were determined using differential scanning calorimetric analysis and were found to be in the range -48 to +1 °C. Chemical oxidation of the materials was carried out in solution using Fe(ClO<sub>4</sub>)<sub>3</sub> or FeCl<sub>3</sub>. The resultant dark, insoluble powders were compressed into pellets, and their electronic conductivities were measured. All the materials were found to be semiconductive with conductivities in the range  $4 \times 10^{-10}$ - $5 \times 10^{-5}$  S cm<sup>-1</sup>. The results of attempted electrochemical oxidation and chemical oxidation using iodine are also described.

### Introduction

In recent years, a growing interest has been evident in the development of electronically conductive organic polymers.<sup>1,2</sup> Such materials are technologically important because they offer the prospect of combining electronic conductivity with other useful properties such as toughness, flexibility, or ease of fabrication into devices. Among

the most intensively studied conductive polymers are poly(pyrrole), poly(thiophene), and their derivatives. Research efforts in numerous laboratories are concentrated on improving the tractability of these materials.<sup>3</sup>

Poly(organophosphazenes) comprise a broad class of inorganic-organic polymers of general structure [NPR<sub>2</sub>]<sub>n</sub>.<sup>4</sup> The possibility that electronic conductivity might be induced in polyphosphazenes has been considered in earlier

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