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Articles

Oxidation of Poly[bis(4-methylphenoxy)phosphazene] Surfaces and Chemistry of the Surface Carboxylic Acid Groups

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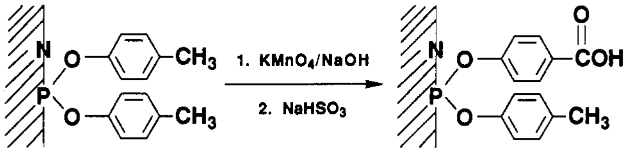
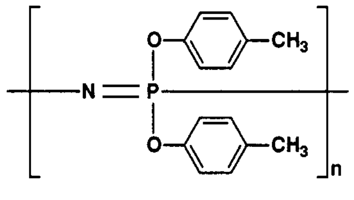
Surfaces of poly[bis(4-methylphenoxy)phosphazene], $[NP(OC_6H_4CH_3)_2]_n$, were oxidized with an aqueous $KMnO_4$/NaOH solution, analyzed, and used as substrates for surface reactions. The small-molecule cyclic trimer, $[NP(OC_6H_4CH_3)_2]_3$, was also oxidized as a model system. Analysis of the small-molecule reactions by solution state ^{13}C, ^{31}P, and ^1H NMR spectroscopy and mass spectrometry confirmed that the methyl groups were oxidized to carboxylate groups. The oxidized polymer film surfaces were examined by contact angle measurements, ATR-IR, SEM, TEM, and XPS methods. The maximum depth of oxidation was 1 μm. Relationships between the reaction parameters, percent oxidation, and the contact angle have been established. The oxidized surfaces were also examined for cation exchange capability. Carboxylic acid surface units were reduced to benzylic alcohol groups. In addition, various coupling reactions were used to link 4-nitrofuroic acid and the tetrapeptide, Arg-Gly-Asp-Ser, to the polymer surfaces.

Introduction

The oxidation of an inert polymer surface is known to enhance both its adhesion and its biocompatibility.[1,2] For example, oxidized surfaces have enhanced blood compatibility[3] and are excellent substrates for cell attachment and growth.[4] Chromic acid has been used to oxidize polyethylene or polypropylene surfaces, and plasmas have been employed for the modification of polystyrene and other inert polymer surfaces.[5-10] A disadvantage of these systems is that several different surface functional groups are generated by the reaction. Thus, alcohol, ketonic, aldehyde, and carboxylic acid units are formed on the modified polymers. Plasma modifications are also sensitive to numerous experimental parameters. For these reasons, we have investigated the surface oxidation of a specifically tailored poly(organophosphazene) in which the backbone bonds are expected to be stable to oxidation, and the side groups bear only one type of oxidizable site. Specifically, we report a mild, controllable method to oxidize poly[bis(4-methylphenoxy)phosphazene] (1) films in a way that apparently generates only carboxylic acid functionalities at the surface (Scheme I).

Scheme I





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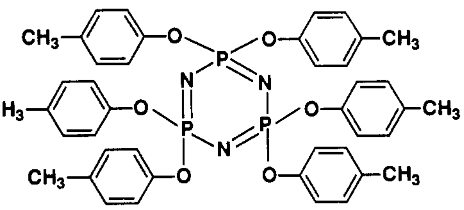

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(1) Landrock, A. H., Ed. *Adhesives Technology Handbook*; Noyes: Park Ridge, NJ, 1985.

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

(3) Hastings, G. W., Ducheyne, P., Eds. *Macromoleclar Biomaterials*; CRC Press: Boca Raton, Fl, 1984.

(4) Ramsey, W. S.; Hertl, W.; Nowlan, E. D.; Binkowsi, N. J. *In Vitro* **1984**, *20*, 802.

(5) Whitesides, G. M.; Ferguson, G. S. *Chemtracts* **1988**, *1*, 171.

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

(7) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87.

(8) Lee, K.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 309.

(9) See abstracts from the Symposium on Plasma Polymerization and Plasma Interactions with Polymeric Materials in: *Proceedings of ACS Division of Polymeric Materials: Science and Engineering*; American Chemical Society: Washington, D.C., 1990; Vol. 62.

(10) Hudis, M. Plasma Treatment of Solid Materials. In *Techniques and Applications of Plasma Chemistry*; Hollahan, J. R., Bell, A. T. Eds.; John Wiley & Sons: New York, 1974; pp 113–147.

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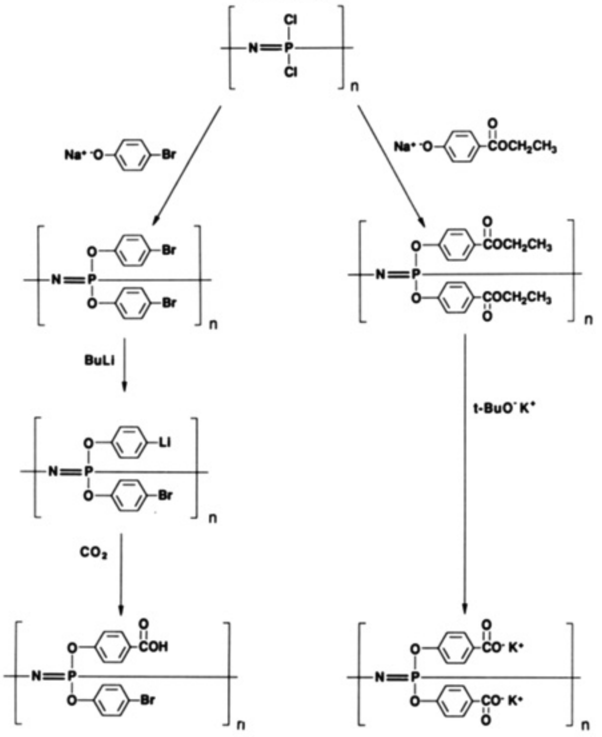
Scheme II



Poly(organophosphazenes) with carboxylic acid-containing side groups had been prepared previously in our laboratory by two other routes (Scheme II).[11,12] These polymers have several important properties such as water solubility, cation-exchange capability, and polyelectrolyte behavior.[13] However, if the percentage of carboxylate units is high, the solid polymers lack materials strength and flexibility and have only modest film- or fiber-forming qualities. As with previous work,[14-16] our goal was to retain the beneficial bulk physical characteristics (flexibility and toughness) of the starting polymer while, at the same time, modifying the polymer surface.

Answers to the following questions were sought: (1) What is the most effective method for oxidation of a poly(organophosphazene) surface? (2) What chemistry is involved in the modification? (3) Does the surface reaction cause polymer chain cleavage? (4) What relationships exist between the reaction parameters, the percent oxidation, and surface characteristics such as contact angles? (5) Can the functional groups generated on the surface be employed for the ionic or covalent binding of biologically interesting species?

Results and Discussion

Small-Molecule Model Reactions. Initially, finely divided crystalline cyclic phosphazene **2** in a heterogeneous system was used as a model for the surface chemistry that occurs on polymer films. Thus, powdered trimer **2** was allowed to come into contact with aqueous permanganate in a heterophase system. The material isolated from these crystal surface reactions consisted of a mixture of oxidized and unoxidized trimers of the type $N_3P_3(OC_6H_4CH_3)_{6-x}(OC_6H_4CO_2H)_x$, where $x = 2\text{–}6$. Thin-layer chromatographic analysis indicated the presence of at least four products, which were identified by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. A decrease in the methyl proton resonance at 2.1 ppm in the ^{1}H NMR spectra was accompanied by the appearance of a resonance at 12.1 ppm, which was assigned to the carboxylic acid proton. In the ^{13}C NMR spectra, the methyl carbon resonance at 20.7 ppm decreased in intensity, while a resonance that was assigned to the carboxylic acid carbon appeared at 171.1 ppm. The ^{31}P NMR spectra of the oxidized trimers were indistinguishable from the spectrum of the starting compound **2**. Mass spectra of the isolated materials contained the molecular ion peaks for all six products with from zero to six carboxylic acid units per molecule. The model reactions indicated that oxidation occurs solely at the methyl groups, with no detectable side reactions.

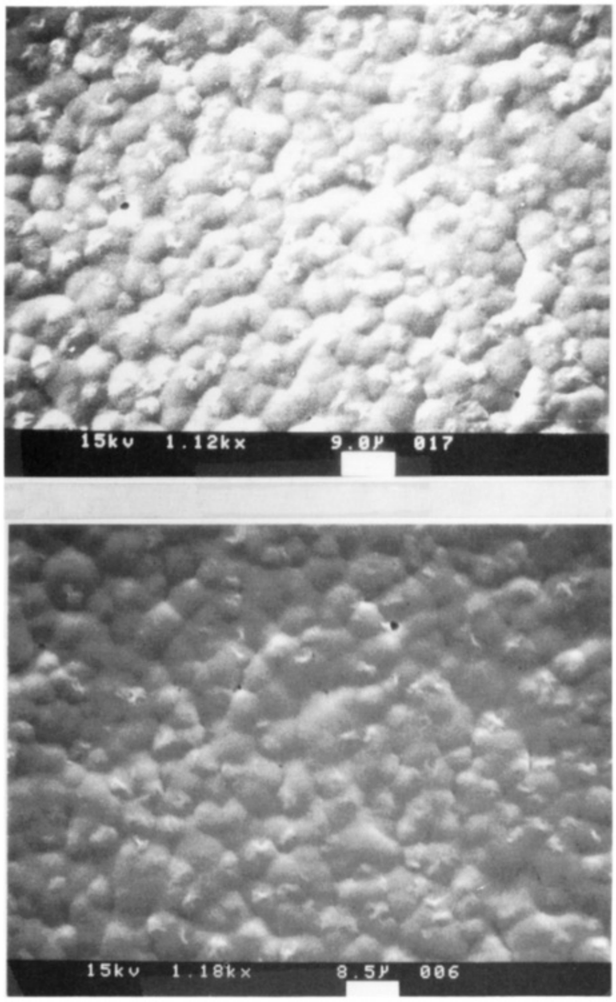


Figure 1. Electron micrographs of a film of polymer 1 before (upper) and after oxidation at 25 °C for 11 days (lower).

Polymer Surface Oxidation. Films of polymer **1** were immersed in solutions of $KMnO_4$ and NaOH for various times and temperatures. The films treated for the longest times and at the highest temperatures had a noticeable deposit of MnO_2 on their surfaces. The MnO_2 was removed by soaking the films in an aqueous solution of $NaHSO_3$. All the treated films had an appearance identical to that of the starting films.

Characterization of the Oxidized Surfaces. The analytical studies revealed a surface that was physically similar to that of the starting material, but chemically

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[11] Allcock, H. R.; Kwon, S. *Macromolecules* **1989**, *22*, 75.

[12] Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules* **1980**, *13*, 1325.

[13] For biomedical and biotechnology applications of carboxylatophosphazene polymers, see: Cohen, S.; Bano, M. C.; Visscher, K. B.; Chow, M.; Allcock, H. R.; Langer, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 7832. Bano, M. C.; Cohen, S.; Visscher, K. B.; Allcock, H. R.; Langer, R. S. *Biotechnology* **1991**, *9*, 468.

[14] Allcock, H. R.; Rutt, J. S.; Fitzpatrick, R. J. *Chem. Mater.* **1991**, *3*, 442.

[15] Allcock, H. R.; Fitzpatrick, R. J. *Chem. Mater.* **1991**, *3*, 450.

[16] Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.* **1991**, *3*, 1120.

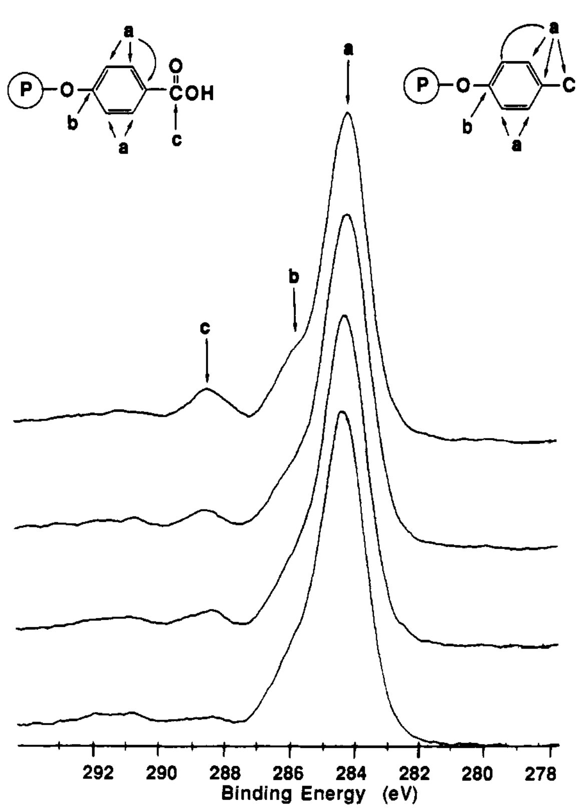


Figure 2. XPS C(1s) region of films of 1 after oxidation at 50 °C for 1 h (bottom), 5 h, 10 h, and 24 h (top). The spectrum for an unoxidized sample was virtually indistinguishable from that of the sample oxidized for 1 h. The broad peaks near 291 eV are present in the unoxidized sample and are due to π–π^* "shakeup" noise from the phenyl rings.

different. The oxidized surfaces were significantly more hydrophilic than those of the starting films. Water easily spread out over the oxidized surfaces but beaded on the surfaces of the starting films. The contact angle data will be discussed in more detail in a later section. Scanning electron micrographs of the untreated film surfaces and those modified at 25 or 50 °C were indistinguishable from each other (Figure 1). Films treated at 80 °C for periods of 5 or more hours had rougher surfaces than did the starting films.

Several surface-oxidized films were dissolved in THF and were analyzed by solution methods. The GPC molecular weight distribution was unchanged from that of the starting polymer (3×10^6). Solution ^{13}C NMR spectra contained resonances for both oxidized and unoxidized 4-methylphenoxy groups, although the oxidized side groups constituted only a small percentage, as would be expected from the fact that most of the repeating units in solution originated from the bulk material.

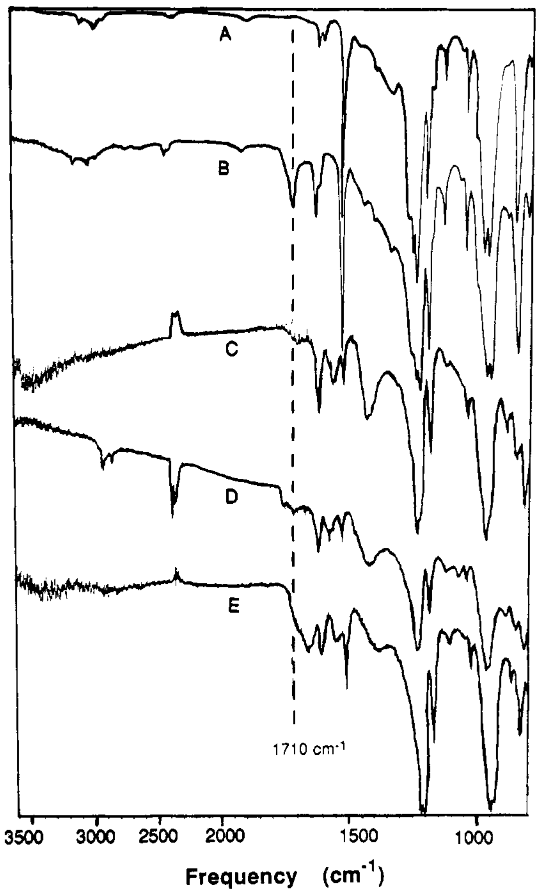


Figure 3. ATR-IR spectra of films (A) before oxidation, (B) after oxidation for 24 h at 50 °C, (C) after reduction with $LiAlH_4$, (D) with covalently bound 4-nitrofuroic acid, and (E) with immobilized tetrapeptide ARG-GLY-ASP-SER.

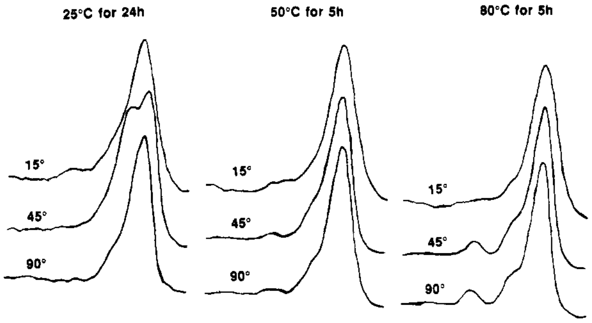


Figure 4. XPS C(1s) region of films of 1 after oxidation under various conditions and analyzed at angles of 15°, 45°, and 90°.

The oxidized film surfaces were also analyzed by XPS and ATR-IR spectroscopy. The XPS spectra of the oxidized surfaces contained a single new C(1s) peak at 288.7 eV. The intensity of this peak increased with both reaction time and temperature (Figure 2). The peak was assigned to the carbonyl carbon of carboxylic acid units. The ATR-IR spectrum of the oxidized surface was similar to that of the initial film surface, except for the presence of a new peak at 1710 cm^{-1} (Figure 3). This peak corresponds to the carbonyl group of a carboxylic acid unit. Some of the XPS spectra also contained Na(1s) and K(2p) peaks, presumably from alkali-metal ions associated with the carboxylate salts. The absence of alkali-metal peaks in the XPS spectra of some oxidized samples was attributed to protonation of the carboxylate group during exposure to $NaHSO_3$ solutions. No manganese or sulfur peaks were present in the XPS spectra. As with the model reactions, the surface oxidation generated no products from side reactions and yielded carboxylic acid groups in place of methyl units. The possibility exists that other oxidized species such as alcohol or aldehyde units may also be formed by the process, but they were not detected by the methods of analysis used for the polymers or the model compounds.

The depth of oxidation was examined with the use of both XPS and TEM techniques. For the samples oxidized at 25 °C, oxidation was primarily in the outer 40 Å of the polymer film. Angle-dependent XPS studies on the surfaces oxidized at 50 or 80 °C indicated that no difference existed between the percent oxidation in the outer 60- and 100-Å regions (Figure 4). However, the oxidation level was significantly *lower* in the outer 20 Å, and this anomaly will be discussed later. TEM analysis of the oxidized films

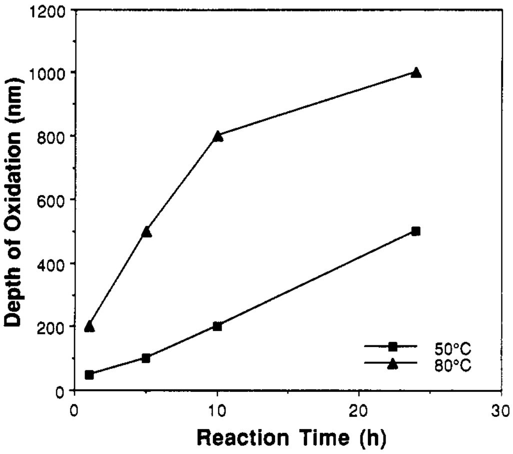


Figure 5. Depth of oxidation of 1 (determined by TEM analysis of film cross sections) as a function of oxidation time and temperature.

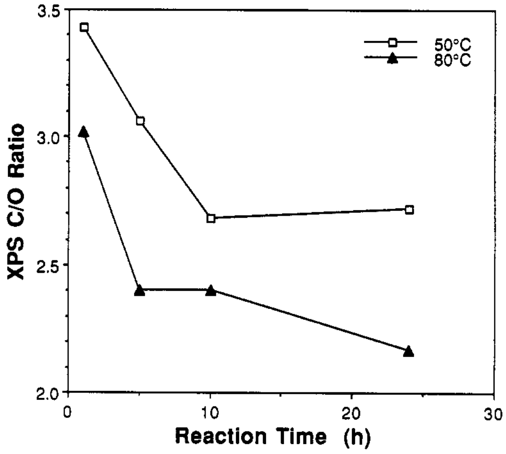


Figure 6. Carbon/oxygen ratio as a function of reaction time and temperature, determined by XPS techniques.

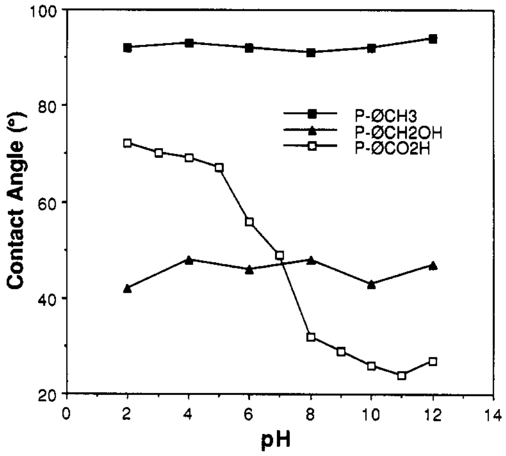


Figure 7. Contact angle of film surfaces as a function of the pH of the applied solution.

Table I. Effect of Reaction Time and Temperature on Percent Oxidation

temp of oxidation, °C	reaction time, h	XPS C/O ratio	surface O–$C_6H_4CH_3$ groups oxidized, %
25	24	3.45	67
25	132	3.03	77
25	264	2.99	78
50	1	3.43	68
50	5	3.06	76
50	10	2.68	87
50	24	2.72	86
80	1	3.02	77
80	5	2.40	97
80	10	2.40	97
80	24	2.17	~100

also clearly revealed the oxidation depths in the various samples, as shown in Figure 5. Use of this technique indicated that the depth of oxidation for reactions carried out at 25 °C was consistently less than 50 nm. The depth of oxidation for reactions at 50 or 80 °C was between 50 nm and 1 μm and progressed to deeper regions with increases in reaction time and temperature.

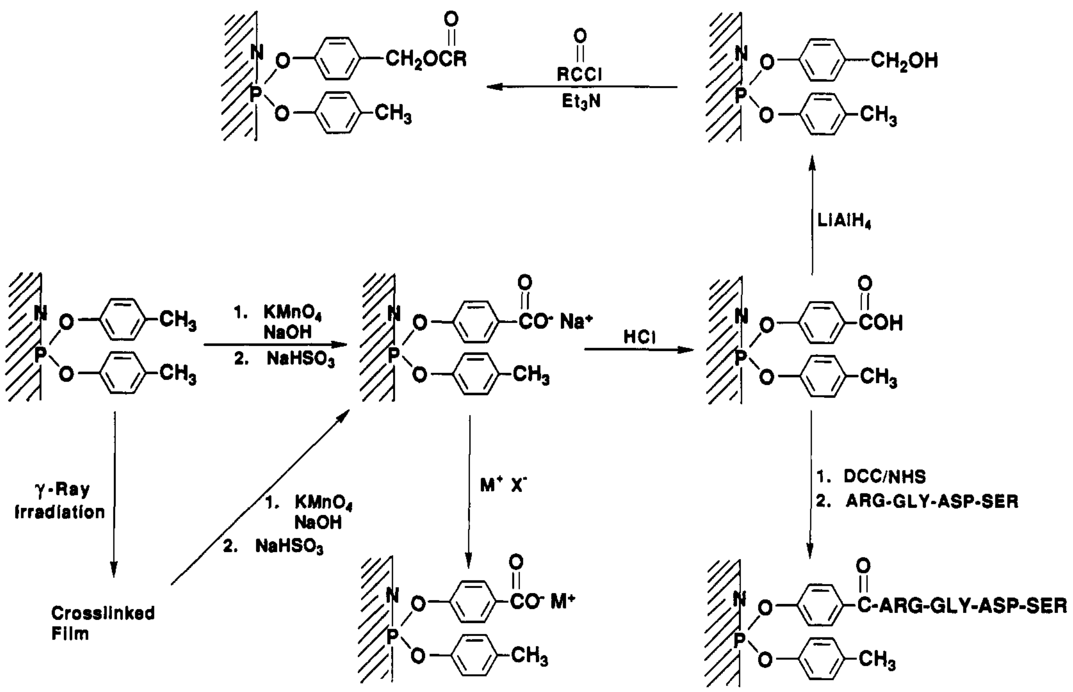
Effect of Reaction Time and Temperature. Variations in reaction times and temperatures allowed some control to be exercised over surface roughness, degree of surface oxidation, and depth of oxidation. Surface roughening was evident when the films were oxidized at 80 °C, but no roughening could be detected after extended reaction times at 25 or 50 °C (Figure 1).

The percentage of methyl groups converted to carboxylate units was estimated from the carbon/oxygen atomic ratios measured by XPS analysis. A ratio of 7:1 corresponds to an unoxidized system and a ratio of 7:3 to 100% conversion of methyl groups to carboxylic acid units. Using this method, it was found that the percentage of oxidized groups increased linearly with increasing reaction time at 80 °C (Figure 6 and Table I) until approximately 85% of the tolyl side groups at the surface were converted to arylcarboxylate groups. Further exposure to the reagent did not increase the number of oxidized sites. At 25 °C, the oxidation was significantly slower than at 50 or 80 °C, but the extent of oxidation increased slowly from 67% to 78% of the surface groups as the reaction time increased from 1 to 11 days. Thus, increases in reaction temperature dramatically increased the rate of the surface reaction. To reach a 75% conversion of surface methyl to carboxylate groups required 11 days at 25 °C, 5 h at 50 °C, and 1 h at 80 °C. Increases in reaction time and temperature also affected the depth of oxidation (Figure 5). Overall, the depth of oxidation was limited by the hydrophobic nature of the starting material, the aqueous nature of the medium, and the deposition of MnO_2. The hydrophobic surface limits the initial interaction with the aqueous reactant. The deposited MnO_2 layer, which forms during oxidation, appears to function as a barrier to retard the penetration of the $KMnO_4$ solution.

Contact Angle Measurements. The contact angle at the oxidized surface was dependent on pH, while the value for the unoxidized film (92°) was independent of pH (Figure 7). When the pH of the applied liquid was highly acidic, the contact angle at the oxidized surface was 70°. Strongly basic aqueous solutions generated a contact angle of 25°. Intermediate contact angle values were found when the pH of the droplet solution was between 5 and 8. Under acidic conditions, the surface carboxylic groups are protonated and are thus less hydrophilic (higher contact angles). Under basic conditions, the carboxylate groups are ionized in their salt form, and the surface is more hydrophilic (lower contact angle).[6] Intermediate contact angle values formed between droplet pHs of 5 and 8 can be explained by the presence on the surface of both the protonated and salt forms of the carboxylic acid groups.

Increases in the loading of carboxylate groups in the surface regions generated lower contact angles to water. Since the degree of oxidation could be estimated from the XPS C/O ratio data, it was possible to show that a modest decrease in contact angle occurred as the carboxylic acid loading at the surface rose from 0% to 65% (Figure 8), but

Scheme III



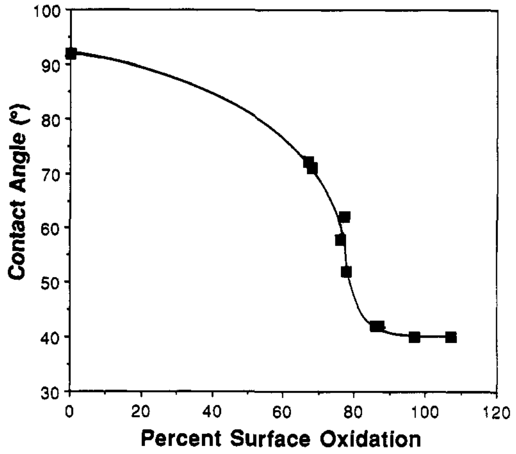


Figure 8. Contact angle as a function of the percent surface oxidation of the film.

a sharp decrease in angle (to 40°) then occurred as the percentage of oxidized groups rose to 85%. Beyond that point increases in carboxylic acid loading had little effect.

Surface Reconstruction. The process of surface reconstruction, in which new functional units formed at the surface are subsequently buried by macromolecular motions, must be considered for any polymer surface reaction. In the present case, the results are ambiguous, as illustrated by the following observations. Variable angle XPS analysis revealed a surprising feature of the oxidized film surfaces (Figure 4). First, XPS spectra taken at an angle of 15° for highly oxidized samples contained essentially no C(1s) peak that corresponded to carboxylic acid carbon atoms. XPS spectra of the same sample taken at angles of 45° and 90° contained obvious C(1s) carboxylic peaks. This might suggest that the carboxylic acid units, once formed, retreat from the surface and are detected only below the outer 20 Å of the polymer film surface. This trend was found for all the samples with a high loading of COOH groups (formed by oxidation at 80 °C) but was not as obvious for the less oxidized surfaces formed at 50 °C. For samples oxidized at 25 °C, more carboxylic acid groups were detected in the upper 20 Å than in the lower layers. An explanation is that the most highly oxidized surfaces undergo a reconstruction that buries the carboxylate units in order to minimize their interfacial energy and that this process occurs more readily at the higher reaction temperature of 80 °C. The possibility also exists that the XPS data reflect the effects of surface etching by the oxidation medium.[17]

However, the contact angle data, obtained immediately after oxidation, indicated that oxidized units remained at the surface. Thus, unless surface turnover occurred at 25 °C during the 1–2-week period before the XPS data were measured (and this appears to be unlikely), it must be concluded that the results cannot be interpreted in terms of a simple surface reconstruction model.

Chemistry of the Oxidized Surfaces. Carboxylic acid groups serve as a useful starting point for additional surface reaction chemistry. Acid–base interactions, cation-exchange reactions, reductions, and coupling reactions took place at the oxidized surfaces of 1 (Scheme III).

The protonation of the surface carboxyl groups and their reactions with basic solutions have already been mentioned. Surfaces bearing sodium carboxylate groups exchanged cations with a solution of $CaCl_2$ to yield calcium carboxylate groups. The XPS spectra of these surfaces contained a $Ca(2p_{3/2})$ peak at 347.5 eV but no Na(1s) or Cl(2p) peaks. The exchange of cations between the film surface and the solution appeared to be complete.

The carboxylic acid groups at the polymer surface could also be reduced by $LiAlH_4$ to obtain surface benzylic alcohol units. This reduction process was accompanied by vigorous gas evolution. The absorption at 1710 cm^{-1} in the ATR-IR spectra (C=O units) nearly disappeared after treatment with the $LiAlH_4$ (Figure 3). The XPS spectrum of the reduced surface contained a small residual peak at 288.7 eV from the carboxylic acid carbon. The shoulder at 285.3 eV on the main C(1s) peak increased in intensity following formation of the benzylic alcohol methylene group. The contact angle of the new surface was 46°, and was independent of pH (Figure 7). As a control for the

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(17) We are indebted to one of the referees for the alternative explanations of these results.

reduction process, the ATR-IR and XPS spectra of an unoxidized film treated with $LiAlH_4$ were identical to those of the starting film. Thus, $LiAlH_4$ does not reduce the polyphosphazene backbone.

The antibiotic, 4-nitrofuroic acid, was converted to its acid chloride, and this reacted with surface benzylic alcohol groups to form an ester linkage. The ATR-IR spectra of the surface now contained new infrared peaks which matched those of 4-nitrofuroic acid (Figure 3). The new resonances at 1725 cm^{-1} were assigned to the carbonyl group of the immobilized species. Absorptions at 1545 cm^{-1} were attributed to the nitro group. The ATR-IR spectrum of a control unoxidized film exposed under similar conditions to 4-nitrofuroyl chloride contained none of these peaks. The XPS spectrum of the 4-nitrofuroyl-bearing surface contained a new N(1s) peak (405.1 eV) and showed an increase in the C(1s) peak (291–293 eV), both of which corresponded to highly oxidized species. The changes in the XPS spectra are consistent with the presence of a nitro group, a carbonyl carbon, and a carbon that bears a nitro group.

The surface carboxylic groups were also used for the covalent immobilization of a tetrapeptide, Arg-Gly-Asp-Ser. The reaction involved exposure of surface-activated ester units to the tetrapeptide (Scheme III). This tetrapeptide is one of several sequences that are recognized by cellular membrane proteins as a suitable attachment site. ATR-IR spectra of the peptide-linked surface contained new peaks at 3400–3000 cm^{-1} and showed an increase in the intensity of the peak at 1710 cm^{-1} (Figure 3). The peaks at 3400–3000 cm^{-1} were assigned to the N–H units of the peptide amide bonds and to its pendent amino group. The increase in intensity of the peak at 1710 cm^{-1} corresponds to the presence of peptide carbonyl groups. ATR-IR spectra of a control, surface-oxidized, film that was simply soaked in a solution of the tetrapeptide showed no changes. Thus, the peptide is not simply adsorbed onto the oxidized polymer surface. XPS spectra of the peptide-bearing surface contained a new peak in the N(1s) region at 399.5 eV, which corresponds to the amide nitrogen of the peptide. An increase in intensity in the 285–292-eV region of the C(1s) peak corresponded to the presence of the peptide carbonyl groups and the α-carbons to the amide linkage.

It should be noted that films of polymer 1 can be cross-linked by γ irradiation before surface modification. The cross-linking adds physical stability to the film but does not affect the subsequent chemistry. ATR-IR and XPS spectra of un-cross-linked and cross-linked samples were identical.

Experimental Section

Equipment and Materials. A Buchi BEP 280 stirred autoclave was employed for elevated temperature (160 °C) polymer synthesis reactions. ^{60}Co γ irradiation experiments were carried out at the Breazeale Nuclear Reactor at The Pennsylvania State University. ^{31}P spectra were obtained with the use of a JEOL FX-90Q spectrometer. ^{13}C amd ^{1}H NMR spectra were recorded with a Bruker 200-MHz NMR spectrometer. A Perkin-Elmer Model 1710 infrared Fourier transform spectrometer was used to obtain infrared spectra, and a Harrick variable-angle twin-parallel mirror reflection attachment equipped with a 45° Ge crystal (50 × 10 × 3 mm) was used for ATR-IR spectra. Contact angles were measured with the use of a Rame-Hart Model 100 Goniometer. SEM analyses were obtained with the use of an ISI SX-40A instrument.

All phosphazene syntheses were carried out with the reaction mixtures under an inert atmosphere of dry nitrogen (Matheson). Hexachlorocyclotriphosphazene (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 tube.[18,19] Sodium metal stick (Aldrich) was stored and used in a glovebox. Dioxane (Aldrich) and tetrahydrofuran (THF, Aldrich) were both distilled from sodium/benzenophenone immediately before use in the reactions. 4-Methylphenol (Aldrich) was sublimed and stored in a dessicator. Arg-Gly-Asp-Ser (Sigma), $LiAlH_4$ (0.96 M in Et_2O) (Aldrich), $CaCl_2$ (Aldrich), and dicyclohexylcarbodiimide (Aldrich) were used as received. *N,N*-Dimethylformamide (DMF) was vacuum-distilled and stored over molecular sieves (4 Å). *n*-Hydroxysuccinimide (NHS, Aldrich) was recrystallized from ethanol, vacuum-dried, and then stored in a desiccator. 4-Nitrofuroic acid (Lancaster Synthesis) was vacuum-dried and also stored in a desiccator. This was converted to the acid chloride by standard techniques. Alternatively, 4-nitrofuroyl chloride was obtained from Lancaster Synthesis and was used as received. Triethylamine (Aldrich) was distilled from CaH_2 before use.

GPC Methodology. A Hewlett-Packard HP 1090 liquid chromatograph equipped with a refractive index detector was used to determine GPC molecular weights. PLgel columns were used for THF-soluble polymers. A solution of Bu_4NBr (0.1%) in THF was the eluent. The polymers were dissolved in THF to obtain a 1% solution. The instrument was calibrated against secondary polystyrene standards.

XPS Technique. X-ray photoelectron spectra were obtained at the Perkin-Elmer Physical Electronics Laboratory. An Mg anode (Mg Kα = 1486 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. Measurements were made using a Rame-Hart Model 100 contact angle goniometer equipped with an environmental chamber. The sessile drop method was employed in which a 1-μL drop of distilled water was placed on the polymer surface. Contact angles were determined at various times after the application of the 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.

Preparation of Cyclic Trimer $[NP(OC_6H_4CH_3)_2]_3$ (2). Sodium metal (12.05 g, 0.524 mol) was placed in a dried 3-L flask equipped with a condenser. Dry THF (600 mL) was distilled into the flask. 4-Methylphenol (62.0 g, 0.659 mol) was dissolved in dry THF (400 mL) in a separate flask and was then added dropwise to the sodium. The salt solution was stirred for 12 h at room temperature and was then heated for 12 h until all the sodium had reacted. At that time, hexachlorocyclotriphosphazene (15.0 g, 0.129 mol) was dissolved in dry THF (500 mL) and was added to the salt solution. The reaction mixture was refluxed for 48 h, cooled, and filtered through silica gel. The filtrate was concentrated, dissolved in diethyl ether, and extracted with 2 × 150 mL portions of 0.05 M aqueous NaOH, and with 3 × 150 mL portions of distilled H_2O. The ethereal layer was concentrated, and the oily residue was crystallized from hexane. Characterization data: ^{1}H NMR 7.0 (d), 6.8 (d), and 2.2 ppm (s); ^{13}C NMR 148.5, 134.0, 129.7, 120.9, and 20.7 ppm; ^{31}P NMR 9.2 ppm (s); mp = 116–117 °C; mass spec calcd 777, found 777.

Preparation of $[NP(OC_6H_4CH_3)_2]_n$ (1). A 10.0-g (8.62×10^{-2} mol) sample of poly(dichlorophosphazene) was dissolved in warm dioxane (500 mL). In a separate flask, 4-methylphenol (55.2 g, 0.587 mol) was dissolved in dioxane and was added to an ice-bath-cooled suspension of sodium (11.1 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 the autoclave reactor. The reaction mixture was stirred and heated in the autoclave at 160 °C for 24 h at 60 psi. The mixture was then concentrated and precipitated into deionized water. The polymer was reprecipitated from THF

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[18] Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

[19] Allcock, H. R.; Kugel, R. J.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

into deionized water (3×), hexane (3×), and ethanol (1×). A tough, white polymer was recovered. Characterization data: ^{1}H NMR 7.0–7.5 (m), 2.3 (s); ^{13}C NMR 149.6, 132.1, 129.1, 121.0, and 20.6 ppm; ^{31}P NMR 19.6 ppm (s); $T_g = -2$ °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 °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}C γ 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 KMnO$_4$ (0.04 M) and NaOH (0.02 M) for 24 h at 80 °C. The excess KMnO$_4$ was deactivated with ethanol, and the MnO$_2$ precipitate was removed by reduction with 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 KMnO$_4$ (0.04 M) and NaOH (0.02 M) for various times and temperatures. The films were then removed from the reaction solution and were soaked in an aqueous NaHSO$_3$ solution for 5 h in order to remove the 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 HCl solutions (pH = 3) for 24 h at room temperature. The films were then rinsed and stored in deionized water.

Reduction of the Oxidized Surfaces with LiAlH$_4$. Oxidized film samples that had been protonated were vacuum-dried overnight and then placed in a 0.5 M solution of 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 °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 °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 °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}Co γ-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 obtaining 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[1–4] surface oxidations have

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