REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
March 16, 1996

3. REPORT TYPE AND DATES COVERED
Manuscript

4. TITLE AND SUBTITLE
Controlled Formation of Carboxylic Acid Groups at Poly phosphazene Surfaces: Oxidative and Hydrolytic Routes

5. FUNDING NUMBERS
N00014-91-J-1194
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R&T Code: 3132007

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

19960404 047

11. SUPPLEMENTARY NOTES
Submitted for publication to CHEMISTRY OF MATERIALS

12a. DISTRIBUTION/AVAILABILITY STATEMENT
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12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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14. SUBJECT TERMS
Surfaces, polymers, polyphosphazenes, surface reactions, carboxylates, alcohols, XPS, SEM

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
UL

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 1

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std Z39-18
298-102

OFFICE OF NAVAL RESEARCH

Grant No. N00014-91-J-1194

R&T Project 3132007

Dr. Kenneth J. Wynne, Program Manager

Technical Report No. 33

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by

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Prepared for publication in *Chemistry of Materials*

March 16, 1996

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Abstract

Two methods have been developed for the controlled formation of carboxylic acid units at the surfaces of aryloxyphosphazene high polymers. The first involves a permanganate-induced oxidation of p-methylphenoxy side groups, with the surface density of carboxylic acid units being controlled by the ratio of p-methylphenoxy to phenoxy groups along the polymer chains. The second approach involves a base-induced hydrolysis of carboxylate ester functions at the para-positions of surface aryloxy side groups. In this method the surface density of carboxyl units is controlled by the reaction conditions, especially by the temperature and the solvent for the base. The same ester functions were converted to alcohol moieties by surface reductions using lithium aluminum hydride in diethyl ether. The surface structures before and after these reactions were studied by a combination of contact angle measurements, X-ray photoelectron spectroscopy, scanning electron microscopy with X-ray microanalysis, and ATR-IR spectroscopy.

Introduction

The development of selective chemical reactions at polymer surfaces is an expanding frontier in the chemical sciences with broad ramifications in theoretical, synthetic, and technological chemistry.[1-6] Properties, such as adhesion, wettability, composite formation, permeability, and biocompatability can depend critically on the surface character. For this reason, it is vitally important to be able to control the surface composition of materials in a rational manner.

Until fairly recently the control of polymer surfaces was accomplished by the choice of different polymers which already had inherently different surface compositions. Thus, the generation of a material with a specific surface response often required the design and synthesis of an entirely new polymer. In many cases, a polymer chosen for its bulk properties lacked the appropriate surface characteristics, and *vice versa*. Hence materials design involved a compromise. The alternative approach is to select a polymer on the basis of its bulk properties and then modify the surface of the material in a predictable manner to enhance specific interfacial characteristics.

Many methods have been developed to modify polymer surfaces.[1-12] For example, plasma treatment of polyethylene to oxidize the surface, or the introduction of sulfur groups at the surface of polybutadiene has been used to increase the adhesion of these materials.[13-15] Some of these processes involve the use of harsh conditions which leads to the formation of several different functional species at the interface. Hence, understanding the mechanisms by which such surfaces interact with their environment becomes difficult.

The purpose of the present work was to develop chemical reactions that will lead to predictable and controllable structures on the surfaces of a broad class of polymers known as polyphosphazenes (**1**)[16-20]. These macromolecules contain a backbone of alternating phosphorus and nitrogen atoms, with two (usually organic) side groups linked to each phosphorus. The main method of synthesis involves macromolecular substitution reactions carried out on a reactive polymeric intermediate, poly(dichlorophosphazene) (**3**). Polyphosphazenes are almost unique with respect to the wide range of side groups that can be introduced. By the beginning of 1996, more than 700 different polyphosphazenes had been synthesized and characterized, with materials properties that span the range from elastomers, surface coatings, and glasses to fibers. Different polymers are soluble in organic media or water, and the surface properties vary with different side groups from hydrophobic or amphiphilic to hydrophilic. The surface properties of polyphosphazenes are particularly important for their uses in advanced elastomers, membranes, protective coatings, and biomedical materials.

A sub-class of these polymers is especially important from the viewpoint of secondary reactions. These are species that bear aryloxy side groups attached to the inorganic polymer chain. Many organic substitution reactions can be carried out on the side groups of these polymers in solution without disruption of the backbone, mainly because the aryloxy side units protect the backbone from attack by aggressive reagents.[21-23] In particular, oxidation and ester hydrolysis reactions are known that convert organic-soluble polymers to water-soluble species.[24,25]

The specific objective of the present work was to devise methods for the controlled introduction of carboxylic acid units at the surfaces of aryloxyphosphazene polymers. The purpose was to generate hydrophilic surfaces on hydrophobic polymers in ways that would improve adhesion, change the response to the surface by microorganisms or marine organisms, and provide linkage points for the binding of biologically active molecules, bases, or metal cations.

The challenges in this work were: (1) to develop reaction conditions that restrict the transformation to the surface of the material without altering the chemical structure of the interior regions (this usually requires the use of mild reaction conditions), (2) to control the degree of reaction at the surface to influence the concentration or coverage of the new functional units (this, too, requires the use of mild conditions), (3) to analyze the surface structure and determine both the species present and the depth of the transformation; and (4) to ensure that the newly formed surface is not buried by the turnover of flexible macromolecules in the surface regions.

The two different surfaces and reaction types shown in Scheme 1 were employed as starting points and pathways that lead to carboxylic acid formation. An additional transformation, that involves the reduction of an ester group, leads to alcohol formation and is also shown in Scheme 1. The individual polymers were synthesized by the routes shown in Scheme 2. The starting point for this present work was the knowledge that p-methylphenoxy groups linked to phosphazenes can be oxidized by permanganate to aryloxycarboxylic acid units, but that the course of surface reactions is difficult to control. The present work seeks to apply additional controls by the presence of two types of side groups - oxidatively reactive p-methylphenoxy groups and inactive phenoxy groups. The plan was to vary the ratios of these two side groups through the polymer synthesis process, and to use the ratios to control both the depth of the surface reaction and the concentration of carboxylate units at the surface. An additional idea was to utilize this arrangement to ensure the retention of hydrophobicity in the bulk material and hence discourage burying of the acid groups by surface reorganization.

The second route to carboxylic acid formation was via the hydrolysis of aryloxy propylcarboxylate groups. This reaction has been developed for phosphazene high polymers as a solution state process,[25] but had not been applied to surface modification studies. Because of the mildness and ease of control over this surface reaction it was not necessary to utilize a second, unreactive hydrophobic side group, although in principle this is also possible.

Experimental Section

Materials Hexachlorocyclotriphosphazene (**2**) was supplied by Ethyl Corp. and was purified by one recrystallization from heptane and two fractional vacuum sublimations at 50 °C and 0.05 mm Hg. Poly(dichlorophosphazene) (**3**) was synthesized by the thermal polymerization of hexachlorocyclotriphosphazene in an evacuated sealed tube at 250 °C in an oven equipped with a rocking shelf. Phenol (Aldrich) and p-cresol (Aldrich) were sublimed and stored under argon. Propyl 4-hydroxybenzoate (Aldrich) was recrystallized from methylene chloride/hexane before use. Sodium hydride (60% dispersion in mineral oil, Aldrich), $KMnO_4$ (Aldrich), KOH (1M solution in water, Aldrich), KOH (1M solution in methanol, Aldrich), and $LiAlH_4$ (1 M solution in ether, Aldrich) were used as received. Dioxane and tetrahydrofuran (THF) were distilled into a reaction flask from sodium benzophenone-ketyl from a grease-free still under an atmosphere of dry argon or nitrogen. Ethyl acetate was distilled before use in a grease-free apparatus. Sodium phenoxide and sodium p-methylphenoxide were synthesized by standard procedures and were concentrated, dried under vacuum, and stored under nitrogen.

Equipment ^{31}P nuclear magnetic resonance (NMR) spectra were recorded with a JEOL FXQ90 NMR spectrometer operated at 36.2 MHz or with a Bruker WM-360 NMR spectrometer operated at 146 MHz. ^{31}P NMR spectra are relative to 85% phosphoric acid as an external reference with positive values downfield from the reference. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WM-360 NMR spectrometer operated at 360 or 90.27 MHz respectively. ^{1}H and ^{13}C NMR spectra were referenced to internal $CDCl_3$. Elemental microanalyses were obtained by Galbraith Laboratories (Knoxville, TN). Surface contact angle measurements were obtained with the use of distilled, deionized water as 1 μL sessile drops or by the addition or removal of liquid from a 2-4 μL drop with use of a Ramé-Hart contact angle goniometer, model 100-00, fitted with an environmental chamber. The humidity was maintained at 100%, with the temperature between 18-25 °C. Polymer molecular weights were estimated with the use of a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with two Phenomenex Phenogel linear 10 columns, and a Hewlett Packard 1047A refractive index detector. Data collection and calculations were accomplished with use of a Hewlett

Packard Chemstation equipped with Hewlett Packard and Polymer Laboratories software. The GPC samples were eluted with a 0.01 M solution of tetra-n-butylammonium nitrate in THF and are reported versus polystyrene standards. Glass transition temperatures were obtained with use of a Perkin-Elmer DSC-7 differential scanning calorimeter controlled by a PE7500 computer. Heating rates of 10-30 °C/min. and sample sizes of 20-30 mg were used. Some polymer samples were crosslinked by exposure to 10 Mrads of ^{60}Co γ-radiation at the Breazeale Nuclear Reactor at The Pennsylvania State University. Scanning electron micrographs were obtained with use of a JEOL JSM 5400 microscope. X-ray microanalyses were obtained with use of a Pgt Imix Version 6 system attached to the scanning electron microscope. Samples were prepared by freeze fracture techniques to obtain cross sections of the film. The cross sections were mounted on a carbon stub and were coated with carbon with use of a Fisons Polaron PS-2 sputter coater. X-ray photoelectron spectroscopy (XPS) measurements were obtained with use of a Hewlett Packard 5950A XPS spectrometer outfitted with a monochromated Al $K_{\alpha 1,2}$ X-ray source (1486.6 eV).[26] The base pressure of the instrument was 8×10^{-10} Torr and an operating pressure of 1×10^{-8} Torr. A pass energy of 117 eV was utilized. The electron emission angle was fixed at 52^{o}. All data analysis (curve fitting and Shirly background subtraction) was accomplished using Surface Science Instruments version 6.12 software. Curve fitting was achieved with a Gauss-Lorentzian function after background subtraction with a minimum of 15 iterations to achieve a χ^2 convergence. The oxygen/carbon atomic sensitivity factor used was 2.93, which was verified with reference samples.

Synthesis of $[NP(OC_6H_4CH_3)_{1.5}(OC_6H_5)_{0.5}]_n$ (6) and Related Polymers 4 and 5. All three polymers were prepared by similar techniques, but with variations in the reactant ratios. The details for the preparation of **6** are given as an example. Sodium phenoxide (2.46 g, 21.3 mmol) in dioxane (150 mL) was added slowly dropwise to a rapidly stirred solution of poly(dichlorophosphazene) (4.92 g, 42.5 mmol) in dioxane

(500 mL) under an inert atmosphere in a 1000 mL three-neck round bottom flask fitted with a reflux condenser, gas inlet, and addition funnel. A white precipitate formed. The reaction mixture was heated to reflux for 48 hours allowed to cool, and then transferred to an autoclave. Sodium p-methylphenoxide (26.02 g, 200 mmol) in dioxane (500 mL) was added. The reaction mixture was heated to 155 °C for 18-24 hours in a closed reactor system, cooled, concentrated to a viscous liquid, and precipitated into water to isolate the crude, white polymer. The undried polymer was redissolved in THF and was precipitated into water (3x), hexane (3x), and 95% ethanol (2x). The yields were typically 50-75%. Polymer **5** was synthesized in a similar manner. Polymer **4** was synthesized at reflux in dioxane (102 °C) without the use of an autoclave. ^{1}H ($CDCl_3$) 6.8 (br s, ar), 6.78 (br m, ar), 6.67 (br m), 2.06 (s, CH_3); ^{31}P ($CDCl_3$) -20 (s); ^{13}C ($CDCl_3$) 152.0 (ipso-aromatic, phenoxy), 149.5 (ipso-aromatic, methylphenoxy), 132.4 (p-aromatic, methylphenoxy), 129.1 (m-aromatic, methylphenoxy), 128.6 (m-aromatic, phenoxy), 123.2 (p-aromatic, phenoxy), 121.3 (o-aromatic, phenoxy), 121.0 (o-aromatic, methylphenoxy). The NMR spectra of polymers **4-6** contained the same number and types of peaks with different relative intensities related to the ratios of the side-groups. The ^{1}H integration is shown in Table 2-O.

Synthesis of $[NP(OC_6H_4CO_2C_3H_7)_2]_n$ (7): Sodium 4-(propoxycarbonyl)phenoxide was prepared under an inert atmoshphere by the dropwise addition of propyl 4-hydroxybenzoate (43.6 g, 0.242 mol) in THF (250 mL) to a stirred suspension of NaH (8.37 g, 0.209 mol NaH) in THF (250 mL) cooled in an ice bath. The mixture was stirred until a homogenous solution was obtained. This solution was added dropwise to poly(dichlorophosphazene) (5.95 g, 51.3 mmol) in THF (1000 mL) in a 2000 mL three-necked round-bottom flask fitted with a reflux condenser, gas inlet, and addition funnel. The formation of a white precipitate occurred. The reaction mixture was then heated to reflux for 48 h and was then allowed to cool. It was then concentrated to a viscous liquid and was precipitated into water. The polymer was redissolved in THF or ethyl acetate without drying and was precipitated into water (3x), hexane (3x), and 95% ethanol (2x). ^{1}H ($CDCl_3$) 7.5 (br s, 2H, aromatic), 6.6 (br s, 2H, aromatic), 4.1 (br s, 2H $CO_2C\underline{H}_2$), 1.67 (br d, 2H, $C\underline{H}_2CH_3$), 0.92 (br t, 3H, $C\underline{H}_3$); ^{31}P ($CDCl_3$) -20 (s); ^{13}C ($CDCl_3$) 165.1 ($\underline{C}O_2R$), 154.0 (ipso-aromatic), 130.8 (m-aromatic), 126.8 (p-aromatic), 120.0 (o-aromatic), 63.8 ($CO_2\underline{C}$), 21.9 ($\underline{C}H_2CH_3$), 10.4 ($\underline{C}H_3$) ; T_g -20 °C; M_n 1.6 x 10^6, Mw 2.2 x 10^6. EA (Calc'd; found) C 59.55, H 5.50, N 3.47, Cl 0.00; C 58.77, H 5.48, N 2.99, Cl 0.33.

Film Preparation: Solution-cast films were prepared by the slow evaporation of 2 g/50 mL of polymers **4-6** in THF or of **7** in ethyl acetate within aluminum frames cemented to glass. The frame was covered by an inverted tray or metal foil and the atmosphere was saturated with THF or ethyl acetate to ensure slow evaporation. After 2-5 days, the films were dried under vacuum (0.01 mm Hg) for 3 days.

Spin cast films were prepared from THF (for the methylphenoxy polymers) or ethyl acetate solutions on gold substrates. Concentrations and spin rates were chosen to yield thin films to minimize charging in the XPS apparatus. However, the films were sufficiently thick that gold was not detected in the spectra.

Surface Reactions: (a) Oxidations Solutions of a mixture of 5 mL of 1.08 M NaOH (aq) and 25 mL of 0.48 M $KMnO_4$ (aq) were equilibrated to the desired temperature in a glass jar fitted with a cap perforated with slits. Films of the polymers were immersed in the solutions for specific times at different temperatures, rinsed with water, soaked in $NaHSO_3$ (aq) for 3-8 hours, rinsed again with water, and stored in water until analyzed. **(b) Hydrolyses** Approximately 15-35 mL of KOH (1 M in H_2O) was equilibrated to the desired temperature in a glass jar fitted with a cap that was perforated with small slits. Bulk or spin cast films of **7** were immersed in or floated on the solution for specified times. The films were then rinsed with water, and were soaked and stored in water until analyzed. (c) **Reductions** Bulk or spin cast films of **7** were immersed in $LiAlH_4$ solution (1 M in ether) for specific times and temperatures under an inert atmosphere. The films were then rinsed and soaked in cold ethanol (100%) and were stored in water until analyzed.

Results and Discussion

(A) Oxidation Reactions.

Overall Approach. The synthesis of the p-methylphenoxy/phenoxyphosphazene polymers was carried out with the use of reaction conditions that resulted in a maximum random distribution of the two types of side groups along the chain (Table 1).[29] The disposition of two or more different side-groups along the chain can influence the distribution of groups formed at the polymer surface. In this synthesis protocol, slow addition of the first nucleophile, sodium phenoxide, to a rapidly stirred solution of poly(dichlorophosphazene) at room temperature resulted in an even distribution of phenoxy side groups along the chain as determined by ^{31}P NMR spectroscopy. The subsequent replacement of the remaining chlorine atoms by p-methylphenoxy groups then favored a retention of this distribution. In other words, the conditions used for the substitution made it unlikely that blocks of one substituent existed in the final polymer. The steric and electronic similarities between the two types of side groups was also expected to discourage the formation of domains in which one side group or the other predominated. However, in principle, any cosubstituent group that is stable to the surface reaction conditions could be utilized, and this would allow for significant changes to the bulk polymer properties.

The similarity of polymers **4-6** in the bulk state was indicated by the similarily of the glass transition temperatures, T_g, which were within 10°C of each other (Table 1). However, the films of these polymers have different solid state characteristics. The 75% methylphenoxy films (**6**) were tough and flexible, whereas the 25% methylphenoxy (**4**) and 50% methylphenoxy (**5**) polymers were rubbery and flexible. Moreover, contact angle measurements and XPS spectra revealed differences in wettability and carbon to oxygen ratios (C/O) respectively, even before the oxidation reactions took place. Even so, the polymers were similar to each other in most respects, and comparisons of the modified surfaces are significant.

The oxidations of the methylphenoxy cosubstituent polymers (**4-6**) (Scheme 1) were accomplished by immersion in 0.4 M $KMnO_4$/0.18 M NaOH at 50 °C. The surface reactions were monitored by contact angle goniometry, x-ray photoelectron spectroscopy (XPS), and attenuated total reflectance infrared spectroscopy (ATR-IR). In general, the oxidation of polymers with varying ratios of methylphenoxy groups proved to be an effective strategy to control the number of carboxylate groups formed at the polymer surface.

General Characterization of the Oxidized Surfaces . The following general observations summarize the basic data obtained regarding the surface oxidation of polymers **4-6**. Contact angle measurements with water indicated an increase in wettability of the oxidized surfaces. ATR-IR investigations detected absorbances at 1695 cm^{-1} characteristic of PhC=O (υ) and consistent with results from the earlier oxidations of polymer **8**. XPS spectra also detected electrons with a binding energy that corresponds to $\underline{C}$=O groups at the treated polymer surface. The overall C/O ratio decreased with the introduction of the additional oxygen atoms of the carboxylic acid, and the O_{1s} region of the spectra revealed a second oxygen environment assigned as C=$\underline{O}$. X-ray microanalysis and electron microscopy provided evidence of a surface specific, mild oxidation. No significant morphological differences between the treated and untreated surfaces were detected by SEM. Thus, the behavior of polymers **4-6** was consistent with the formation of carboxylic acid groups at the surfaces. The specific details and explanations are as follows.

Contact Angle Investigations. The results of the contact angle measurements are shown in Figure 1. The initial, unreacted polymers showed higher advancing contact angle, θ_a, values with increased phenoxy content of the polymer. Specifically, polymers

6, 5, and **4** have θ_a values of 91°, 102°, and 110° respectively. Subsequent oxidation of the polymer surfaces with permanganate, to form carboxylic acid groups, resulted in a decrease in θ_a. The θ values were uniform over the surface of the modified films, which indicated a homogenous oxidation. However, a significant feature of these systems was the change of the θ_a values as a function of the time during which the chemically modified films were subsequently soaked in water. Reproducible results were achieved only when the oxidized films were soaked in water for long periods of time. This change in the θ values with exposure to water was evidence of a surface reconstruction process to minimize the interfacial surface free energy by the movement of carboxylate groups to the interfacial region over a period of weeks.[30] For the oxidized species formed from **6** after 24 hours at 50 °C, the difference in θ_a values was 32° after a soaking time of 2 days (73°) and 4 weeks (41°). The oxidized 75% methylphenoxy polymer (**6**) and a 100% methylphenoxy polymer (**8**) showed similar wettability behavior. The minimum θ value of 41° was detected after 10 hours surface oxidation for both systems. Polymers **4** and **5**, with a higher phenoxy content, had minimum θ_a values of 61° and 50° respectively. Polymers **4, 5,** and **6** showed the same trend of a decrease in contact angle with an increase in oxidation time, which is consistent with the increased conversion of methylphenoxy groups to aryloxy carboxylic acid groups at long reaction times. The difference in θ_a values corresponds to the difference in the ratio of phenoxy and carboxylate groups at the surface, and this indicated that the surface density of carboxylate groups can be controlled by the composition of the polymer.

XPS Spectroscopy. Attempts to obtain XPS spectra for oxidized surfaces formed by contact with 0.4 M $KMnO_4$/0.18 M NaOH solutions were hampered by delamination of the thin polymer films from the gold substrates. Therefore, investigations were undertaken using a 10-fold decrease in the concentration of reagents. XPS analysis of reactions that utilized these concentrations, 0.04 M $KMnO_4$/0.02 M NaOH, were evaluated initially with use of polymer **8**. Oxidation of **8** with the use of 0.4 M

$KMnO_4$/0.18 M NaOH for 1 and 24 hours resulted in 67% and 86% conversion of the methyl groups to carboxylic acid units respectively.[24] The use of the milder 0.04 M $KMnO_4$/0.02 M NaOH resulted in 14% and 83% conversion of the surface methyl groups at two temperatures respectively. Oxidations of **8** carried out with the more concentrated oxidant for 24 hours at 50 °C resulted in an 800 nm depth of reaction[24] which would lead to film delamination. No film delamination was detected for the spin-cast films treated with the weaker reagents. Use of these milder conditions induced no change in the ATR-IR spectra. This suggested that only a very thin layer of oxidized species had been formed, a layer that could be detected by a decrease in the θa contact angle. However, the scatter of the θ measurements suggested the presence of patches of oxidized side groups and/or of facile surface reconstruction. All the XPS data were obtained for materials oxidized under the milder conditions.

With respect to polymers **4**, **5**, and **6**, the XPS spectra showed an increase in conversion of methylphenoxy groups to carboxylic acid groups with an increase in oxidation time for all three polymers. Figure 2 shows the percentage of methyl units converted to carboxylate groups at the surfaces. The maximum possible number of carboxylate groups at the surface of **4** is 25%, **5** is 50%, and **6** is 75%. For the 1 hour reactions, approximately 30% of the available surface methyl groups were converted to carboxylate groups for each polymer. Thus, the number of carboxylate groups relative to the *total* aryloxy species at the surface of **4** was 9%, **5** was 18%, and **6** was 23%. It was clear that the use of the same reaction conditions for all three polymers generated different concentrations of carboxylic acid groups at the three surfaces, with the total amount of these groups limited by the number of methylphenoxy groups available for oxidation. The conversion increased with time and to a maximum percentage of carboxylate groups relative to all surface aryloxy groups (for the mild conditions) of 25% for **4**, 41% for **5**, and 54% for **6**. Reactions carried out at higher reagent concentrations would probably result in higher conversions for **5** and **6**.

Conclusions Regarding the Surface Oxidations. The XPS data illustrate the differences that can be obtained in the control of surface structure by (a) an alteration of reaction conditions (reaction time or temperature) or (b) by variations in the polymer composition. The modification of any of these polymers with use of the appropriate conditions can result in surface regions in which ~25% of all the side groups present are carboxylic acid units. However, the bulk properties and the distribution of the groups at the surfaces may be different for each substrate. Attempts to control the number of carboxylic acid groups through the use of milder reaction conditions alone may lead to patches of reacted and unreacted groups at the surface.[8,31] For example, the generation of a surface that contains only 25% carboxylate groups by the oxidation of **5** or **6** may result in a nonhomogeneous distributution of carboxylic acid groups clustered in groups on the surface. Such clusters could form in response to the increased wettability of the modified areas and to an autocatalytic generation of the carboxylic acid groups in regions of prior reaction in preference to the hydrophobic, unreacted portions of the film. However, the oxidation of **4** should yield a surface with a homogenous distribution of carboxylic acid groups arising from the initial homogeneous distribution of methylphenoxy groups at the surface. Although these factors were difficult to evaluate due to the surface reconstruction in these polymers, θ measurements for the surface oxidations of polymers **4**, **5**, and **6** with 0.4 M $KMnO_4$/ 0.18 M NaOH indicated uniform oxidation at high conversions of methylphenoxy groups to carboxylic acids.

Hydrolysis Reactions.

Overall Approach. The homogeneous *solution* hydrolysis of polymer **7** has been reported previously.[25] The surface hydrolysis of **7** was accomplished by the immersion of solution-cast films (~150-200 μm thick), or thin films spun cast on glass or gold substrates, in aqueous 1 M potassium hydroxide. The reactions were monitored by x-ray photoelectron spectroscopy (XPS), contact angle (θ) goniometry, and scanning electron microscopy (SEM). In general, the basic hydrolysis of **7** proved to be a mild and effective strategy to generate a surface layer of carboxylic acid groups.

Solvent Effects. The course of the hydrolysis could be altered dramatically by the choice of the reaction solvent. The solvent for the base controls the response at the interfacial region. A solvent that swells the polymeric substrate may generates a deep interface, whereas a medium that does not lead to swelling would be expected to give a more sharply defined surface region. In addition, the wettability of the surface by the solvent will affect the interaction of the solid substrate with the liquid phase reagent.[32]

The hydrolysis of **7** was investigated with the polymer in contact with 1M KOH in water and in methanol. The use of methanol was investigated for the following reason. Although both the initial ester polymer and the product carboxylated surface are insoluble in methanol, this solvent wets the surface of the polymer more effectively than does water, and methanol has been found by other investigators to be an effective solvent for the surface hydrolysis of ester groups.[31] Thus, it was of interest to establish the importance of surface wettability in these reactions.

Treatment of **7** at 50 °C with 1 M methanolic KOH for 18 hours led to hydrolysis of the ester groups throughout the bulk material. Although no swelling was detected while the film was immersed in the methanolic solution, these films dissolved when subsequently exposed to water. Polymer films that had been previously crosslinked before methanolic hydrolysis swelled to form hydrogels as they absorbed water. The crosslinked hydrogel systems also underwent a pH sensitive swelling. The bulk reaction of the polymer during treatment with methanolic KOH suggests that surfaced-hydrolyzed domains can act as conduits to transport the methanolic KOH to ester groups in the interior of the material. By contrast, treatment of the solid polymer with *aqueous* KOH does not lead to a reaction of the bulk material, even though the surface-modified areas swell in water. This behavior highlights a key difference between these techniques.

It also illustrates a difference between the approach described in this paper and the behavior of polymeric solids in which ester groups are present only at the surface of unreactive polymers such as poly(chlorotrifluoroethylene) or polyethylene.[13,31] Polymers that bear only a thin surface layer of ester groups cannot yield carboxylic acid groups in the interior (except by surface reorganization). For these systems, the use of methanol as a solvent provides an effective medium for hydrolysis of the ester. For the modification of **7**, water is a more effective solvent to control the surface reaction. Thus, the following discussion refers to ester hydrolysis brought about by aqueous base.

Structure of the Surfaces Generated by Aqueous Hydrolysis. The presence of surface carboxylic acid groups generated by the aqueous hydrolysis of the ester groups in **7** by 1M aqueous KOH was established by contact angle measurements and by XPS experiments.

A study of the contact angles revealed that the hydrolysis process yields a surface with a higher hydrophilicity than that of the starting material (Figure 5). This is consistent with the generation of surface carboxylate groups. In addition, advancing contact angle values, θ_a, varied as a function of the pH of the applied probe liquid from 45 to 18° (Figure 6). This suggests the presence of ionizable groups at the polymer surface. No such pH dependence was found for the θ_a contact angles at the unhydrolyzed surface.

XPS spectra of the hydrolyzed surfaces revealed a decrease in the carbon/oxygen ratio (C/O) compared to the initial polymer, and this is consistent with the loss of propyl groups. The O_{1s} region of the spectra for the hydrolyzed surfaces was consistent with the presence of surface carboxylate structures. In addition, potassium was detected at the modified surfaces. No potassium was detected at unreacted ester polymer surfaces or at surfaces treated with KOH under conditions that did not bring about hydrolysis.

The surface changes were evaluated by XPS and contact angle measurements as a function of the reaction time and temperature. Treatment of **7** with 1 M KOH in water at 25°C resulted in no detectable change based on XPS and θ measurements. Moreover, no potassium was detected by x-ray microanalysis of these surfaces. However, treatment at 50 °C generated an increasingly hydrophilic surface as the reaction progressed (Figure 5). Both the advancing, θ_a, and receding, θ_r, contact angle measurements revealed this increase in hydrophilicity. The θ_r values decreased rapidly from 67° at 0 hr, to 30° at 2 hr, 12° at 6 hr and to <5° for reactions carried out during 12 hours. Thus, the θ_r values were not useful for following the progression of the reaction for longer reaction times. The θ_a value for **7** is 91°. After treatment at 50 °C for 24 hours, the θ_a had fallen to 41°. Further treatment at 50 °C did not result in a lower θ_a value and this represented the minimum for this reaction. Figure 5 depicts the change in θ_a as a function of reaction time at 50 °C and 80 °C.

An increase in the reaction temperature to 80 °C required the use of a polymer crosslinked by ^{60}Co γ radiation to prevent bulk deformation and flow at this temperature. The reaction proceeded more rapidly at 80 °C and resulted in a minimum θ_a value of 40° after 6 hours. Treatment for 1 week at 80 °C resulted in no further change in the value of θ_a.

The extent of conversion of ester to carboxylic acid groups within the surface zone was determined by peak fitting XPS spectra by two methods. First, the carbon to oxygen ratio (C/O) for the initial and treated surfaces was used to evaluate the percentage of carboxylate groups. The ratio of carbon atoms to oxygen atoms in unmodified **7** is 10/3. The corresponding C/O ratio for a 100% conversion of ester groups would be 7 carbon atoms and 3 oxygen atoms, or 7/3, which reflects the loss of the propyl group from the ester structure. The total areas of the carbon and oxygen regions in the XPS spectra were evaluated and the percentage conversion calculated as the reaction progressed with time (Figure 7).

In addition to this, a second method was used to calculate the percent conversion of ester to carboxylate groups, which involved curve-fitting the high resolution O_{1s} spectra. The peak assignments are shown in Table 2. Peak assignments were facilitated by the referencing of spectra to similar chemical moieties.[27,28] The P-$\underline{O}$-C area is not changed by the reaction conditions and is constant at 531.4 eV in the initial and modified surfaces. Thus, the comparison of the C=$\underline{O}$, C-$\underline{O}$-C, and C(O)-$\underline{O}$H with the P-$\underline{O}$-C area provides this additional method to calculate conversion. The C-$\underline{O}$-C, and P-$\underline{O}$-C peaks have very similar binding energies of 531.4 eV. The ratio for the initial O_{1s} peak fit is therefore 2 (C-$\underline{O}$-C and P-$\underline{O}$-C) to 1 (C=$\underline{O}$, 529.9 eV) (Figure 3a). For the hydrolyzed surface, the two oxygen atoms of the carboxylic acid unit have very similar binding energies of 525.5 eV. Thus, a conversion of 100% would yield a ratio of 1 (P-$\underline{O}$-C) to 2 (C=$\underline{O}$, and C(O)-$\underline{O}$H). The conversion determined by the integration of the peaks in the O_{1s} region was consistently higher than that determined by the C/O ratio. Nevertheless, both methods indicate ~80% conversion after 24 hours at 50°C.

The observations that follow suggest that the O_{1s} may provide a more accurate evaluation of the percentage conversion. First, a comparison of the θ_a results with the XPS data indicates that the O_{1s} data are more consistent with the contact angle than are the C/O data. XPS results from the O_{1s} region for a 12 hour reaction indicated an 80% conversion, which is slightly less than the maximum conversion of 84%. This agrees with the θ_a value of 46° for a 12 hour reaction, which approaches the minimum of 41°. However, it must be noted that θ measurements detect changes in the outer 10 Å of the surface whereas the XPS conditions used in this work detect changes at the surface to a depth of 20 Å. Therefore, any correlation between θ and XPS results may be artificial. In addition to the consistency between the O_{1s} data and the θ measurements, the O_{1s} data avoid interference from carbon contamination. The ratio of the areas of the O_{1s} region peaks for **7** for the two types of oxygen environments was more consistent and easier to evaluate than that for the three carbon environments in the C_{1s}. Finally, the O_{1s} region was also the region of greatest change in the XPS spectra (Figure 3a and b). While the C/O ratio changed, the change to the C_{1s} region was not as pronounced as the change in the O_{1s} region (Figure 3a and b and 4a and b). Although differences exist between the results suggested by the different methods of analysis, both sets of XPS data indicate increased conversion with hydrolysis time and a maximum conversion of ~80% at 24 hours. As with the θ measurements, these XPS data did not reveal increased conversion with further treatment at 50 °C.

One experiment at 50 °C using a very thin film of polymer (with the thinness evidenced by the detection of the gold substrate in the XPS spectrum) indicated a 100% conversion. This result implied that the aqueous hydrolysis process had penetrated through a layer less than 20 Å thick. When thicker films were analyzed, the calculated conversion was less than 100% which suggests that the hydrolysis was confined to the outer 20 Å of the films. An increase of the reaction temperature to 80 °C led to a conversion of 90%. The surfaces generated at 50 and 80 °C, with 80 and 90% conversions respectively, had $\theta_a = 41°$. Thus, both the XPS and θ data suggest a surface-confined transformation of ester to acid groups within an outer 20 Å thick region.

Investigations of the surface of these polymeric substrates by SEM, before and after treatment with KOH, revealed no significant differences. 1 μm holes were evident and were most likely due to evaporation of the solvent during film preparation. In a further attempt to discern the depth of the hydrolysis reaction, hydrolyzed films were equilibrated with 0.1 M cesium hydroxide to selectivley stain the hydrolyzed portion of the film. Cross sections of the film were analyzed by SEM. No differences were detected between the hydrolyzed and bulk, unreacted polymer. However, X-ray microanalysis confirmed the presence of cesium at the surface of the hydrolyzed film. Potassium was also detected in films not stained with cesium. The lack of any contrast in the SEM or TEM images suggested that the layer of modification was very thin. The TEM results were of only marginal value since the samples melted in the electron beam, but the data obtained in the brief period before melting agreed with the conclusions from the SEM data. These results, in conjunction with XPS data, again suggest that the depth of reaction was less than 20 Å. This provides a marked contrast to the carboxylic acid bearing films produced by the permanganate-induced oxidation of a methylphenoxyphosphazene single substituent polymer (**8**).[24] The depth of reaction for those surface oxidations ranged from <50 nm for room temperature reactions, to more than 400 nm for a 24 hour 50 °C oxidation, and 1 µm for 80 °C reactions.

Attenuated total reflectance infrared spectroscopy (ATR-IR) studies of the hydrolyzed materials were hampered by the presence of the ester functionalities that remained near the surface. Their absorptions masked the carboxylate species at the surface.

Thus, the hydrolysis of **7** by treatment with aqueous KOH is a mild, effective method for the generation of carboxylic acid groups at a polymer surface. It can be contrasted with the surface carboxylic acid groups generated by the permanganate oxidation of methyl groups in poly(methylphenoxy-phenoxy-phosphazene) **6.** The θ and XPS data for the surfaces of these two polymers after reaction were very similar. The main difference between the two was the depth of penetration. The aqueous base hydrolysis method led to a very surface-specific modification with a depth of reaction of less than 20 Å, which was not detectable by SEM or TEM. The depth of reaction for the oxidation-generated surfaces ranged from several nm's to ~1µm.

Reduction Reactions

Alcohol functionalities were introduced at the surface of **7** by reduction of the ester units using $LiAlH_4$. This was accomplished by immersion of solution- or spin-cast films of **7** in solutions of $LiAlH_4$ in diethyl ether at room temperature. The reactions were monitored by XPS, contact angles, and ATR-IR techniques. This process proved to be an effective method for the generation of alcohol groups at a polyphosphazene surface.

ATR-IR spectra of the dried, modified surfaces detected the characteristic OH stretch as a broad absorbence at 3420 cm^{-1}. XPS spectra revealed an increase in the C/O ratio: the O_{1s} region of the spectra showed predominantly a single oxygen environment, and the C_{1s} region revealed a loss of the C=O peak, all consistent with the reduction of ester groups (Figures 3c and 4c). Traces of aluminum were occasionally detected by XPS. The presence of aluminum was minimized by extensive washing with cold ethanol (100%). Contact angle measurements revealed an increase in hydrophilicity, but with no dependence of θ on the pH of the probe liquid (Figure 5 and Table 3).

These surface reductions were evaluated by both XPS and θ measurements as a function of the time and temperature of the reaction. After 1 hour reaction time at room temperature, a 79% conversion to hydroxyl groups was detected by the XPS analysis of the O_{1s} region. The θ_a value for these conditions was 46°. Increases in the reaction time to 24 hours yielded no change beyond that of the 1 hour reaction, with a 75% conversion estimated by XPS and a θ_a value of 45°. A reduction of the temperature to 12 °C for a 1 hour reaction led to a conversion of 58%. The contact angle measurements for these (12°C) samples indicated a patchy surface, since the data revealed a large scatter for the θ measurements. Increases in the reaction time to 6 hours at 12 °C yielded a similar scatter. A further temperature reduction to 0 °C resulted in no detectable reaction as determined by XPS. Attempts to discern the depth of the reaction by electron microscopy were unsuccessful.

Conclusions

The alteration of side group ratios provided a convenient method for the control of the surface oxidation of methylphenoxy-phenoxy-phosphazenes. The concentration of phenoxy groups at the polymer surface limited the number of carboxylate groups formed by surface oxidations. The utilization of the same reaction conditions to modify polymers **4**, **5** or **6** resulted in different concentrations of carboxylic acid groups in the surface regions. This method may offer more control over the number and distribution of functional groups at the surface of these polymers than previous oxidative processes. The presence of both hydrophobic and hydrophilic groups led to reconstruction to minimize the interfacial surface free energies.

The surface hydrolysis of **7** can be carried out with the use of mild basic hydrolysis or reduction conditions. Treatment of the polymer with KOH (1M in H_2O) at 50 or 80 °C resulted in the formation of a very thin layer bearing carboxylic acid groups, with an increased conversion occurring over time. The course of the reaction was monitored by θ and XPS measurements and was found to be nearly complete after 12 hours at 50 °C. The surface was similar to the one produced by surface oxidation of **8** except that the zone of reaction was shallower. The use of methanol as a solvent for the hydrolysis led to a bulk reaction which produced a water-soluble carboxylate bearing polymer. The reduction of **7** at 12 °C and room temperature led to the formation of surface hydroxyl groups as detected by XPS, contact angle measurements, and ATR-IR. No reaction was detected after treatment with $LiAlH_4$ (1M in ether) at 0 °C. A 58% conversion was achieved at 12 °C and a 79% conversion occurred at room temperature.

Overall, these two approaches to carboxylic acid formation provide a sound starting point for studies of both materials and biological adhesion and offer a platform for extended synthesis and cation coordination at polymer surfaces. It also provides access to materials with surfaces that are of considerable interest in biocompatibility research.

Acknowledgments

H.R.A and C.T.M thank the Office of Naval Research, and W.K.W and N.W. achnowledge the NSF for the support of this research. We also thank D.A. Shirley for the use of the XPS spectrometer and R. Walsh for helpful discussions regarding the electron microscopy.

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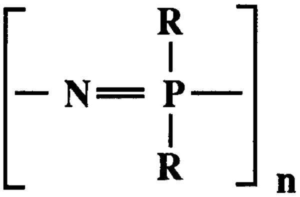
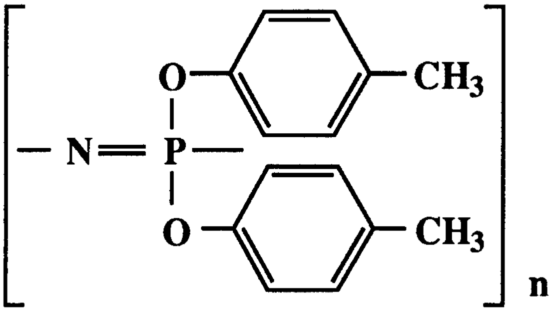


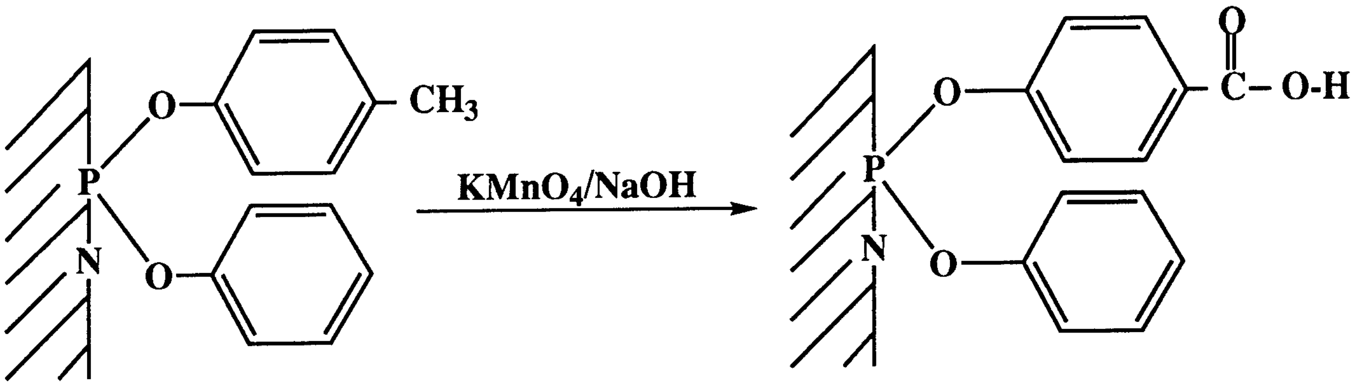
$\left[-N{=}PR_2-\right]_n$

1

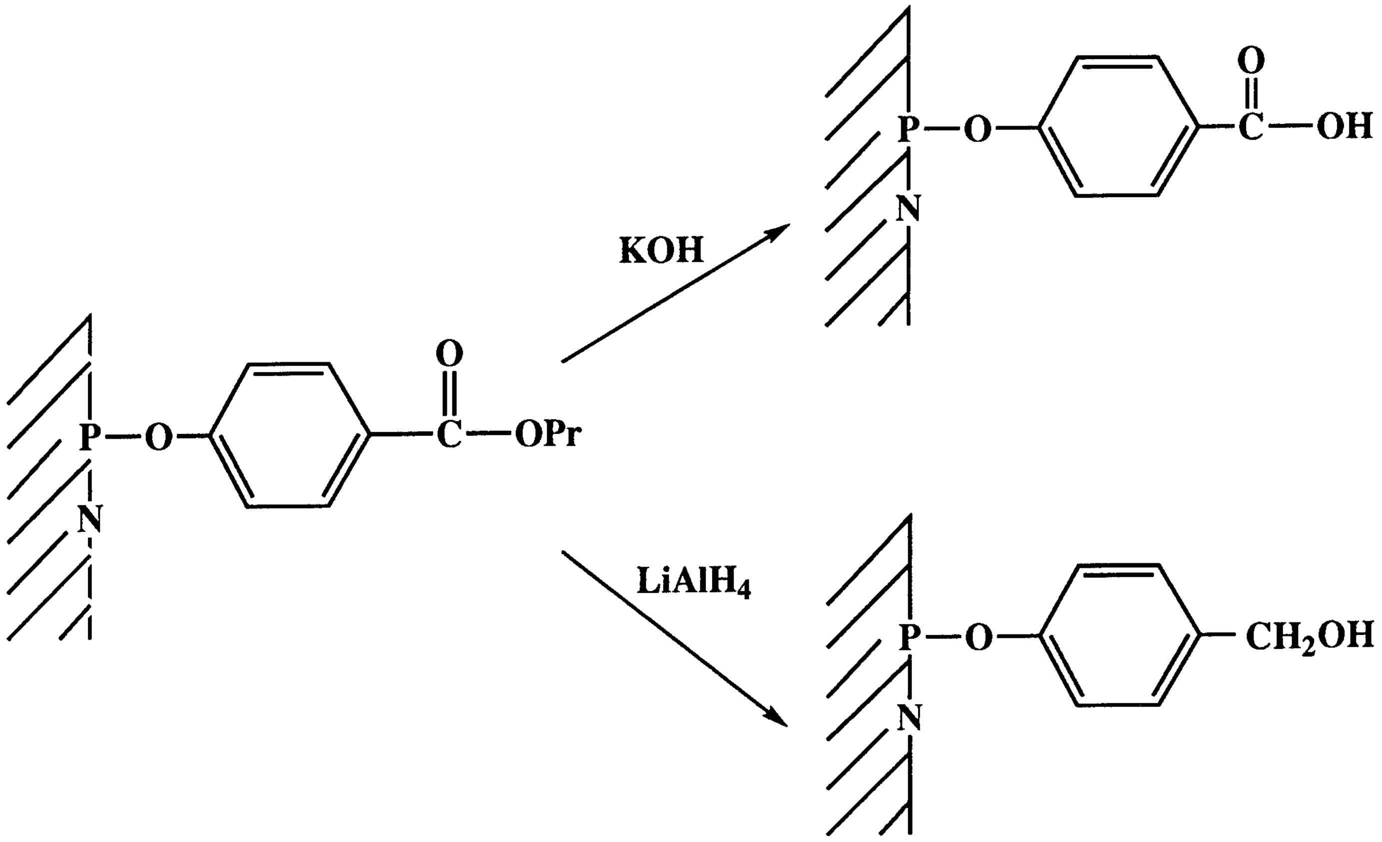


8

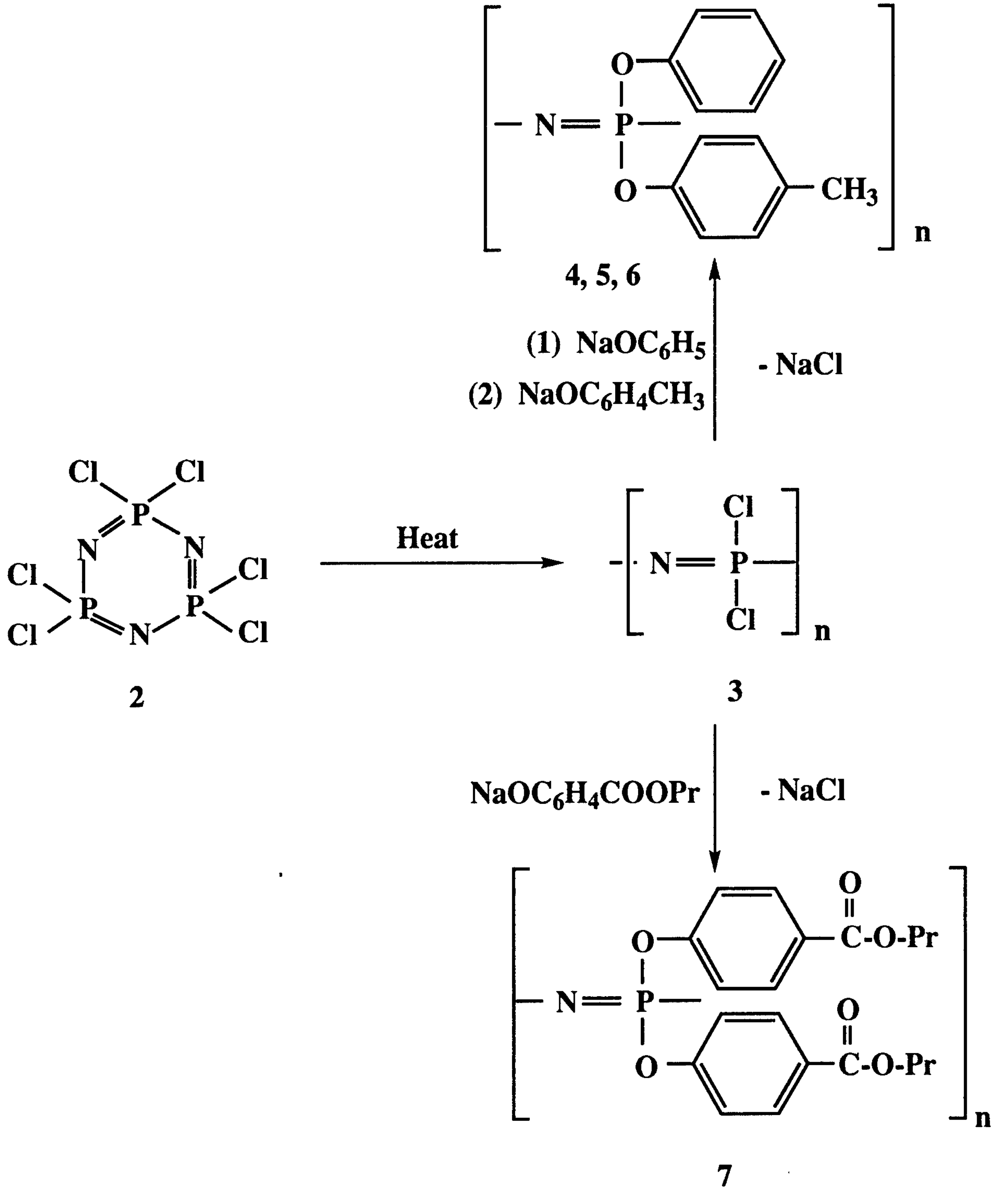
Scheme 1



25, 50, 75% methylphenoxy groups



Scheme 2



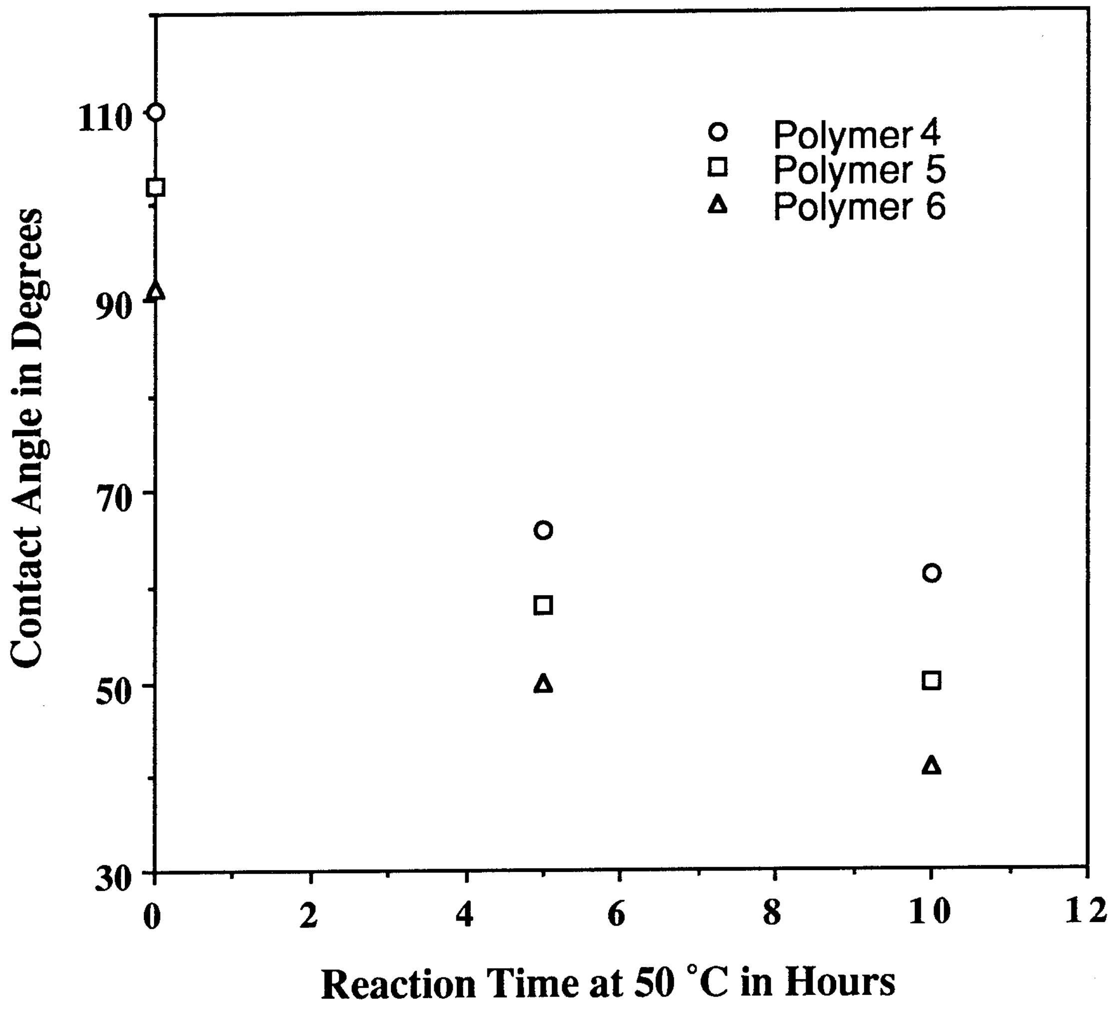

Contact Angle in Degrees
110
90
70
50
30
0
2
4
6
8
10
12
Reaction Time at 50 °C in Hours
○ Polymer 4
□ Polymer 5
△ Polymer 6

Figure 1

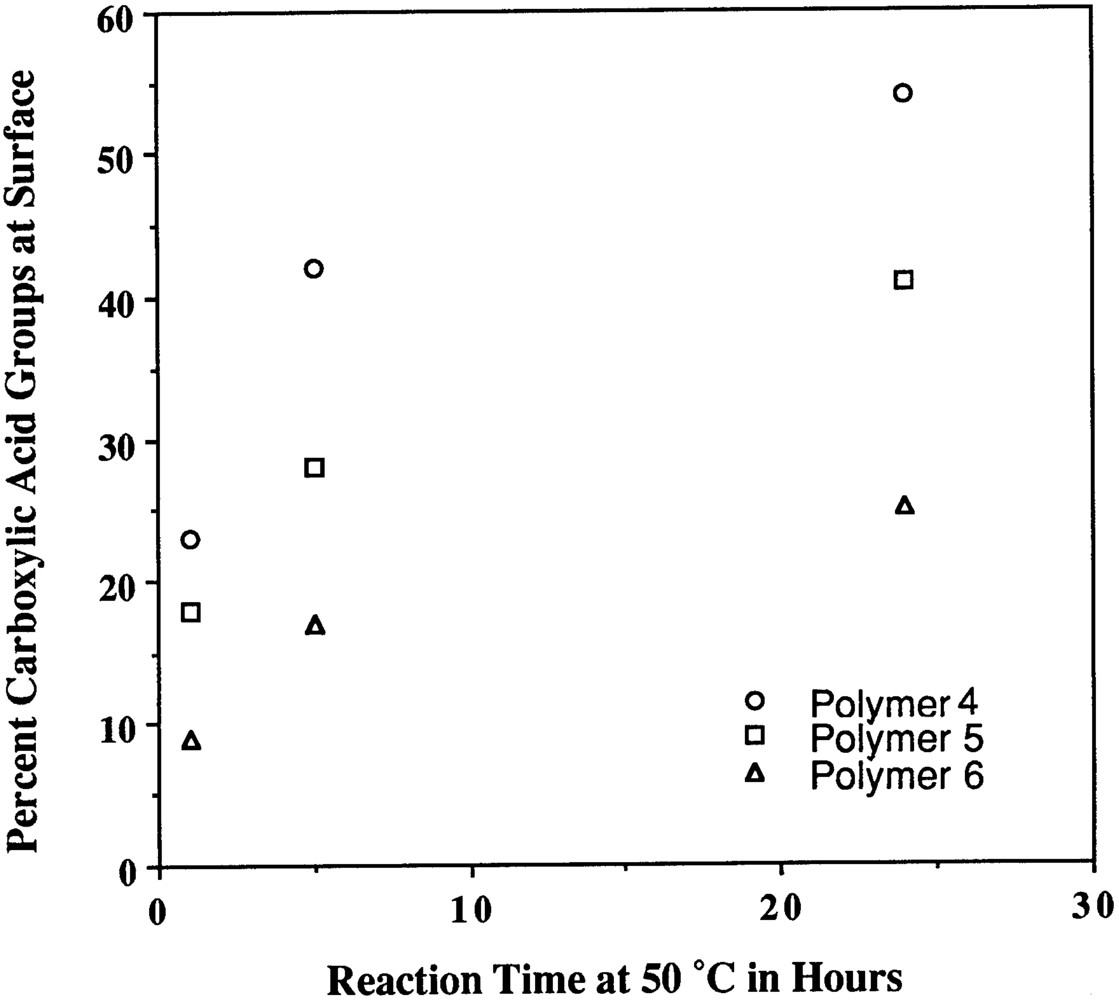

Percent Carboxylic Acid Groups at Surface
0
10
20
30
40
50
60
0
10
20
30
Reaction Time at 50 °C in Hours
○ Polymer 4
□ Polymer 5
△ Polymer 6

Figure 2

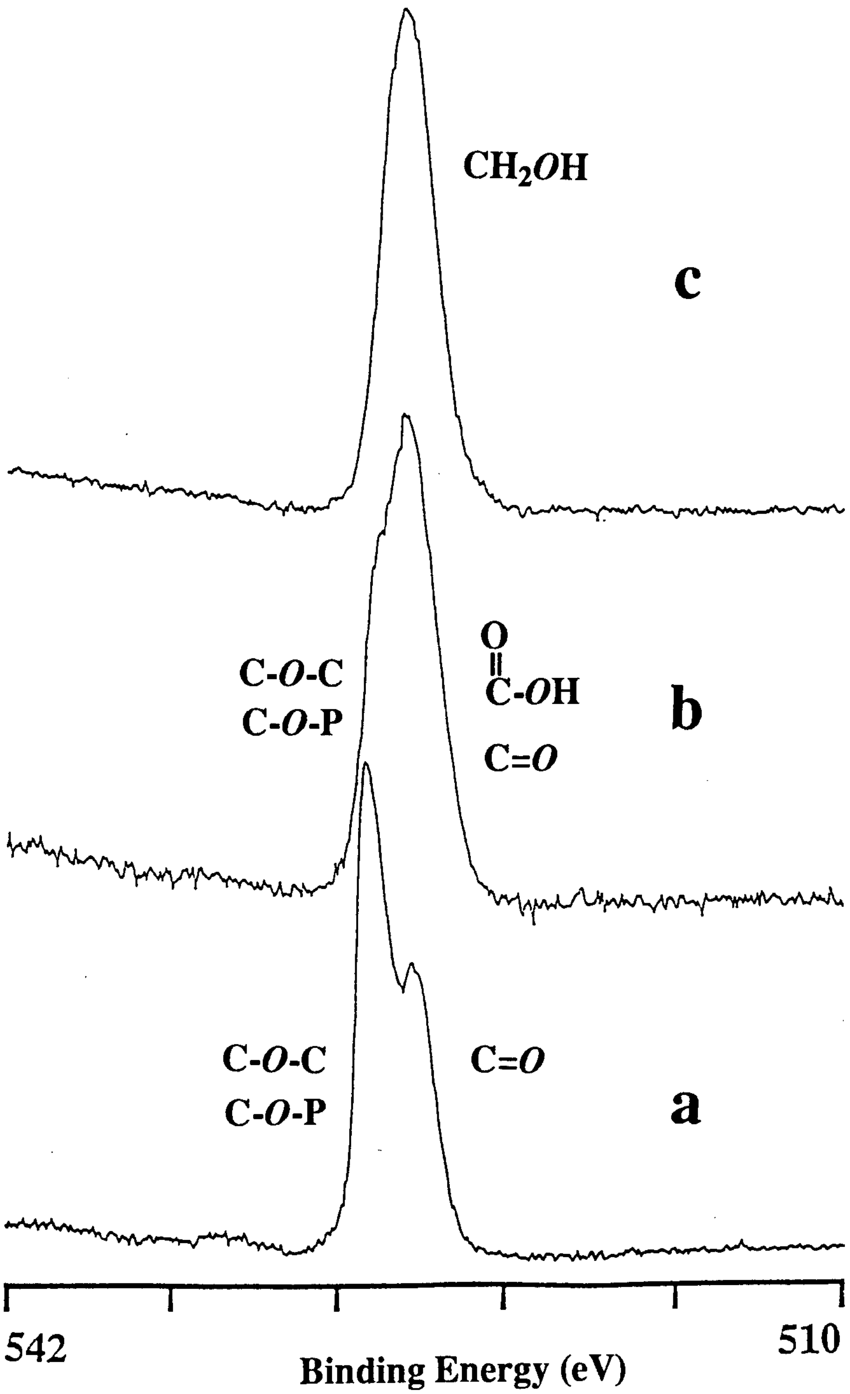


Figure 3

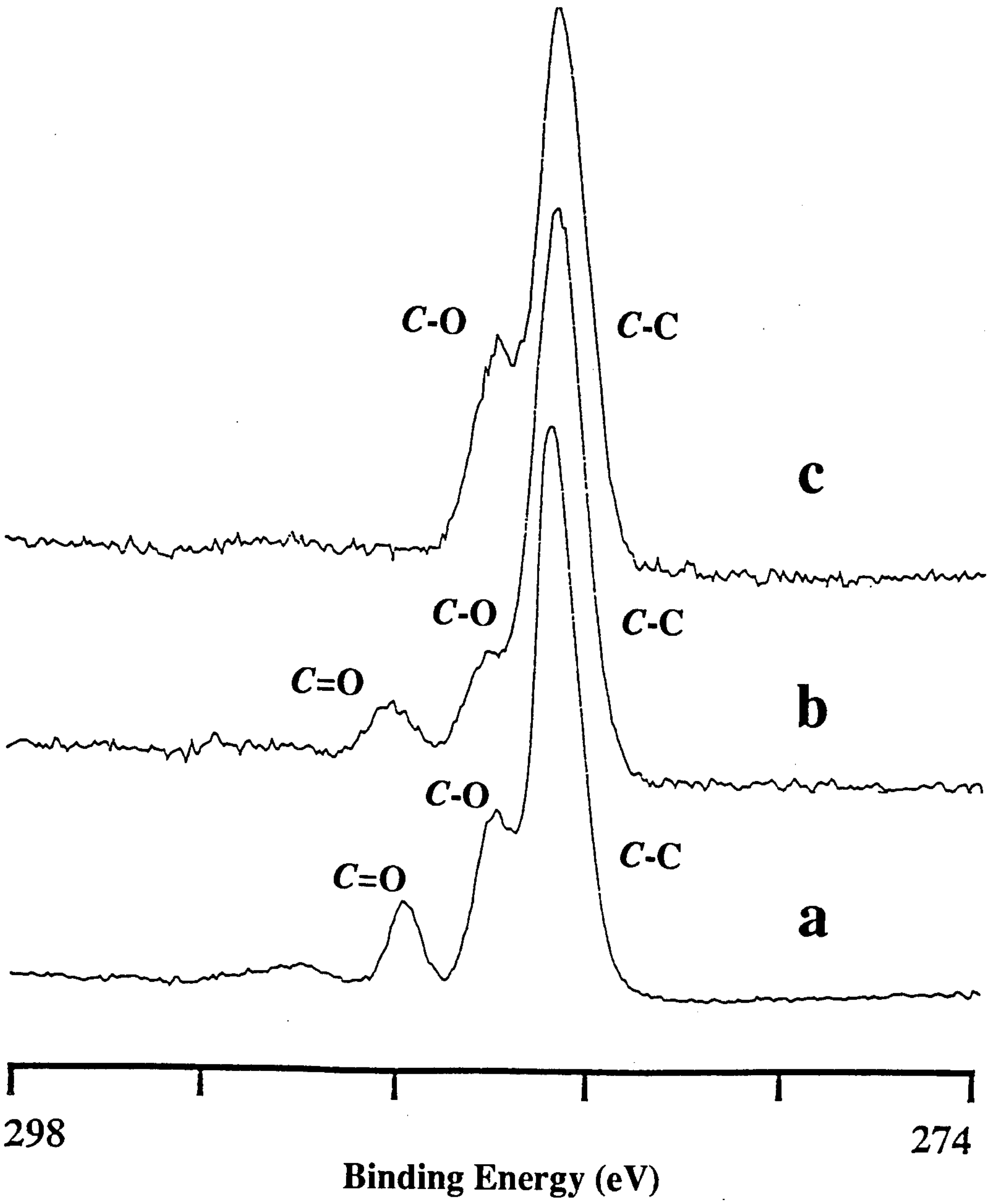
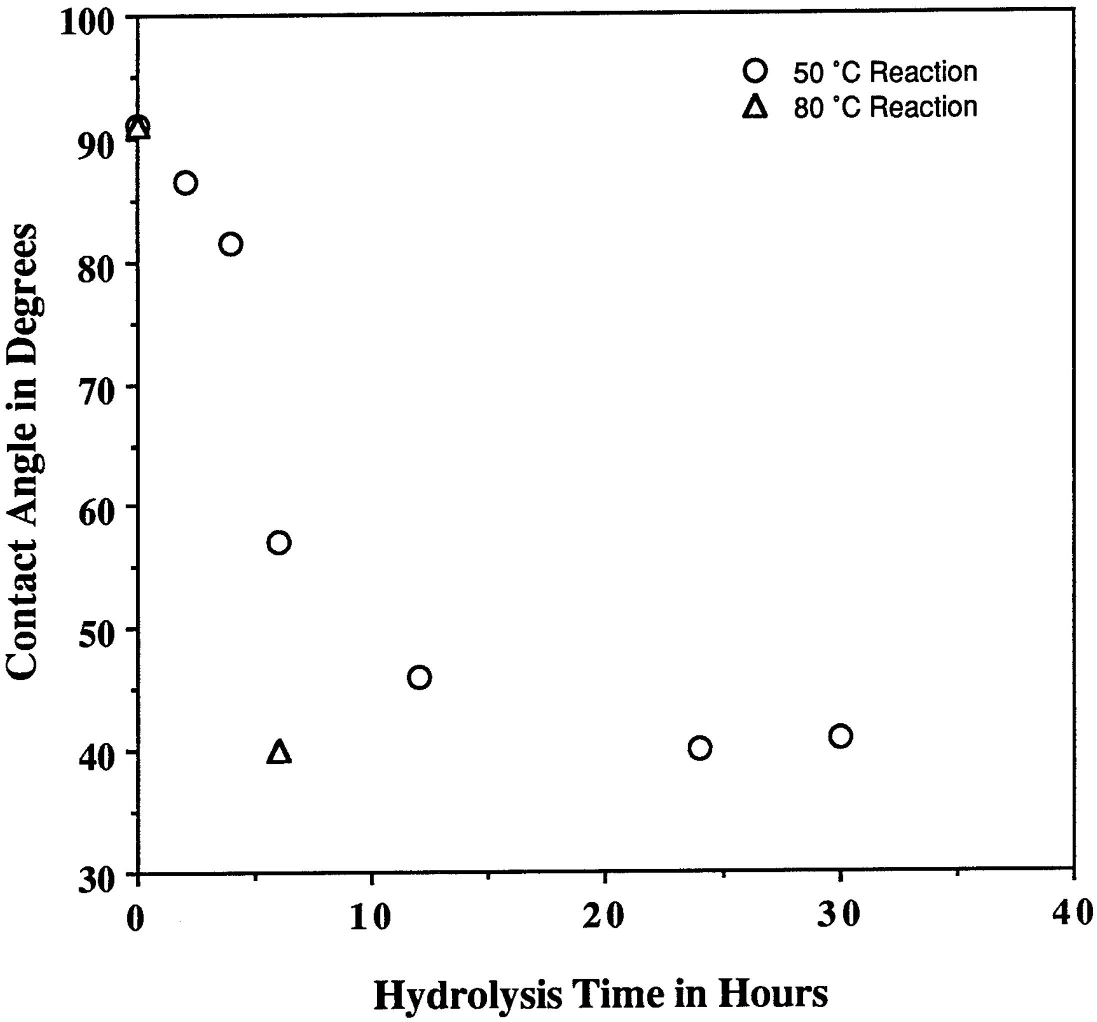
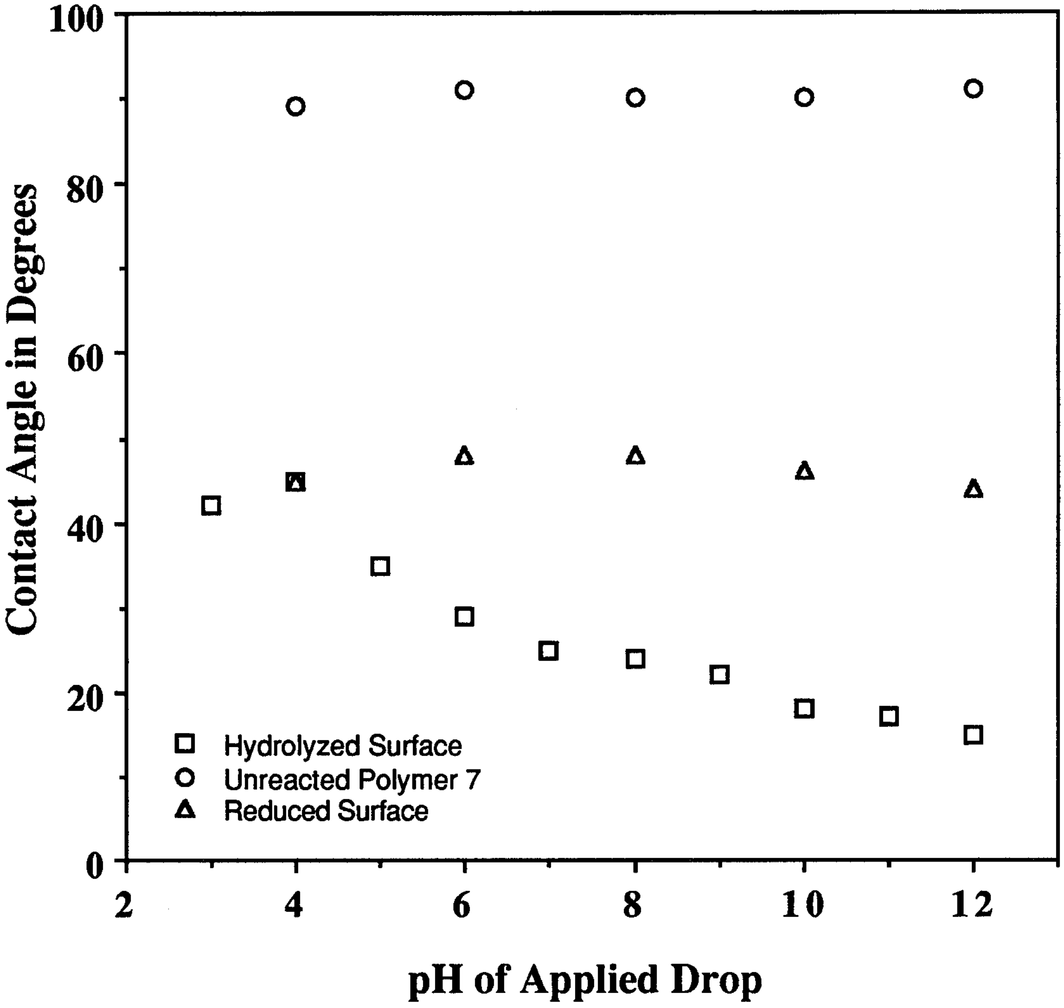


Figure 4



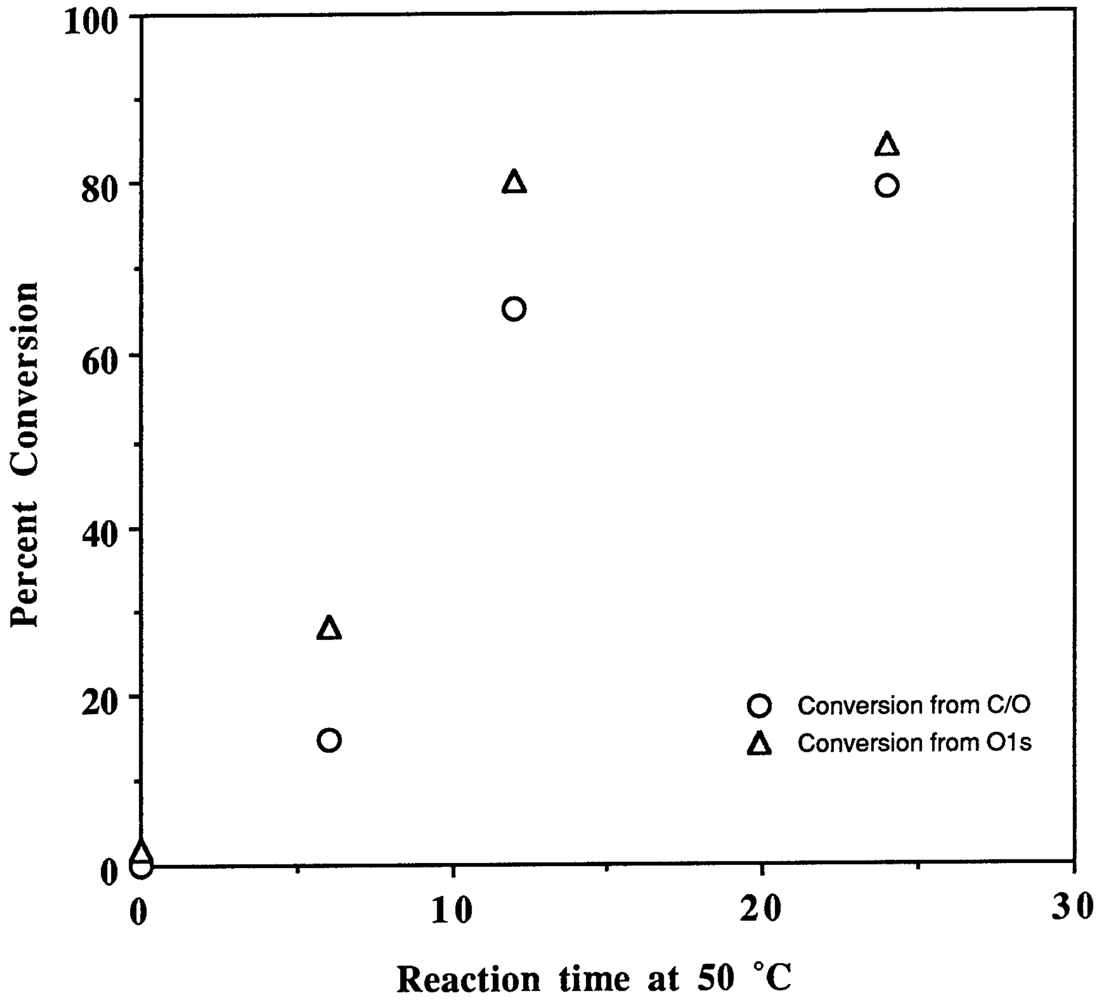
100
90
80
70
60
50
40
30
0
10
20
30
40
Contact Angle in Degrees
Hydrolysis Time in Hours
○ 50 °C Reaction
△ 80 °C Reaction

Figure 5



100
80
60
40
20
0
Contact Angle in Degrees
2
4
6
8
10
12
pH of Applied Drop
□ Hydrolyzed Surface
○ Unreacted Polymer 7
△ Reduced Surface

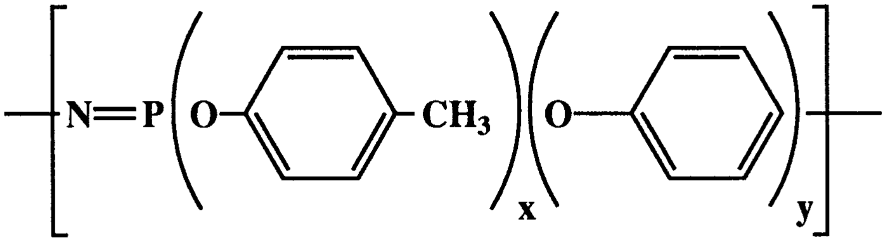
Figure 6



100
80
60
40
20
0
Percent Conversion
0
10
20
30
Reaction time at 50 °C
○ Conversion from C/O
△ Conversion from O1s

Figure 7

Table 1 Composition of Polymers 4 - 6 and Characterization Data



Polymer	x, y	H_{aryl}/H_{Me}	Mol Wt	Tg (oC)	Elemental Analysis (%)
			Mw, Mn		
---------	----	------------	---------	----	--
4	0.44, 1.56	7.24	4.5×10^5	-10	calc'd C 63.03, H 4.65, N 5.88, Cl 0.00
			6.0×10^4		(found) (61.81) (5.06) (5.61) (0.52)
5	0.98, 1.02	3.06	2.3×10^6	-7	calc'd C 63.67, H 4.93, N 5.71, Cl 0.00
			1.3×10^5		(found) (63.54) (5.03) (5.59) (0.00009)
6	1.50, 0.50	1.92	3.1×10^5	-1	calc'd C 64.29, H 5.19, N 5.55, Cl 0.00
			7.9×10^4		(found) (63.57) (5.52) (5.43) (0.0067)

Table 2. XPS-Derived Binding Energies for the Various Functional Groups

Functional Group	Binding Energy (eV)
$C\text{-}\underline{C}\text{-}C$	284.0
$C\text{-}\underline{C}\text{-}O$	285.6
$C\text{-}\underline{C}{=}O$	287.9
$C\text{-}\underline{O}\text{-}C$	531.4
$P\text{-}\underline{O}\text{-}C$	531.4
$C{=}\underline{O}$	529.9
$O{=}C\text{-}\underline{O}H$	529.9
$CH_2\underline{O}H$	531.5

Table 3: XPS-Derived Conversion Data and Contact Angle Values for the Surface Reduction of **7**

Time	Temperature	Conversion	Contact Angle
1 hour	25 °C	79%	46°
24 hours	25 °C	75%	45°
1 hour	12 °C	58%	a
6 hours	12°C	60%	a

a) Contact angles varied from location to location on the surface

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