

The Introduction of Alkyl, Ester, Carboxylate, Amino, Hydroxyl, and Phosphate Functional Groups to the Surface of Polyethylene

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SYNOPSIS

The surface of polyethylene was derivatized with ester, carboxylate, amino, hydroxyl, and phosphate functional groups. α , ω bifunctional alkanes, containing on one end a primary amine, were coupled to oxidized polyethylene through an amide linkage. Polyethylene was first oxidized with chromic acid, the carboxylate groups were converted to the acyl chloride with phosphorus pentachloride, and then reacted with a primary amine to give the covalently bound amide. The opposing ends of the bifunctional alkanes were the methyl, tertiary amine, ester, and hydroxyl groups. The ester was converted to the carboxylate by acid cleavage and the hydroxyl group converted to the phosphate by treatment first with phosphorus oxychloride and then aqueous base. Attenuated total reflection FTIR, XPS, and pH-dependent contact angle wetting were used to characterize the surfaces. The FTIR data were used to confirm the formation of the amide and to detect an undesired carboxylate/ammonium ion complex formed in the presence of trace amounts of water. XPS data were used to confirm expected changes in elemental composition and to provide quantitative estimates of the yields. Oxidation of the polyethylene introduced 5×10^{14} carboxylate groups/cm² in the 25 Å XPS sampling depth. Of these, up to 98% could be converted to the amide. The advancing contact angle data confirmed the acid/base behavior of the functional groups.

INTRODUCTION

Polymer surfaces prove technically important in a wide variety of applications where control of adhesion, wetting, environmental degradation, and adsorption are important.^{1,2} The composition of polymers is most often tailored to achieve desired mechanical properties with little consideration of surface properties. Hence post-processing surface treatments are typically used and are designed to clean the surface of unwanted constituents or in-

roduce specific functionality to the polymer backbone. The methods used are often expedient to the desired result and limited to simple treatments. Such ad hoc treatments are too limited in scope to contribute to a deeper understanding of the relationship of polymers surface composition to surface properties. More extensive studies would compare a wide variety of surface compositions with attention to type of surface functional groups, density of these groups, local environment effects, and surface structure. The systematic variation of surface composition has received less attention, in part from the paucity of organic synthetic schemes targeted specifically for polymer surfaces and the problems encountered in analysis of the "product." An enhanced understanding of the relationship between surface composition and interfacial properties will result

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from availability of synthetic schemes and reliable surface characterizations.

Our interest is in derivatization of surfaces with a series of common organic functional groups. Specifically, we wish to relate surface composition to the ability of these surfaces to induce heterogeneous nucleation of minerals from solution.^{3,4} Carboxylate, sulfonate, phosphate, amino, hydroxyl, and thiol groups are of specific interest for their acid, base, or polar properties. These groups have been identified as important in controlling heterogeneous nucleation and crystal growth in biomineralization—e.g., formation of bone, dentin, and mollusk shell.^{5,6} Besides our specific interest, a series of well-characterized surfaces differing only in functional group type and density should prove valuable in the study of adhesion, wetting, adsorption, and other basic surface phenomena.

In order to systematically explore the effect of variation of functional group attached to the surface, it is necessary to use a polymer substrate which is not soluble nor swells appreciably in the solvents which are used in surface synthetic schemes. This allows a wide variety of schemes to be used and, more importantly, allows derivatization to be confined to the surface or near surface region. Secondly, the introduction of each functional group should be based upon a single derivatization scheme except for steps which control the type of functional group. This assures that the measured physical property is more properly related to the type and density of functional group rather than the underlying substrate or than in variation in functionality introduced by different derivatization schemes.

Polyethylene (PE) provides a suitable substrate as it is not soluble nor does it swell appreciably in most solvents—provided that the temperatures are kept below about 50°C and immersion times are limited to a few hours. The lack of reactive functionality in PE is overcome by introducing carboxylate groups. To these carboxylate groups stable ester or amide linkages can be formed which provide a route of attaching the desired functional group.^{2,4,7-13} Conversion of the carboxylate group to the acyl chloride improves the reactivity. Thus, for example, a tertiary amine can be introduced to the surface by reaction with α, ω bifunctional alkane, containing on one end a primary amine and on the other the tertiary amine. The primary amine forms an amide linkage to the surface with the tertiary amine extending from the surface. This scheme is applicable to any end group which does not compete with the primary amine.

Oxidation of PE has been achieved by both physical and chemical methods; these methods were reviewed by Brewis and Briggs.¹ Etching with dichromate/sulfuric acid solutions (chromic acid) is a simple method which favors introduction of carboxylate groups and which has been explored in detail in the literature.^{1,7,14-16} By comparing the etching of high density polyethylene (HDPE), low density polyethylene (LDPE), and polypropylene (PP); Blais et al.¹⁴ determined that etching occurred by cleavage of exposed carbon chains. Little etching occurred on HDPE as the crystalline regions are resistant to chromic acid attack. Presumably this was due to the inability of the reagent to penetrate the polymer. PP etched rapidly by cleavage at the methyl appended tertiary sites. Few oxidized groups remained attached to the surface, however, as frequent cleavage resulted in short oligomers, which were lost from the surface. LDPE resulted in the highest density of retained functional groups. The amorphous regions in LDPE provided sterically reactive secondary methylene sites and tertiary cross-linking sites which did not cleave so frequently as to be lost from the surface. Prolonged etching resulted in loss of material, but the oxidation site density became constant after some minimum etching time. As determined by Rasmussen et al.,⁷ approximately 60% of the oxidized sites were carboxylate, and 40% were ketones or aldehydes. Alcohol groups were not found in significant fraction.

These same authors developed a nomenclature scheme which is followed in this report. Surface etched PE is designated PE—(C=O)COOH to reflect the presence of both keto and carboxylate groups. Since in most cases the keto groups are unimportant, the designation is abbreviated here as PE—COOH to reflect the focus on the reactive carboxylate group. Similar nomenclature applies to derivatives; for example, the tertiary amine formed by coupling of *N,N*-dimethylethylenediamine would be designated PE—CONHCH₂CH₂N(CH₃)₂.

In a series of papers,⁷⁻¹³ Whitesides and co-workers have reported on the reactivity of PE—COOH. For the formation of amides, of the general formula, PE—CONH(CH₂)_{*n*}R, the carboxylated surface was first reacted with sulfonyl chloride or phosphorus pentachloride to give the acyl chloride, PE—COCl. This was then reacted with basic, aqueous solutions of the primary amine or reacted with a methanol solution of the amine containing triethylamine base to scavenge the evolved acid. Holmes-Farley and Whitesides¹¹ reported that both hydroxide ion and methanol react rapidly with the acyl chloride. Hence

strong competition with the amine for the acyl chloride was expected. Despite this Holmes-Farley, Bain, and Whitesides¹³ reported successful formation of the amide from an aqueous basic solution using taurine (2-aminoethylsulfonic acid), glycine, methylamine, dimethylamine, glucosamine, 2-aminoethanethiol, aspartic acid, 4-aminopyridine, and 2-aminophenol. From methanolic solutions the amides of 4-aminobenzoic acid, 2-aminoethylphosphonic acid, 2-aminoethylphosphate, 2-aminoethyl hydrogen sulfate, (3-aminophenyl) boronic acid, and dansylcadaverine were reported.

The physical characteristic of derivatized PE are complex and the definition of the surface requires some care. Holmes-Farley and Whitesides¹¹ proposed the formation of an interphase region approximately 20 Å thick, which is very probably graded from essentially polyethylene to dangling carboxylate groups on short alkyl chains. Depending on the physical method used to probe the interface, very different results were obtained. For example, ATR-FTIR spectroscopy penetrates deeply into the surface and gives only qualitative information on functional group identity. The XPS escape depth of an electron is of the same order as the interface region thickness and allows a better estimate of the extent of reaction. Advancing contact angle wetting generally probes only the outermost few angstroms of the surfaces. In this sense, contact angle wetting is very useful in monitoring the physical and chemical parameters relevant to heterogeneous nucleation, cation adsorption, wetting, and other highly surface specific physical phenomena.

The reactivity of PE-COOH or its derivatives depends on the ability of solvent and/or reagent to penetrate into the surface region.¹¹ For this reason, a single method of derivatization applicable to many desired functional groups promotes uniformity of reaction for a series of functional groups. The structure of the surface may also be dependent on environment. For example, mild heating in dry atmosphere promoted extensive rearrangement of the surface and migration of carboxylate groups into the interior of the sample.^{8,12}

In this work we report on the functionalization of PE with a series of simple organic functional groups using a consistent derivatization scheme. The formation of the amide occurred by reaction of the amine with the acyl chloride. We were not able to achieve reaction in the presence of water as previously reported¹³ and utilized a dry pyridine/triethylamine solvent. The surfaces were characterized by ATR-FTIR spectroscopy, XPS, and the pH depen-

dence of contact angle wetting. These methods provided confirmation of the success of the reactions and preliminary information on the physical characteristics of the surface.

EXPERIMENTAL

General Methods. All solvents were reagent grade; triethylamine, Et₃N, and diethyl ether were distilled under nitrogen from Na metal before use; pyridine was used as received (HPLC grade, 99.99%, Aldrich Sure-Seal). Water was purified to 18 MΩ cm by reverse osmosis and carbon and ion exchange filtering using a Millipore system. Polyethylene (PE) (low density powder, melt index 0.22, *T_m* 115°C) and Chromium(VI) oxide (99.9+%) were purchased reagent quality from Aldrich and not purified further. The liquid amines, *n*-propylamine (99+%, Aldrich), dimethylethylenediamine (95%, Aldrich), and 3-amino-1-propanol (99+%, Aldrich), were purified by vacuum distillation onto a column of 4 Å molecular sieves. β-Alanine ethyl ester hydrochloride (98%, Aldrich) was purified by recrystallization with hot absolute methanol and cold ether. The free amine was obtained by adding a several fold excess of triethylamine to a pyridine solution of β-alanine ethyl ester hydrochloride. Triethylamine hydrochloride precipitated from the solution. After centrifugation the supernate containing the free amine in triethylamine/pyridine solution was used directly in the synthesis.

Polyethylene Film (PE). Microscope slides (VWR select grade) were cleaned and pretreated by roughening the surface with 280 grit sandpaper, ultrasonication in absolute methanol, and vapor depositing a layer of hexamethyldisilazane (98%, Alfa Products) on the surface. The surface preparation was completed by bonding the hexamethyldisilazane to the slide by heating the samples to 150°C for 120 min. A solution of polyethylene in *o*-xylene (98%, Aldrich) in a ratio of 1 g to 25 mL at 110°C was used to dip coat the surface of microscope slides. The resulting polyethylene film was approximately 1 mm thick after two dip coats. To smooth the surface of the film and to insure good adhesion between the polyethylene and the slide, the slide underwent an annealing procedure; the samples were heated at 105°C for 30 min; the temperature was raised to 150°C over a period of 10 min and maintained at 150°C for 20 min; next the temperature was raised to 163°C over a period of 5 min and maintained at 163°C for 20 min; finally the samples were cooled

to room temperature by allowing the samples to sit overnight in the closed oven without application of power. A small convection oven (Blue M) was used for annealing and the temperature maintained to within 2°C of the setpoint by an Omega CN9111 miniature microprocessor temperature controller with a type K thermocouple. After annealing, the samples were allowed to stand at room temperature for 2–3 days in atmosphere prior to the chromic acid oxidation step.

Surface reactions on the polyethylene films were performed using glass microscope slide racks (Wheaton) which held 10 slides each. Stirring of solutions was accomplished by magnetic stirrers and stir bars at low speed. The samples were handled using polypropylene locking forceps on the end of the slide not coated by polyethylene. All samples were dried in a desiccator under vacuum prior to spectral analyses.

Polyethylene Carboxylic Acid (PE-COOH).

PE samples were immersed in a chromic acid solution ($\text{CrO}_3/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ in a 29 : 42 : 29 w/w/w formulation) at 72°C for 1 min with stirring. The samples were washed with water (1 min), a solution of 10% nitric acid (1 min), and finally a water soak (2 min). The samples produced in this manner, PE-COOH, were the basis for all further studies. Each batch was tested by ATR-FTIR spectroscopy to insure reproducibility. The PE-COOH samples were also tested by XPS for contamination by chromium, sulfur, or nitrogen in this step.

Formation of the Carboxylate Salt (PE-COOK). PE-COOH samples were immersed in a solution of 0.5M KOH in absolute methanol for 1 h with stirring to obtain the potassium salt. The samples were removed and washed in clean absolute methanol.

General Preparation of PE-Amides. The conversions of PE-COOH to the acid chloride, PE-COCl, and further to the amide, PE-CONH(CH₂)_nR, were done in a series of three glove bags (Instruments for Research and Industry, Model SS-20-20H), each equipped with dry nitrogen and vacuum lines, connected with quick-clamp closures. The first bag was used for the acid chloride derivatization, the middle bag for an ether rinse, and the final bag for the amide derivatization step. The specific procedures are discussed below.

PE-COCl. The acid chloride group, PE-COCl, was prepared by immersing PE-COOH film samples in a 0.05M solution of phosphorus pentachloride (98%, Aldrich) in ether for 20 min with stirring. The samples were moved directly to the ether rinse

for 5 min and on to the amide step without spectral analysis. After three sets of samples (30 slides), the phosphorus pentachloride/ether and ether rinse solutions were replaced.

PE-CONH(CH₂)_nR. The PE-COCl samples were immersed in a solution of 10 mL of the desired liquid amine or a solution containing the free amine isolated from 10 g of the original amine hydrochloride and 250 mL of triethylamine/pyridine solution (1 : 1 v/v). The samples were treated for 20 min with stirring. The samples were removed to atmosphere and rinsed briefly in water and finally in absolute methanol. After three sets of samples (30 slides), the solution was replaced. The appended group, R, was -CH₃, -N(CH₃)₂, -OH, or -COO-C₂H₅ while *n* was equal to 2 or 3.

PE-CONH(CH₂)₂COOH. PE-CONH(CH₂)₂COOC₂H₅ samples were soaked in 0.1M HCl solution for 3 h with stirring. The samples were rinsed in water several times to remove any remaining HCl.

PE-CONH(CH₂)₃OPO₃H₂. The PE-CONH(CH₂)₃OH samples were treated with 6.0 mL (0.065 mol) phosphorus oxychloride (J. T. Baker) and 9.0 mL (0.065 mol) triethylamine in 500 mL dichloromethane (99.9%, Aldrich) for 24 h with stirring. After a brief rinse in water, the samples were soaked in a 0.20M sodium carbonate (Spectrum Chemical Manufacturing) solution for 30 min with stirring. After another water rinse, the samples were soaked in water for 1 h to remove any impurities or unreacted reagents.

ATR-FTIR Spectroscopy. ATR-FTIR spectra were measured on a Nicolet 740 spectrophotometer. Films were mounted in a solid sample holder against a ZnSe plate (45°, 50 × 10 × 3 mm). An internal reflection attachment was used to position the sample for maximum transmittance (about 15% of the initial light beam). The sample chamber was purged with dry nitrogen for 1 h prior to spectral taking to remove carbon dioxide and water present in the atmosphere. Between spectra, the sample holder and ZnSe prism were cleaned in absolute ethanol to remove any residues.

XPS Spectroscopy. XPS surveys were obtained on a Perkin Elmer PHI 560 XPS/Auger/SIMS surface analysis system, using the magnesium anode. Films were cut to approximately ½ in. × 1 in. × 1 mm and were mounted on the sample holder using double-sided tape. Some surveys detected small amounts of silicon present, due to glass fragments from cutting on the samples surface.

SEM Spectroscopy. SEM photomicrographs

were obtained with a Joelco JSM-U3 scanning electron microscope. The samples were cut in half and gold sputtered prior to measurements.

Contact Angle Measurements. Advancing contact angle measurements were obtained using a Rame-Hart Model 100-10 contact angle goniometer. Prior to measurement, the samples were stored in a sealed container above a saturated KCl solution to assure hydration of the surface groups. The actual measurements were taken with the samples in a high humidity plexiglass chamber. Each measurement was taken three times in different areas of the surface to obtain an average value for the entire surface. Contact angles on these surfaces were measured using a series of buffer solution of pH 2.0, 4.0, 5.9, 6.9, 7.7, 8.2, 10.75, 10.95, and 12. The pH of the buffers were checked prior to the contact angle measurements using a combination electrode (Orion) and standard pH 4.0, 7.0, and 10.0 buffers (VWR) for calibration.

Calculation of Yields. The yields were calculated from the relative intensities of the XPS O_{1s} , N_{1s} , and the P_{2p} peaks. These values provided the relative elemental compositions (see Table I) when corrected by the appropriate XPS peak height sensitivity factors. The oxygen elemental fraction, O_{xps} , was given by

$$O_{xps} = 2.0 * [PE-COOH] + m * [D1] + n * [D2] \quad (1)$$

where D1 was the primary amide derivative molecular fraction and, where relevant, D2 was a secondary derivative molecular fraction. The multipliers, m and n , were the stoichiometric number of oxygens in the respective derivatives. The nitrogen elemental fraction was given by

$$N_{xps} = p * ([D1] + [D2]) \quad (2)$$

where p was 1.0 for most of the derivatives, except in the case of PE-CONH(CH₂)₂N(CH₃)₂, where p was 2.0.

In the simple case where [D2] equaled zero, the yield Y was given by

$$Y = [D1] / ([PE-COOH] + [D1]) \quad (3)$$

which was solved by substituting in numerical values for [PE-COOH] and [D1] obtained from eqs. (1) and (2).

For the secondary derivative, PE-CONH(CH₂)₃COOH, [D1] was assumed equal to zero based on FTIR evidence and the yield calculated in a manner analogous to that described above. For the secondary phosphate derivative, PE-CONH(CH₂)₃OPO₃H₂, the molecular fraction was given by

$$P_{xps} = 1.0 * [D2] \quad (4)$$

and the yield was calculated from

$$Y = [D2] / ([PE-COOH] + [D1] + [D2]) \quad (5)$$

In this case, the values of m equaled 2.0 and a value for [PE-COOH] + [D1] was calculated from eq. (1) using eq. (4).

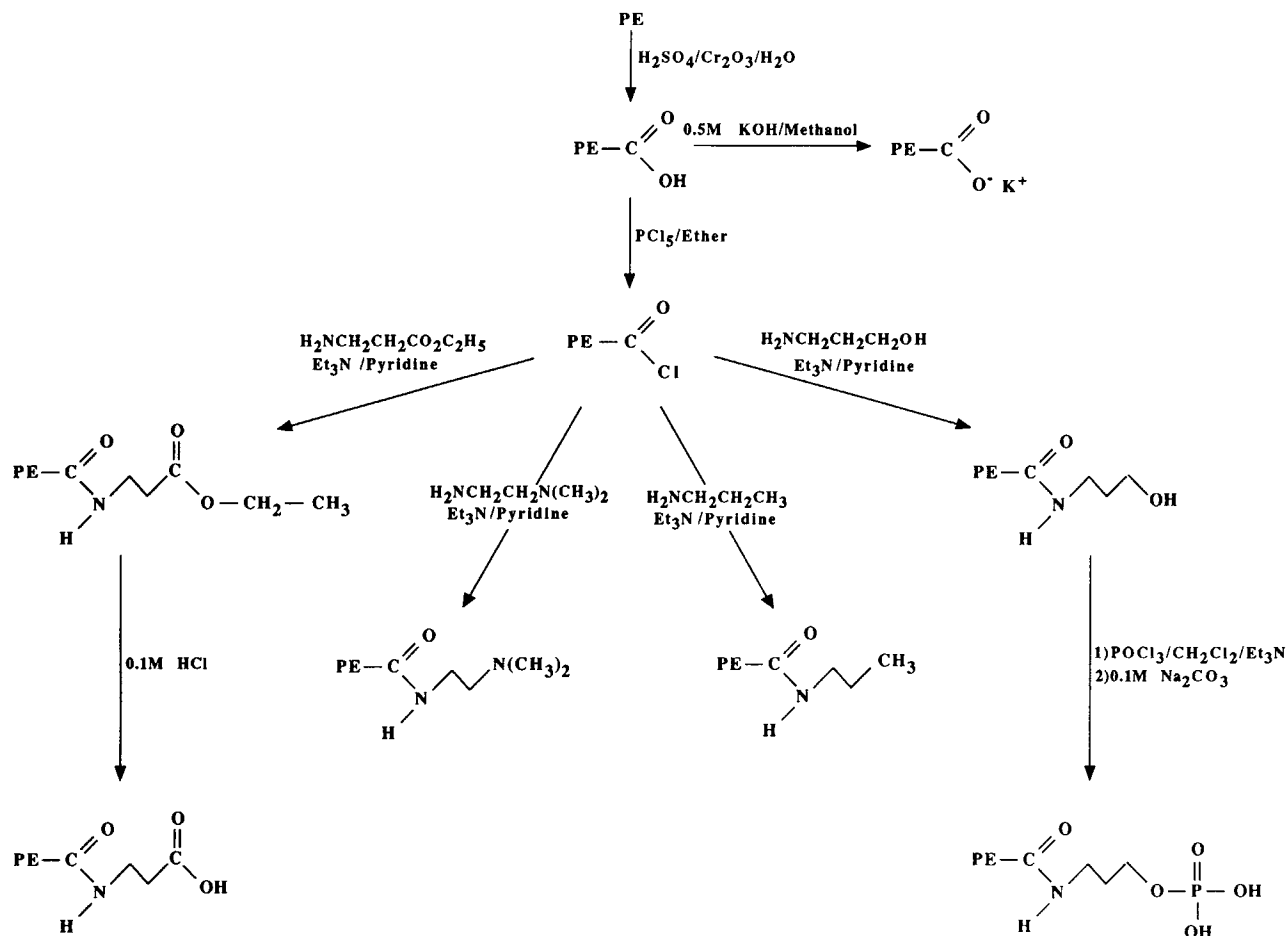
RESULTS AND DISCUSSION

General Considerations

The introduction of functional groups on polyethylene followed that shown in Scheme I:

Table I Elemental Fractions and Selected Yields Derived from XPS Data

Derivative	XPS line					Yield
	C _{1s}	O _{1s}	N _{1s}	P _{1s}	P _{2p}	
PE	0.978	0.022				
PE-COOH	0.910	0.090				
PE-CONH(CH ₂) ₃ OH	0.866	0.096	0.038			79%
PE-CONH(CH ₂) ₃ OPO ₃ H ₂	0.823	0.128	0.030	0.015	0.019	53%
PE-CONH(CH ₂) ₂ N(CH ₃) ₂	0.912	0.045	0.044			66%
PE-CONH(CH ₂) ₂ COOCH ₂ CH ₃	0.738	0.197	0.065			98%
PE-CONH(CH ₂) ₂ COOH	0.840	0.146	0.014			21%
PE-CONH(CH ₂) ₂ CH ₃	0.967	0.027	0.006			36%



Polyethylene was first oxidized in chromic acid to introduce carboxylate groups to the surface, PE-COOH. After vacuum drying, the carboxylate was immersed in a saturated solution of PCl_5 in ether, under a nitrogen atmosphere to form the acyl chloride, PE-COCl. This product was not characterized, but immediately used in one of four different amide formation steps. Some of the desired groups, specifically the methyl, PE-CONH(CH₂)₂CH₃, and the tertiary amine, PE-CONH(CH₂)₂N(CH₃)₂, could be attached directly as no competitive reaction of these groups with the primary amine for the acyl chloride occurred. Despite the possibility of ester formation, the alcohol, PE-CONH(CH₂)₃OH, could be appended directly using the alcohol amine (see below for detail). Attaining other groups required the use of an intermediate. The carboxylate, PE-CONH(CH₂)₂COOH, was formed from the ester, PE-CONH(CH₂)₂COOCH₂CH₃, while the phosphate, PE-CONH(CH₂)₃OPO₃H₂, was formed from the alcohol.

For all the amide formation reactions, the choice of solvent strongly influenced the yield. Here a

1 : 1 volume solution of triethylamine and pyridine was found optimum. With free amines, e.g., *n*-propylamine, dimethylethylenediamine, and 3-aminopropanol some coupling occurred in neat pyridine or in neat triethylamine, but the yield, as determined by FTIR, was low and erratic from batch to batch. For these reagents, triethylamine appeared to be the better solvent for reaction when used alone but was inferior to the 1 : 1 triethylamine/pyridine solution. The commercially available hydrochloride salt of β -alanine ethyl ester, while soluble, showed no reaction in neat pyridine. Presumably, pyridine is not a strong enough base to scavenge the HCl. Triethylamine, however, forms an insoluble salt with HCl as confirmed by melting point and FTIR. Thus, the free amine was formed by dissolving the salt in pyridine, followed by the addition of triethylamine, and separation by centrifugation of the solid triethylamine · HCl. The completion of later reactions was considerably improved by this process.

The presence of water in either the polyethylene films or the solvents hindered the formation of the amide. It was necessary to dry the polyethylene un-

der vacuum and store it over a drying agent prior to derivatization. Thermal drying of the substrates was avoided due to the possibility of surface rearrangement of the carboxylate groups.^{8,12} Occasionally batches showed low yield which was usually overcome by more scrupulous drying of the solvents. Despite this, trace amounts of water could not be entirely avoided. Because this was a surface reaction, the total quantity of reactive acyl chloride sites was comparatively low and, as detailed below, this trace water played a significant role in the surface derivatization reaction.

Polyethylene and Polyethylene Carboxylate

Shown in Figure 1 is the FTIR spectra of the polyethylene samples after the annealing process but before chromic acid oxidation. Present are the expected CH_2 symmetric and asymmetric stretching vibration, 2914 and 2847 cm^{-1} , the CH asymmetric bending at 1462 cm^{-1} , the CH_3 symmetric bending at 1376 cm^{-1} , and the CH_2 rocking, 718 cm^{-1} . No splitting of the 718 cm^{-1} band was observed as expected for amorphous polyethylene,¹⁷ indicating that amorphous characteristics of the "as purchased" low density polyethylene were retained during the *o*-xy-

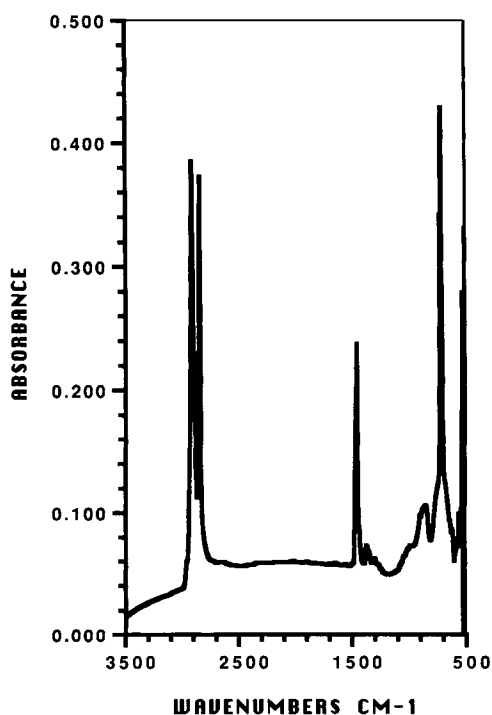


Figure 1 ATR-FTIR spectra of a thick film of low density polyethylene deposited on glass microscope slide by dip coating.

lene dip coating and subsequent annealing steps. None of the bands characteristic of the *o*-xylene dip coating solvent were present at discernable intensities. As the coatings are approximately 0.5–1 mm thick, contribution to the spectra from the underlying glass substrate or the silazane surface treatment could not be detected.

All spectra reported here retained similar characteristics except in the 1500–1800 cm^{-1} region where the major peaks for water, carboxylates, esters, and amides occur. Hence subsequent spectra concentrated specifically on this region. Other peaks characteristic of the attached functional groups often could not be positively identified. This was due to the relatively low concentration of the derivative compared to the polyethylene in the microns thick sampling depth the ATR-FTIR spectroscopy techniques. For example, peaks due to $\text{P}=\text{O}$ bonds near 1150 cm^{-1} was buried in the multitude of small peaks due to polyethylene. The broad, low intensity peaks expected to arise at 3000–3500 cm^{-1} due to $\text{O}-\text{H}$ and $\text{N}-\text{H}$ bonds could not be discerned from relatively small variations in baselines between samples and did not allow unambiguous assignment.

The extent and type of carbonyl groups introduced by chromic acid etching can be estimated by comparing the FTIR spectra of PE, PE-COOH, and PE-COOK (see Fig. 2). In this region no contribution to the spectra from PE was expected and the baseline was comparatively flat and stable. Some fine structure due to water was observed in all three spectra provided the spectra were expanded to $\times 10$ from that shown in the figure. A strong carbonyl peak at 1712 cm^{-1} was observed for PE-COOH; no such peak was observed for PE. Conversion of the acid to the potassium salt resulted in a strong carboxylate ion peak at 1564 cm^{-1} . The remaining 1712 cm^{-1} peak was attributed to ketones and aldehyde groups following previous assignments in the literature.⁷ Comparison of the intensities of the carbonyl peaks of the acid and potassium salt suggested that at least 50%, and up to 80%, of the carbonyl groups are carboxylate groups—in basic agreement with previous work.⁷ Precise quantification was difficult in this case due to the inability to directly compare absorbances of two different ATR-FTIR spectra and the unknown extinction coefficients of carboxylate salts relative to ketone and aldehyde groups.

An etching time of 60 s, at 72°C, in fresh chromic acid solution maximized the intensity of the 1712 cm^{-1} carbonyl peak. Longer etching times or higher temperatures did not significantly change the intensity, but, as revealed by visual inspection and scanning electron microscopy, resulted in unnecessary roughening of the surfaces. Shorter etching times

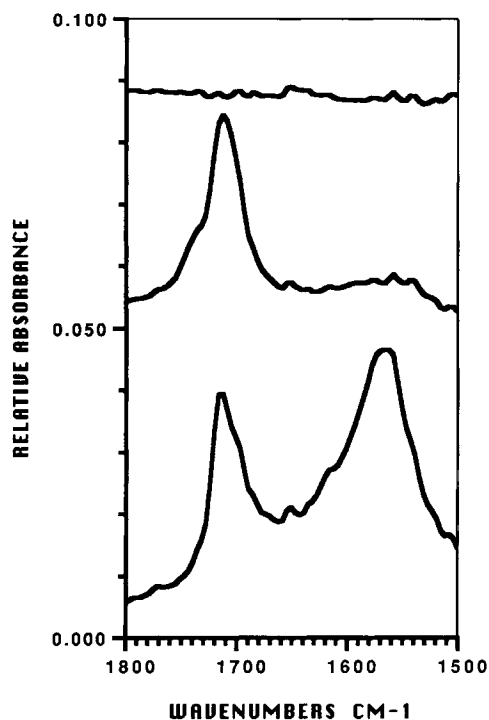


Figure 2 Detail of the ATR-FTIR spectra (1500–1800 cm^{-1}) of polyethylene (top), chromic acid etched polyethylene, PE-COOH (middle), and the potassium salt of the acid etched film, PE-COOK (bottom). Spectra are offset from baseline for clarity.

and/or lower temperatures resulted in a commensurate decrease in the carbonyl peak intensity.

The XPS survey spectra of PE and PE-COOH (Fig. 3) provided confirmation of an expected increase in oxygen content of the carboxylated surface. (Note that the region below 250 eV is enlarged by $\times 4$ in this and all other XPS figures.) A small amount of oxygen was present in PE which may have been due to absorbed oxygen or slight oxidation of the polyethylene. As no keto groups were detected in the FTIR, it is possible that this was absorbed oxygen or alcohol groups arising from air oxidation. A slight contamination by silicon (105 and 153 eV) presumably as SiO_2 , may account for a portion of the oxygen. Chromic acid oxidation introduced about a fourfold increase in the quantity of oxygen. The XPS survey spectra showed no contamination by chromate (Cr $2p_{3/2}$, 576.5 eV) and sulfate (S 2p, 168 eV) due to the etching process. No nitrate (N 1s, 406 eV) was present from the nitric acid wash.

Table I lists the relative elemental composition as determined from the XPS spectra for PE and PE-COOH as well as other samples. Oxygen com-

prised 2.2% of the PE film and 9.0% of the PE-COOH film—an increase by a factor of 4.1 in oxygen content. The C/O ratio on PE-COOH was 10.1 [0.91/0.09]. Assuming that all the oxygen was due to ketone or aldehyde groups, then the ratio of $\text{CH}_2/\text{C}=\text{O}$ is 9.1 [(0.91–0.09)/0.09]. Assuming all the oxidized groups are carboxylates then the CH_2/COOH ratio is 19.2 [(0.91–0.045)/0.045]. Using a density of 0.92 g/cm^3 for low density polyethylene implies an area density for CH_2 groups of $9.9 \times 10^{15}/\text{cm}^2$ in the approximately 25 Å sampling depth of the XPS technique. This translates to a maximum areal density for COOH groups of $5.3 \times 10^{14}/\text{cm}^2$. This number represents an estimate of the possible carboxylate groups available for amide formation. The actual value may be more or less depending on the depth of the reaction relative to the XPS sampling depth. The areal densities were calculated based on geometric area and cannot be interpreted to imply a uniform surface coverage of carboxylate groups. The actual exposed surface area must be corrected by an as yet unknown roughness factor. More importantly the surface had a finite depth and, as will be discussed in the conclusions, was graded in composition.

The contact angle versus pH measurements, shown in Figure 4, provided additional confirmation of the presence of carboxylate groups. As expected, PE showed a high contact angle, approximately 97° , with a small and apparently random pH dependence. PE-COOH showed a sigmoid-shaped curve dependence on pH that was reminiscent of a titration curve. The contact angles were lower than unetched polyethylene but still relatively high at $83\text{--}77^\circ$. The inflection was very gradual and the maximum slope occurred at a pH higher than the acid dissociation constant value, $\text{pK}_a = 4.0\text{--}5.0$, expected for a simple alkylcarboxylic acid. Such dependence can be attributed to coulombic interaction between dissociated groups, and variation in the local dielectric environment of individual groups.¹³ This contact angle data provided physical evidence of the surface activity of the carboxylate groups.

The Alcohol and Phosphate Derivatives

Reaction of the acyl chloride with 3-aminopropanol formed predominately the amide with little evidence for ester formation. Figure 5 (top) shows the FTIR spectra of the “dry” form of this derivative. A strong carbonyl peak, 1716 cm^{-1} , was still present, indicating that conversion to the amide was not complete. Formation of the amide was confirmed by the

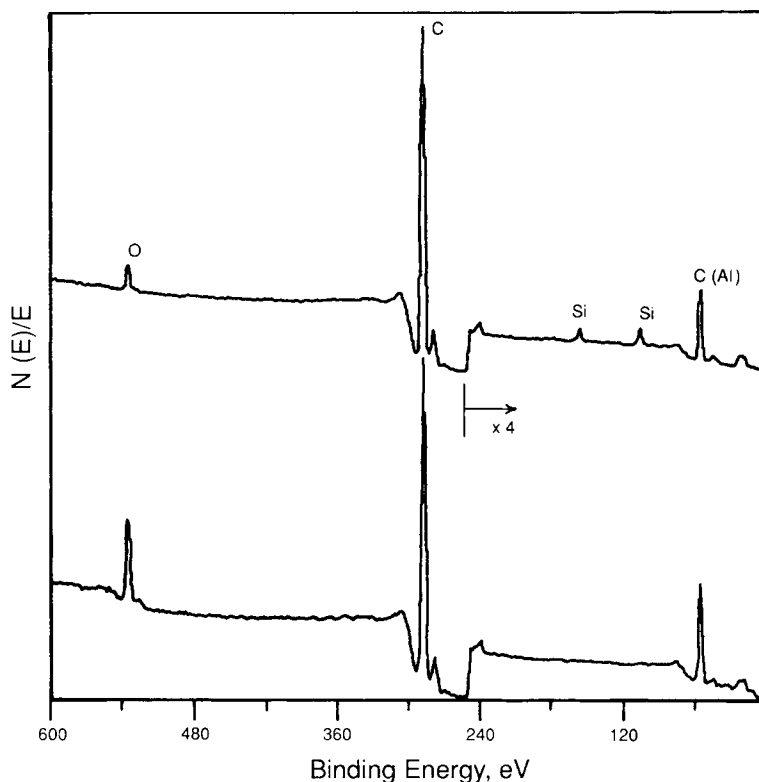


Figure 3 XPS survey spectra of polyethylene (top) and chromic acid etched polyethylene, PE-COOH (bottom).

peak at 1643 cm^{-1} arising from C=O stretch, and the peak at 1558 cm^{-1} which was assigned to both N—H deformation and C—N stretch. Formation of the ester would result in a strong shoulder to the carbonyl peak at about 1740 cm^{-1} . A hint of such a shoulder was observed, but was also present in the spectra of PE-COOH as well as others derivatives where formation of an ester cannot be expected and, hence, cannot be attributed to ester formation. Apparently, amide formation was strongly preferred over ester formation.

Based on FTIR peak height, the yield of amide formation was low, possibly as low as 25% of the available carboxylate groups, which, as noted above, was about 50–80% of the oxidized sites. This is a very crude estimate obtained by directly comparing peak heights of the 1716 cm^{-1} carbonyl and the 1658 cm^{-1} amide carbonyl bands and suffers from lack of precise knowledge of the extinction coefficients of the carbonyl stretch of the amide compared to that of the carboxylic acid and the somewhat arbitrary choice of baseline from which to compare peak areas or intensities. Both bands are typically of strong intensity with the amide band possibly being the

more intense. Hence, direct comparison of peak height may overestimate the yield. The yield may vary with depth and because of the large FTIR sampling depth may not adequately represent the yield in the “near surface” region.

Figure 5 (middle) shows the spectra of the “wet” form of the 3-aminopropanol derivative. A carbonyl peak at 1716 cm^{-1} was present. A much larger broad peak with maximum intensity at 1558 cm^{-1} suggested formation of a carboxylate ion of some form. The particular sample shown in Figure 5 has a small amide carbonyl shoulder and was used in this figure for clarity and emphasis. Frequently, the amide peaks could not be discerned. Upon drying under vacuum and a desiccant for 1–3 days, this particular “wet” film provided the spectra of the “dry” form shown in the top of Figure 5. Occurrence of the carboxylate peak was generally found to be associated with trace amounts of water, giving rise to the “wet” terminology, and could, in most cases, be eliminated by more careful drying of the substrates prior to derivatization. This behavior was not unique to aminopropanol and similar results were observed for other derivatives.

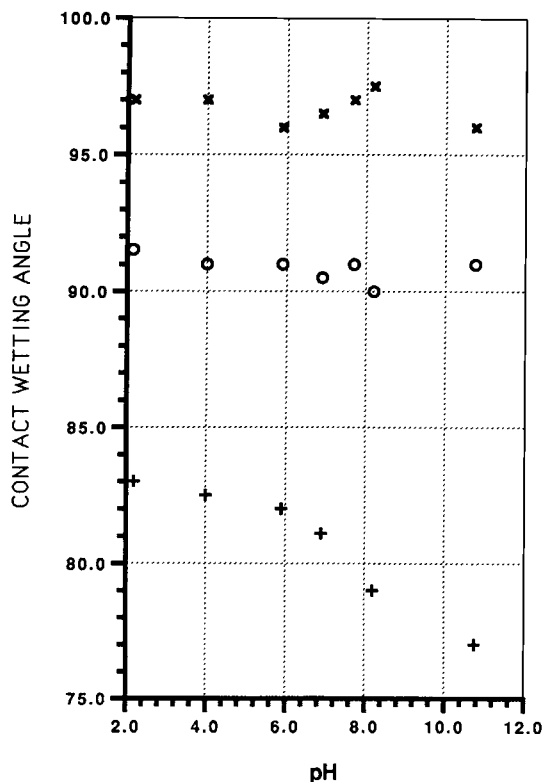


Figure 4 Contact angle values of buffered aqueous solutions on polyethylene (xxx) (top), and the chromic acid etched polyethylene, PE-COOH (+++) (bottom). Also shown is the *n*-propylamine derivative, PE-CONH(CH₂)₂CH₃ (ooo) (middle).

Drying of the “wet” form resulted in a discernable increase in the intensity of the amide bands and implied that drying converted some of the carboxylate ion into the amide. This could be explained if the presence of trace amounts of water resulted in formation of a carboxylate/ammonium ion complex held together by strong electrostatic forces in the low dielectric medium of the essentially hydrocarbon environment. Upon drying, water could be eliminated and the amide subsequently formed. Extended washing of the “wet” form in a neutral aqueous solution before drying resulted in no amide formation. In subsequent derivatization steps, emersion of the “wet” form in dry organic solvents containing reagents which would scavenge water, such as POCl₃ often resulted in conversion of the carboxylate ion to the amide. Apparently the treatment with water was sufficient to solubilize the ion pair, while water sensitive reagents favored formation of the amide.

The XPS spectra of the “wet” and “dry” forms were identical within sample to sample variation

[see Fig. 6 (top)], although the “wet” form surely was converted to the “dry” form in the ultrahigh vacuum chamber. (The small peak at 183 eV was attributed to a previously analyzed and unrelated sample of zirconia.) From the reaction stoichiometry, a 2 : 1 ratio of oxygen to nitrogen was expected. The data from Table I indicate an elemental ratio of oxygen to nitrogen of 2.5 : 1 was obtained. The oxygen content of the film should not change on derivatization as the alcohol compensates for the oxygen displaced during amide formation. Hence the value of *m* in eq. (1) was set to 2.0, and the equation solved for [PE-COOH]. Solving eq. (3) gave a yield of 79%, assuming all the sites containing oxygen were carboxylate groups. This value was at the high end of the 50–80% FTIR estimate for the proportion of carboxylate groups on the surface and implied a yield of 100% or greater if aldehyde and ketone groups were considered. This 79% yield value was much greater than the fairly optimistic, FTIR based, estimate of 25% yield for conversion of these sites to derivatized sites.

The phosphate derivative, PE-CONH(CH₂)₃-OPO₃H₂, was prepared by treating the above described alcohol with phosphorus oxychloride, POCl₃,

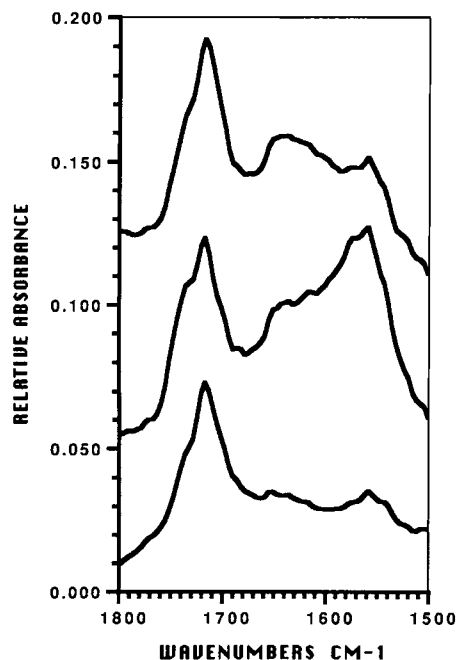


Figure 5 ATR-FTIR spectra of the “dry” form (top) and the “wet” form (middle) of the *n*-aminopropanol derivative, PE-CONH(CH₂)₃OH and the phosphonic acid derivative, PE-CONH(CH₂)₃OPO₃H₂ (bottom). See text for explanation of “dry” and “wet” terminology.

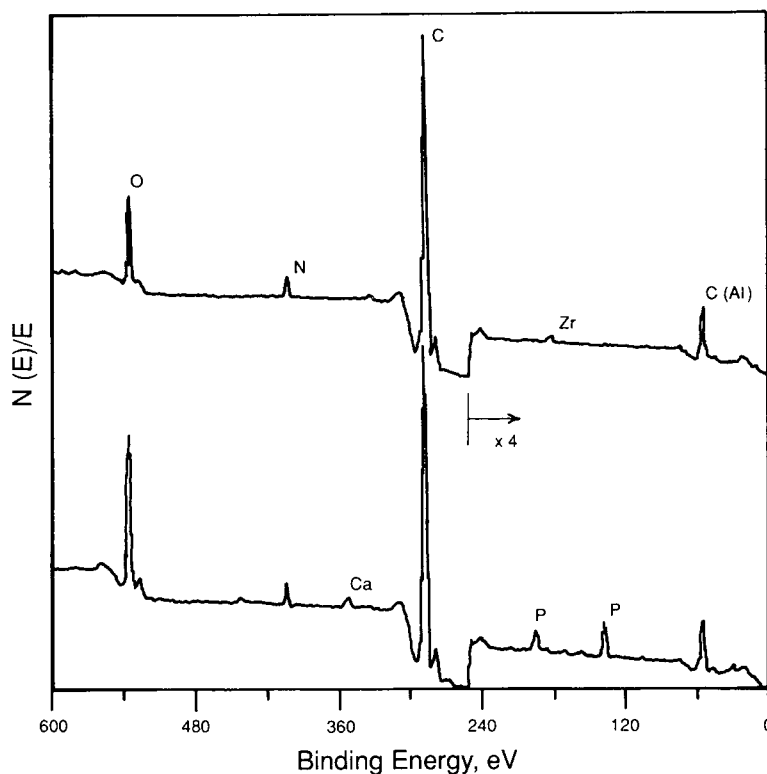


Figure 6 XPS survey spectra of the *n*-aminopropanol derivative, PE-CO-NH-(CH₂)₃-OH (top), and the phosphonic acid derivative, PE-CO-NH-(CH₂)₃-OPO₃H₂ (bottom).

followed by base hydrolysis to the phosphate. The ATR-FTIR spectra [Fig. 5 (bottom)], showed the two amide peaks as well as the 1716 cm⁻¹ carbonyl peak. The amide peaks were considerably reduced in intensity compared to the “dry” aminopropanol derivative. Peaks characteristic of phosphate groups near 1100 cm⁻¹ could not be discerned from the peaks arising from polyethylene. Thus the FTIR spectra provided evidence that the amide functionality was retained during the derivatization step, but provided no evidence of the conversion to the phosphate. Base hydrolysis of the amide linkage probably accounts for the decrease in amide peak intensity.

The XPS spectra [Fig. 6(bottom)] clearly showed the presence of the phosphorus 2s and 2p peaks, and an increase in the oxygen peak over the simple alcohol and the lack of any remaining chloride peak. Analysis of the atomic ratios (Table I) provided an O/N ratio of 4.3 with an expected value of 5.0, and an O/P ratio, based on the P_{2p} line, of 6.7, with an expected value of 5.0. The N/P ratio was 1.6 with an expected value of 1.0.

The phosphate derivative yield was calculated by using eqs. (2) and (4) in eq. (1) to solve for [PE-

COOH] and this value used in eq. (5) to obtain a phosphate derivative yield of 53% upon substituting in the 0.0165 value and the elemental fraction for phosphorus. The overall amide yield for both the alcohol and phosphate derivatives, [D1] + [D2], was calculated as 84%—a value very close to the 79% calculated previously for the simple alcohol. Based on the XPS data, very little if any of the amide groups were cleaved from the surface during base hydrolysis and approximately 63% of the alcohol groups were converted to the phosphate.

Shown in Figure 7 is the multiplex spectra of the phosphorus 2p peak for the phosphate derivative. The binding energy has been corrected for charging by subtracting the charging shift observed for the carbon peak from its well established value.¹⁸ The peak intensity occurred at 133.4 eV and corresponds well to a phosphate group.

The contact angle data for the alcohol derivative is shown in Figure 8 (top); as expected, the data showed no consistent dependence on pH—varying from 59 to 63°. Such values could be expected for a surface without an ionizable functional group and which is modestly hydrophilic. The contact angle

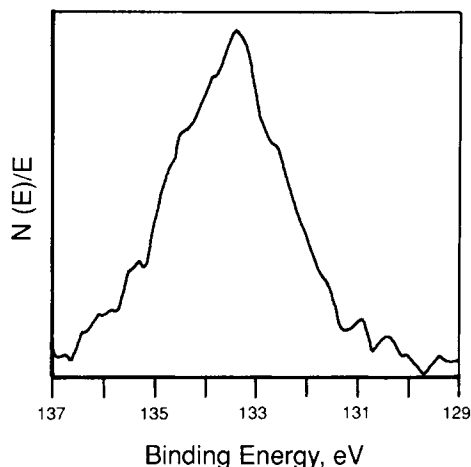


Figure 7 XPS multiplex spectra of the phosphorous 2p peak. Spectra was corrected for charging by observing shift in carbon 1s peak from the standard value for polyethylene.

data for the phosphate derivative, also illustrated in Figure 8 (bottom), showed a steady decrease in angle from 56 to 46° as the pH was raised from 2 to 11. For comparison, phosphoric acid has pKa values of 2.15 and 7.2 and *t*-butylphosphonic acid has pKa values of 2.79 and 8.88. When confined to a surface, coulombic interactions and local dielectric environment effects will spread and shift these values to higher pH ranges. The observed steadily decreasing contact angle data was consistent with this type of behavior.

The Ester, Carboxylate, Amine, and Methyl Derivatives

The PE-CONH(CH₂)₂N(CH₃)₂ derivative was prepared in one step by reaction of *N,N*-dimethylethylenediamine with PE-COCl. The FTIR spectra, middle-bottom of Figure 9, indicated the presence of the amide with similar yields to that observed for the aminopropanol derivative. The XPS spectra, middle-bottom of Figure 10 showed the expected carbon, oxygen, and nitrogen. A 0.5 O/N ratio was expected from stoichiometry. A 66% yield was obtained for this reaction within the XPS sampling depth.

The contact angle data is shown in Figure 11 (bottom). The values ranged from 35 to 44° and showed a sigmoid curve as expected for a basic group. Typical alkyl amines have pKa values of 10–11 in aqueous solution. When confined to a surface the R-NH₃⁺ species should experience coulombic interaction with neighboring groups. The result will be a lowering of the apparent pKa. The observed data were consistent with this qualitative argument.

PE-CONH(CH₂)₂CH₃ was formed by reaction of *n*-propylamine with the acyl chloride in one step. The FTIR spectra [Fig. 9 (bottom)] showed the expected amide peaks in similar intensity to the other amides formed in a single step. The XPS data, [Fig. 10 (bottom)] showed only carbon, nitrogen, and oxygen as expected. Analysis of the elemental fractions gave a yield of 36%—the lowest yield obtained for any of the one step amide reactions. The contact angle data are shown in Figure 4 (middle); the data showed no trend with pH and range from 90 to 92°. These values are only slightly less than that for unmodified PE and suggest that underlying amide linkages play only a slight role in determining the wetting behavior.

PE-CONH(CH₂)₂COOCH₂CH₃ was prepared directly from the ethyl ester of β -alanine. The FTIR spectra [Fig. 9 (top)] showed strong amide peaks. The ethyl ester functionality gave rise to the strong

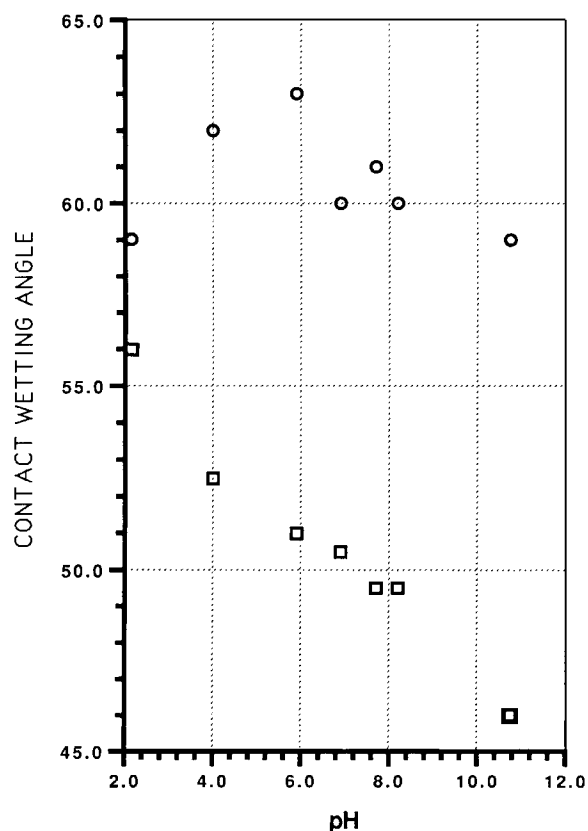


Figure 8 Contact angle values of buffered aqueous solutions on the *n*-aminopropanol derivative, PE-CONH(CH₂)₃OH, (top) (OOO) and the phosphonic acid derivative, PE-CONH(CH₂)₃OPO₃H₂ (bottom) (□□□). The “dry” form of the alcohol derivative was used although samples were stored above a saturated KCl solution prior measurement.

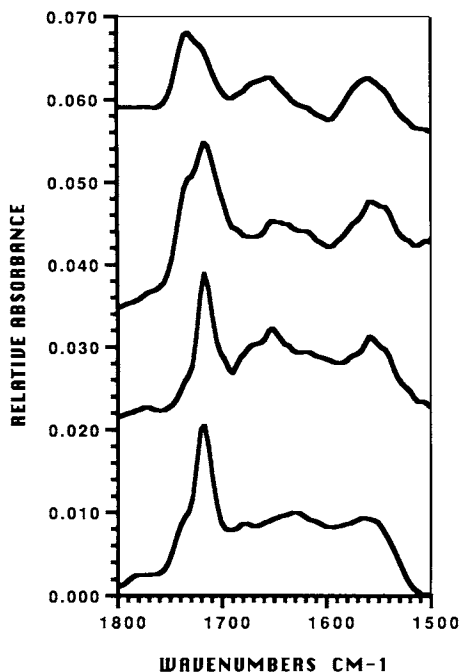


Figure 9 ATR-FTIR spectra of the β -alanine ethyl ester derivative, PE-CONH(CH₂)₃COOCH₂CH₃ (top); the same β -alanine derivative after cleavage of the ester, PE-CONH(CH₂)₃COOH (middle-top); the *N,N*-dimethylethylenediamine derivative, PE-CONH(CH₂)₂N(CH₃)₂ (middle-bottom); and the *n*-propylamine derivative, PE-CONH(CH₂)₂CH₃ (bottom).

peak at 1733 cm⁻¹, which overshadowed that due to unreacted carbonyl groups at 1716 cm⁻¹. The XPS spectra showed the expected atomic constituents. Elemental analysis of the data in Table I revealed a yield of 98% assuming as before all the oxygen arose from unreacted carboxylate groups or reacted carboxylate groups and not from ketones and aldehydes. The contact angle data for this surface [Fig. 11 (top)] showed no distinct dependence on pH and the over all values ranged from 59 to 64°. These data indicated a modestly hydrophobic surface with no active acid/base groups, as would be expected of ester functionalities.

The β -alanine ethyl ester derivative was subjected to acid hydrolysis to provide free carboxylate groups. Acid hydrolysis may also cleave some of the amide groups. However, the amide is generally considered more difficult to cleave than an ester and, in this case, was somewhat protected by an overlying ester group. The FTIR spectra [Fig. 9 (middle-top)] showed a strong decrease in the ester peak at 1733 cm⁻¹ and a prominent rise in the carbonyl peak at 1716 cm⁻¹—indicating successful cleavage of the ester. The amide peaks were, as with the ester, well-

defined. These peaks did appear of slightly less intensity compared to the unreacted carbonyl peak. This suggested some cleavage of the amide groups, although comparison of two ATR-FTIR spectra was not a very reliable method of estimating extent of reaction. Elemental analysis of the XPS data in Table I revealed an O/N ratio of 10.4—a much higher value than the nearly ideal ratio of 3.0 observed for the ester derivative. The yield based on this was 21%, or 79% of the amide groups were cleaved by acid hydrolysis.

The contact angle data indicated the presence of carboxylate groups by the titration curve like data (see Fig. 11). The data have a lower overall angle compared to the simple chromic acid etched film (see Fig. 4). The data also indicated a lower effective pK_a than that observed for the etched film. These data suggested that the two types of carboxylate groups were in strikingly different environments. Presumably the carboxylate groups arising from the ester on the end of the short alkyl chain were freer to interact with the aqueous solution and freer to move away from the hydrophobic polyethylene chains. This more polar environment would allow greater dielectric shielding of the coulombic interaction between ionized groups and consequently a stronger acidity. The lower overall values for the cleaved ester suggest groups more accessible to the buffer solutions.

CONCLUSIONS

The use of a dry triethylamine/pyridine solvent for attaching primary amines to oxidized polyethylene has proved effective for simple amines. The yields for the amide formation step exceeded 65% in all cases except for the *n*-propylamine derivative. As used here, the XPS technique must be considered semiquantitative. The small elemental percentages due to the amide make quantification susceptible to measurement errors, variations in instrumental sensitivity, and spurious contamination. In addition, the possibility of nonuniform distribution of the derivative makes the definition of yield conditional on the depth sensitivity of the technique employed and the depth profile for each derivative. Despite these limitations, XPS provides a more reliable number than ATR-FTIR spectroscopy, if the surface properties of the very first few angstroms are of interest.

Secondary steps involving modification of the amide end group to form the phosphate was accomplished in high yield; however, formation of the alkylcarboxylic acid, PE-CONH(CH₂)₂COOH, by

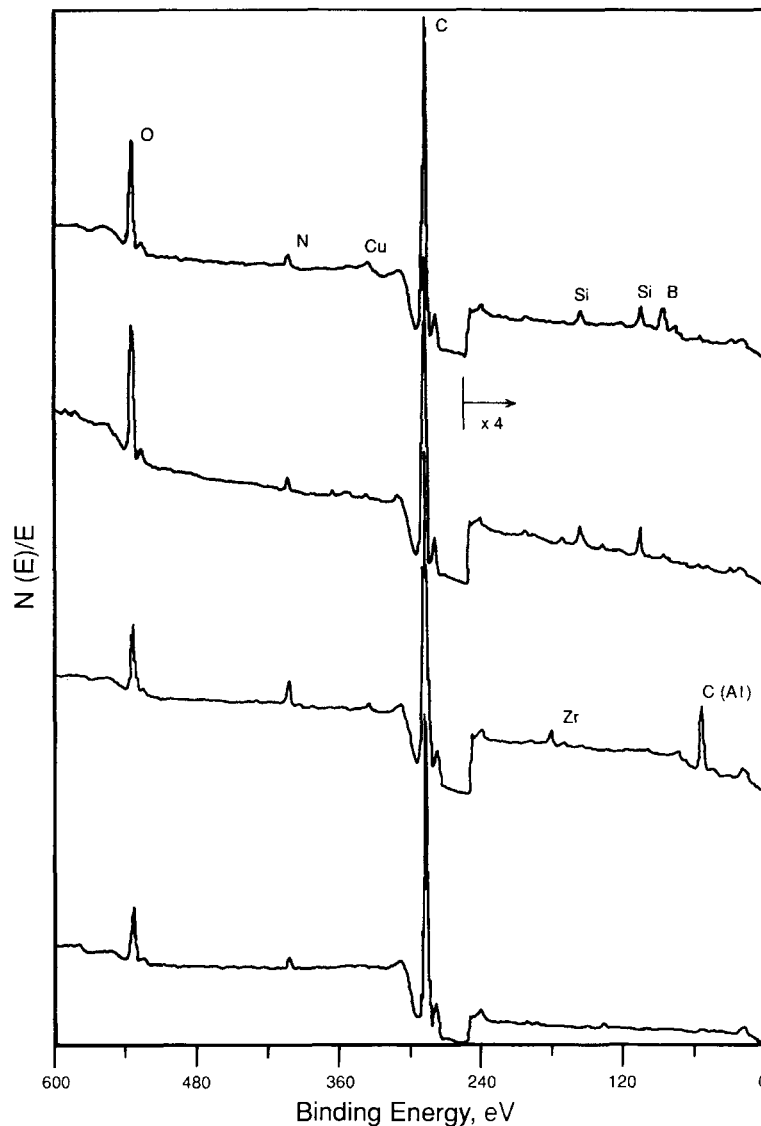


Figure 10 XPS survey spectra of the β -alanine ethyl ester derivative, PE-CONH(CH₂)₃COOCH₂CH₃ (top); the same β -alanine derivative after cleavage of the ester, PE-CONH(CH₂)₃COOH (middle-top); the *N,N*-dimethylethylenediamine derivative, PE-CONH(CH₂)₂N(CH₃)₂ (middle-bottom); and the *n*-propylamine derivative, PE-CONH(CH₂)₂CH₃ (bottom).

cleavage of the ester derivative resulted in a low yield. Presumably the acid hydrolysis of the ester cleaved the amide with greater efficiency than the base hydrolysis used in phosphate preparation. Holmes-Farley and Whitesides¹¹ compared acid and base hydrolysis of PE-COOCH₃ and concluded that base hydrolysis was more effective at cleaving near surface groups while acid hydrolysis penetrated more deeply into the polymer interface. Our observations are in basic agreement with this difference in reac-

tivity. It should be noted that no extensive effort was made to optimize the yields in either the amide formation step or in secondary modification steps. It is likely that much higher yields could be obtained under optimized conditions.

The carboxylate ion postulated to form in the presence of trace amounts of water was suspected as a major reason for low yields. Although some amide formation occurred during dehydration of the "wet" form, substantial amounts of the amine could

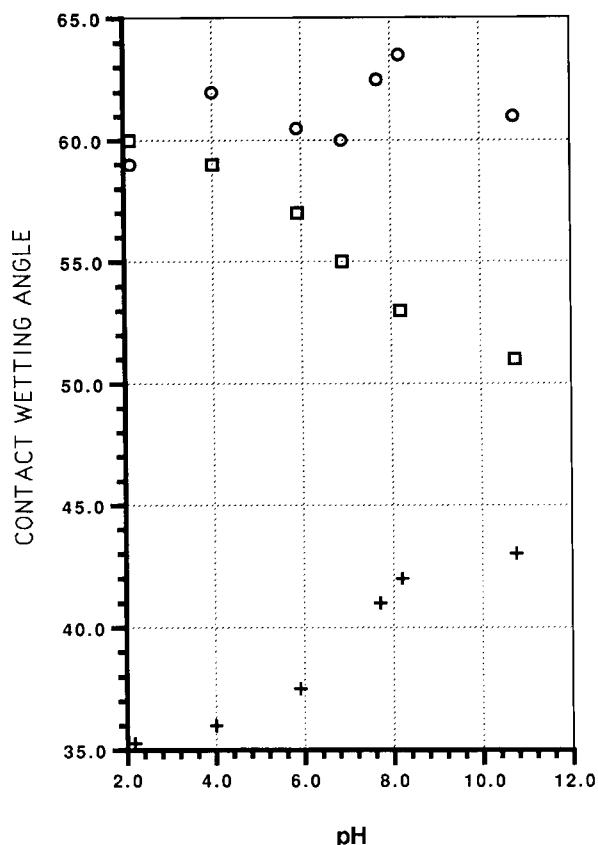


Figure 11 Contact angle values of buffered aqueous solutions on the β -alanine ethyl ester derivative, PE-CONH(CH₂)₃COOCH₂CH₃ (○○○); the same β -alanine derivative after cleavage of the ester, PE-CONH(CH₂)₃COOH (□□□); and the *N,N*-dimethylethylenediamine derivative, PE-CONH(CH₂)₂N(CH₃)₂ (+++).

be lost by volatilization. It is not clear whether water in the film or in the solvent was primarily responsible. Nor is it clear whether water hindered formation of the acyl chloride and attacks the acyl chloride before amide attachment, or promoted HCl cleavage of the amide as soon as the amide is formed. In this laboratory, synthesis using amines dissolved in aqueous base have proved futile.¹³ This, along with the observed influence of water, suggests a dry solvent method should prove superior as a generally applicable method.

The analysis of the "product" proved problematic in that no one single technique provided sufficient evidence of formation of the desired product. ATR-FTIR spectroscopy was valuable in monitoring formation or loss of the amide linkage. Information on elemental species from XPS was especially valuable

in tracking completion of reactions. For example, during hydrolysis of the POCl₃ derivative to the phosphate, completion of the reaction was monitored by disappearance of the chloride XPS signal. Contact angle wetting compliments XPS through identification of the surface species by well-understood acid/base behavior.

The yields as determined by FTIR and XPS were apparently conflicting. FTIR spectra of the potassium salt suggested 60–80% of the carbonyl containing groups were carboxylate groups. Derivative yields from XPS exceeding this value implied much higher densities for carboxylates in the XPS sampling region. In the case of the PE-CO-NH-(CH₂)₂-COOH derivative, a low XPS yield was accompanied by a considerable increase in wetting behavior. This comparison might also suggest higher yields in the contact angle sampling region than overall in the XPS sampling region. These results are in basic agreement with that proposed by Holmes-Farley and Whitesides,¹¹ except that our results suggest that carboxylate and aldehyde/ketone groups are not evenly distributed. The carboxylate groups dominate within the XPS sampling depth, while aldehyde/ketone groups dominate deeper within the polymer. Consequently, much higher yields can be achieved within the surface region than might be suggested by FTIR results.

Although ATR-FTIR spectroscopy samples too deeply for practical purposes, XPS and contact angle measurements proved sufficiently surface sensitive. The "sampling depth" of contact angle measurements has been suggested to be less than 10 Å for these types of surfaces.¹¹ The high contact angles obtained for both underivatized PE and the *n*-propylamine derivative, PE-CONH(CH₂)₂CH₃, suggested that the influence of the amide linkage was minimal. Comparison of the behavior of PE-COOH and the cleaved ester derivative, PE-CONH-(CH₂)₂COOH also suggested that small quantities of groups in the first few angstroms were more influential than underlying groups. Although the study of two alkyl-terminated samples and two carboxyl-terminated samples may seem redundant, these results emphasize the importance of surface structure on otherwise compositionally similar samples. Use of a single derivatization method for attachment of all surface groups will help ensure structural similarity between samples.

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