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Introduction, Modification, and Characterization of Functional Groups on the Surface of Low-Density Polyethylene Film

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Abstract: Initial oxidation of low-density polyethylene film with concentrated chromic acid solution at temperatures between 25 and 75 °C, followed by further oxidation with 70% aqueous nitric acid at 50 °C, generates a surface containing a relatively small number of different types of functional groups. The identities and relative numbers of these functional groups have been established using ATR IR spectroscopy and chemical derivatization. The surface functionality consists primarily of carbonyl derivatives, with approximately 60% of these present as carboxylic acid groups and 40% as ketones or aldehydes. Alcohols do not seem to be present. The absolute number of carboxylic acid groups generated at the surface was assayed using two independent fluorimetric techniques to be approximately $2 \times 10^{15}/cm^2$ of geometrical film area: since the surface is rough, the actual surface density of carboxyl groups is lower than this number. Several procedures have been developed which use these carboxylic acid groups as the basis for further chemical modification of the polymer surface.

The surface composition and structure of solid organic polymers influence many of their properties and uses. Wetting,[2] weathering,[3] permeation,[4] adhesion,[5,6] friction,[6] electrostatic charging,[7] and dye adsorption[5] are examples of processes important in engineering applications of polymers whose characteristics are determined, in part, by surface constitution. Surface functionality influences biocompatibility,[8] especially thromboresistance[9] and cellular attachment.[10] Solid-phase organic synthesis requires high-yield reactions to introduce and modify polymer functionality, and methods to control the interactions between pendant functional sites.[11]

Polymeric materials having particular surface properties are presently developed empirically. It is difficult to construct and test hypotheses relating the molecular structure of a polymer surface to its macroscopic surface properties because it has not been possible to obtain polymers with surfaces having well-defined functionality. The purpose of the work described in this and the accompanying paper[12] is the development of techniques for generating, modifying, and characterizing functionality at the surface of low-density polyethylene film.

The problems encountered in manipulating surface functionality on organic polymers differ in three respects from those familiar in organic solution chemistry. First, to be useful, reactions employed to create or modify groups at a surface must proceed in high yields, because it is impossible to separate and purify the products of these reactions. Second, characterization of surface functionality is difficult, both because the absolute number of surface groups is low and because the bulk polymer must be distinguished from the surface. Third, the three-dimensional spatial distribution of functional groups in the surface region—a problem having no counterpart in solution chemistry—is an important consideration in surface chemistry. In fact, the definition of the word "surface" for an organic polymer is not straightforward. In this paper, we use the words "surface" and "interface" interchangeably, and define both operationally in terms of a particular type of experiment which forms the basis for many of the reactions used: consider a hydrophobic organic polymer (polyethylene) in contact with a polar, nonswelling solvent (water). We define the "surface" of the polymer to be that part which is accessible to reagents that are soluble in water, but insoluble in polyethylene. This definition of a polymer surface has shortcomings: it is not applicable to a polymer which is swelled by the solution. It is ambiguous if thermal motion of the polymer chains at the surface transports functional groups from the bulk to the surface and vice versa with a rate comparable to a process used to test for interaction between a surface functional group and a reagent present in solution. Many water-soluble reagents have low but finite solubility in hydrocarbons, and presumably in polyethylene, and it is difficult to establish that a reagent is completely insoluble in the polymer. Nonetheless, this definition suggests experimental approaches to the generation and modification of surface functionality. It also emphasizes the importance of the *three*-dimensional distribution of functional groups at the polymer–solvent interface. In principle, functional groups at a well-defined polymer surface might be restricted to a coherent monolayer (Figure 1A); alternatively, at a poorly defined surface, the functional groups might be distributed between the polymer–water interface, the bulk polymer, and (by tethering polymer chains) the solvent (Figure 1B). Although these two distributions might not behave differently in many practical applications, the simpler, more ordered one is preferable in studies designed to test the influence of molecular surface structure on macroscopic properties.

We have chosen to investigate the surface chemistry of polyethylene rather than some other polymer for several reasons. It is readily available, inexpensive, and relatively well-characterized.[13-15] It is sufficiently strong mechanically that it can be handled without special precautions, but it is at the same time conveniently flexible. Polyethylene has few functional groups other than carbon–carbon and carbon–hydrogen single bonds, and its chemistry would be expected to resemble the extensively studied solution chemistry of hydrocarbons.
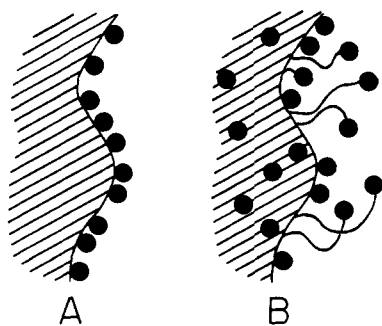
Figure 1. Two idealized schematic views of the interfacial region between a solid organic polymer which has been chemically modified and a solution. The newly introduced functional groups are represented by ●, and the bulk polymer, considered as a homogeneous solid, by the shaded area.

The low solubility of polyethylene in all common solvents at room temperature, and in a number of solvents at elevated temperatures, allows flexibility in the choice of reaction conditions for effecting surface transformations. Since many applications of surfaces (particularly in biochemistry) involve an interface to water, polyethylene, a very hydrophobic polymer,[16] offers an opportunity to separate phenomena occurring at a functionalized, polar surface from those reflecting unfunctionalized surface or bulk polymer. Finally, since polyethylene is widely used industrially, results from the study of its organic surface chemistry may be pertinent to practical problems.

Polyethylene suffers from one serious deficiency as a substrate for these studies: it is structurally heterogeneous. Low-density polyethylene is a mosaic of crystalline and amorphous regions having different structures and different relative reactivities in certain reactions.[17] A typical sample of low-density film with a density $\rho = 0.919$ g/cm^3 is approximately 50% crystalline.[18] We have seen both spectroscopic and kinetic evidence for different populations of surface functional groups on polyethylene.[12] It is not presently clear that these populations arise from polymer regions of different structure, but this heterogeneity remains a complicating factor.

The chemical modification of polyethylene has been the subject of extensive research.[19,20] Most procedures for modification involve reactive species capable of diffusing some distance into the bulk polyethylene, and, as a consequence, introduce functional groups both onto the surface and into the bulk polymer. We have concentrated our efforts on developing those procedures that utilize polar reagents and solvents which do not swell polyethylene in order to restrict functionalization to the polymer surface.

Results and Discussion

Functionalization of the surface of low-density polyethylene film can be accomplished cleanly by initial oxidation with chromic acid and subsequent reaction with nitric acid. The attenuated total reflectance IR (ATR IR) spectrum[21] of commercial low-density polyethylene film that has been extracted with 2-propanol to remove slip agents and antioxidants is shown in Figure 2B. This extracted film was used as the starting material for all procedures described in this work, and is designated by the abbreviation PE-H. Only bands attributable to polyethylene absorbances are visible in the spectrum of PE-H.[22]

The first objective of this work was to develop a procedure that would employ a polar oxidizing solution to convert exposed methylene groups on the polyethylene surface to carboxylic acid moieties. The rationale for this approach to the functionalization of polyethylene rested on five considerations. First, by using a polar (preferably partially aqueous) oxidizing reagent, functionalization should be restricted to the polymer
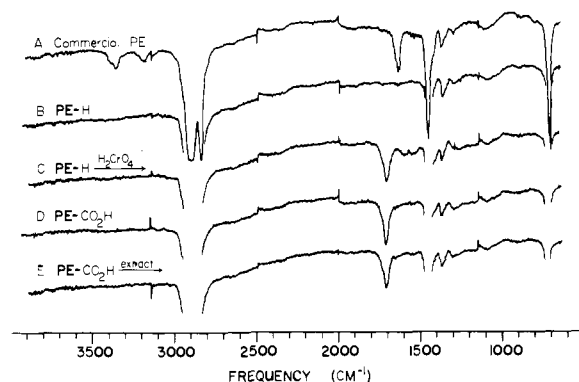

Figure 2. ATR IR spectra of polyethylene films: A, commercial film before extraction of phenolic antioxidants (3450 cm^{-1}) and fatty amide slip agents (3200, 1640 cm^{-1}); B, PE-H, film with these additives removed by extraction with hot 2-propanol; C, PE-H, after oxidation with "concentrated" chromic acid solution (see text); D, PE-CO$_2$H, after treatment with 70% aqueous HNO$_3$ at 50 °C; E, PE-CO$_2$H, after extraction with hot 2-propanol for 2 h. In this figure and those which follow, the complete polyethylene absorptions of the films are only reproduced in the first IR spectrum of the figure.

surface. Second, carboxylic acid groups can be converted in high yields into a number of useful derivatives. Third, carbonyl derivatives have strong IR absorptions at frequencies at which polyethylene is transparent, and are thus well-suited to ATR IR investigation. Fourth, the oxidation procedure could be applied to a variety of forms of polyethylene. Fifth, several oxidative methods for introducing carboxylic acid groups onto polyethylene surfaces were known. Oxidations using chromic acid provided the starting point for this work.[23-26] Of the chromic acid solutions tested, CrO$_3$/H$_2$O/H$_2$SO$_4$ in the ratio 29:42:29 by weight[26] produced a functionalized polyethylene film with the fewest noncarbonyl IR absorptions (Figure 2C). Since precipitation of chromium salts commonly accompanies chromic acid oxidation of polyolefins,[27] the films were further treated with a strong acid to dissolve any inorganic residues. After treatment with 70% aqueous nitric acid at 50 °C or 6 N hydrochloric acid at 50 °C, a colorless polyethylene film was obtained which showed no new functionality detectable by ATR IR other than carbonyl derivatives (Figure 2D). Film prepared by this two-step oxidation is referred to as "polyethylene carboxylic acid", PE-CO$_2$H, and is the subject of the major part of the characterization work that follows. PE-CO$_2$H is visibly etched: optical and SEM micrographs indicate a pitted surface. It is hydrophilic: although we have not measured a contact angle for water on this surface, it seems to be completely wetted. A series of studies, designed to characterize PE-CO$_2$H, concentrated on five questions: (1) Are the surface carbonyl groups firmly bound to the unoxidized, bulk polymer? (2) What is the nature of the functional groups that produce the carbonyl absorptions? (3) What is the concentration or surface density of carboxylic acid groups introduced onto the surface? (4) Is the polymer film derivatized only at the surface layer? (5) What is the morphology of the surface following oxidation?

The majority of the surface carbonyl groups of PE-CO$_2$H are firmly attached. Since chromic acid oxidation of PE-H to PE-CO$_2$H proceeds by cleavage of carbon-carbon bonds,[24] it was possible that the surface carbonyl groups were attached to relatively low molecular weight, soluble, molecules. In fact, no appreciable reduction in the intensity of the carbonyl absorptions in the ATR IR spectrum of PE-CO$_2$H occurred after a 24-h immersion at room temperature in a variety of solvents (THF, CH$_2$Cl$_2$, Et$_2$O, H$_2$O, MeOH, CHCl$_3$, CCl$_4$, DMF, and pyridine). Washing with water at temperatures up to 70 °C had no effect on the intensity of the carbonyl absorption band.
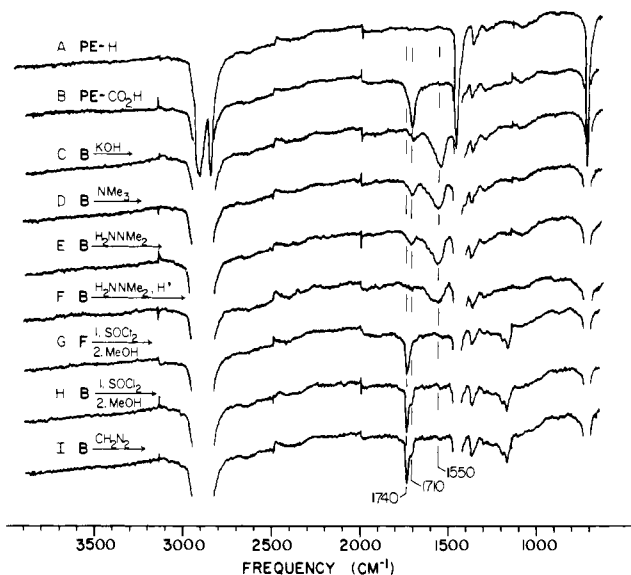
Figure 3. Carboxylic acids are the major contributor to the carbonyl absorption of PE-CO$_2$H, although ketones and/or aldehydes are also present: A, B, reference spectra of PE-H and PE-CO$_2$H, respectively; C-E, PE-CO$_2$H neutralized with 1 N KOH in ethanol (C), 25% trimethylamine in water (D), and 5% dimethylhydrazine in methanol (E) (The residual carbonyl peak at 1710 cm^{-1} in C-E is assigned to ketone and aldehyde absorptions.); F, PE-CO$_2$H after exposure to dimethylhydrazine under conditions in which ketones would be converted to dimethylhydrazones; G, F after conversion of carboxylic acid groups to acid chlorides with SOCl$_2$, followed by treatment with methanol to generate ester groups; H, PE-CO$_2$CH$_3$ generated by reaction of PE-COCl with methanol; I, PE-CO$_2$CH$_3$ prepared by reaction of PE-CO$_2$H with diazomethane.

The effect of extracting PE-CO$_2$H with 2-propanol for 2 h is shown in Figure 2E: the intensity of the carbonyl absorption band was reduced by 10-15%. This decrease in the IR intensity is not due to esterification of the carboxylic acid groups: no ester absorption is observed after extraction, and a similar decrease is observed in the ester carbonyl peak of PE-CO$_2$CH$_3$ (see below) on extraction. More exhaustive extraction (24 h) removes an additional 15-20% of the carbonyl species. Additional evidence is presented later that the major part of the surface functionality remains attached to the film after a 24-h extraction with 2-propanol (Figure 6). Thus the solubility properties of the surface functionality appear to resemble very closely the behavior of unmodified polyethylene. Accordingly, while the use of organic solvents that dissolve polyethylene (e.g., benzene, toluene, THF) at elevated temperatures is not possible during further chemical modifications of PE-CO$_2$H, a wide range of solvents may be employed at room temperature, and many of them at elevated temperatures as well.[28]

The surface functionality of PE-CO$_2$H consists of carboxylic acid and ketone or aldehyde groups: alcohols are not present in significant quantities. Earlier investigations inferred the presence and relative ratio of carboxylic acid, ketone, and aldehyde groups in oxidized polyethylene qualitatively by comparison of the frequencies of the carbonyl absorptions with those of model compounds dissolved in polyethylene.[29] Carboxylic acid groups have also been identified in oxidized polyethylene films by detecting a carboxylate IR absorption band following reaction with ethanolic base, and an acid fluoride absorption following reaction with sulfur tetrafluoride.[31] Ketone (aldehyde) species have been detected by observing the UV absorption of the 2,4-dinitrophenylhydrazine derivative.[25]

When PE-CO$_2$H was treated with either aqueous trimethylamine or methanolic potassium hydroxide, a strong carboxylate signal was observed in the ATR IR spectrum at 1550 cm^{-1} (Figure 3). The extent of conversion of PE-CO$_2$H

to the carboxylate salt, PE-CO$_2$X, depended on the solvent, concentration of the base, reaction time, and wash procedure. In nonpolar solvents (CHCl$_3$, CCl$_4$) trimethylamine did not react with the free acid to form PE-CO$_2^-$Me$_3$NH$^+$:[32] proton transfer from a carboxylic acid to an amine base is thermodynamically favorable only if the medium is capable of solvating the resulting ions. In polar solvents (H$_2$O, EtOH) the carboxylate salt formed, although slowly: when PE-CO$_2$H was immersed in 25% aqueous trimethylamine, 10 h was required to obtain maximum salt formation. We attribute (without direct evidence) the slow reaction rate to the necessity to solvate the surface acid groups, since the nonpolar bulk polyethylene no doubt discourages the formation of ionic species. Other spectroscopic techniques establish that swelling of a functionalized polyethylene surface and loss of solvent from a swelled surface may be slow.[12] In addition, a slow surface rearrangement may be occurring to allow maximum spacing between charged groups,[33] or to uncover groups partially buried in the bulk polymer. Neutralization of the carboxylate ions was rapid: exposure of PE-CO$_2^-$Me$_3$NH$^+$ to 1 N aqueous HCl for 1 min converted the salt quantitatively back to PE-CO$_2$H (determined by ATR IR spectroscopy). Exposure to distilled water (pH 7) converted 20-30% of the carboxylate salt to the free acid.

In all preparations of PE-CO$_2^-$Me$_3$NH$^+$, a significant carbonyl peak remained at 1710 cm^{-1}. This absorption could be either carboxylic acid groups which were not converted to carboxylate ions due to steric or pK_a constraints, or noncarboxylic acid carbonyl species. In addition to carboxylic acid moieties, ketone, aldehyde, alcohol, olefin, and other more complex functionalities are generated during chromic acid oxidations and may be present on the film surface at the completion of the oxidation. To determine the nature of the 1710-cm^{-1} absorption, PE-CO$_2$H was refluxed gently in methanolic 1,1-dimethylhydrazine (5%). In the presence of an acid catalyst—reaction conditions that promote hydrazone formation—a surface was generated whose ATR IR spectrum contained only a very small residual carbonyl peak at 1710 cm^{-1} (Figure 3F). When the acid catalyst was omitted, a much stronger carbonyl signal remained at 1710 cm^{-1} (Figure 3E). This result is strong evidence that the carbonyl remaining at 1710 cm^{-1} in the ATR IR spectrum of PE-CO$_2$H following treatment with base consists primarily of ketone (and/or aldehyde) groups. Using the reported ratio of the extinction coefficients of acids and ketones dissolved in polyethylene film,[29] $\epsilon_{acid}/\epsilon_{ketone}$ = 2.4, we estimate that the carbonyl moieties of PE-CO$_2$H consist of approximately 60% acid and 40% ketone (aldehyde) groups.

The ketone peak was also observed in the spectrum of a number of derivatives of PE-CO$_2$H. For example, reaction of PE-CO$_2$H with diazomethane, or of a polyethylene acid chloride surface, PE-COCl[SOCl$_2$] (vide infra), with methanol produced esterified films, PE-CO$_2$CH$_3$, having indistinguishable ATR IR spectra (Figure 3H and 3I). The ketone absorption peak is clearly visible at 1710 cm^{-1} as a shoulder on the ester carbonyl absorbance (1740 cm^{-1}) of PE-CO$_2$CH$_3$. If PE-CO$_2$H is allowed to react with 1,1-dimethylhydrazine to convert the surface ketone groups to hydrazones prior to esterification, the ketone shoulder is absent (Figure 3G).

Attempts to convert the ketone present in PE-CO$_2$H to carboxylic acid have been unsuccessful. No significant improvement in the acid/ketone ratio was observed after treatment of PE-CO$_2$H with alkaline permanganate, concentrated nitric acid in the presence of vanadium catalysts, or trifluoroperacetic acid followed by base hydrolysis.

Chromic acid oxidation of polyethylene has been reported to introduce surface hydroxyl groups.[24,34] Although the ATR IR spectrum of PE-CO$_2$H showed no hydroxyl absorption, it

seemed possible either that hydroxyl groups were present in small quantities, or that the O–H stretching absorption was too broad to be detected. An indirect technique established that no significant amount of surface hydroxyl moiety is present on $PE-CO_2H$. Reaction of $PE-CO_2H$ with 1 M diborane in THF generated a product, $PE-CH_2OH$, whose ATR IR spectrum (Figure 4B) showed a weak hydroxyl absorption (3360 cm^{-1}) and only a small residual carbonyl peak. Since diborane reacts rapidly with acid, but only slowly reduces ketones,[35] it seemed likely that the remaining carbonyl signal was due to ketone groups. As expected, this carbonyl band disappeared when the film was refluxed with methanolic 1,1-dimethylhydrazine and an acid catalyst (Figure 4C). Several derivatives of $PE-CH_2OH$ were prepared. The disappearance of the alcohol absorptions and the appearance of IR bands characteristic of the derivatives indicated that the reactions proceeded in good yield. The IR spectra of the trifluoroacetyl and tosylate derivatives are shown in Figure 4. The carbonyl (1790 cm^{-1}) and trifluoromethyl absorptions (1165, 1230 cm^{-1}) of $PE-CH_2OCOCF_3$ are sufficiently intense that they would be detectable at concentrations <5% of those giving rise to Figure 4E. Since the conversion of $PE-CH_2OH$ to $PE-CH_2OCOCF_3$ proceeds cleanly and the trifluoroacetyl absorption is easily detected, the quantity of hydroxyl groups present in the original $PE-CO_2H$ can be estimated by trifluoroacetylation and examination by ATR IR spectroscopy. When $PE-CO_2H$ or $PE-CO_2CH_3$ was treated with trifluoroacetic anhydride, no detectable IR absorption at 1790, 1230, or 1165 cm^{-1} was generated. Thus, if hydroxyl groups do exist on the surface of $PE-CO_2H$, their concentration is <5% of that of the acid groups.

Figure 4. $PE-CO_2H$ contains no detectable alcohol groups: A, PE–H reference spectrum; B, $PE-CH_2OH$, generated by reduction of $PE-CO_2H$ with 1 M diborane in THF; C, $PE-CH_2OH$ after treatment with dimethylhydrazine, under conditions which convert ketones to hydrazones; D, $PE-CH_2OTS$, prepared by reaction of $PE-CH_2OH$ with toluenesulfonyl chloride; E, $PE-CH_2OCOCF_3$, generated by treatment of $PE-CH_2OH$ with trifluoroacetic anhydride; F, $PE-CO_2H$ after treatment with trifluoroacetic anhydride under the same conditions used to generate the spectrum in E. No CF_3CO_2R absorptions are evident.

We have not assayed $PE-CO_2H$ for the presence of either nitro groups or olefins. Nitro groups are characterized by strong absorption at 1555 cm^{-1}; no peak at this frequency is apparent in the spectrum of $PE-CO_2H$, although absorption at this frequency is evident in polyethylene oxidized with 70%

Scheme I. Reactions Involved in the Fluorimetric Assays of Surface Carboxyl Groups on Oxidized Polyethylene Film. In This Scheme, "Extract" Indicates That the Film Is Treated for 18 h in a Soxhlet Apparatus with Hot (72–76 °C in the extraction thimble) 2-Propanol
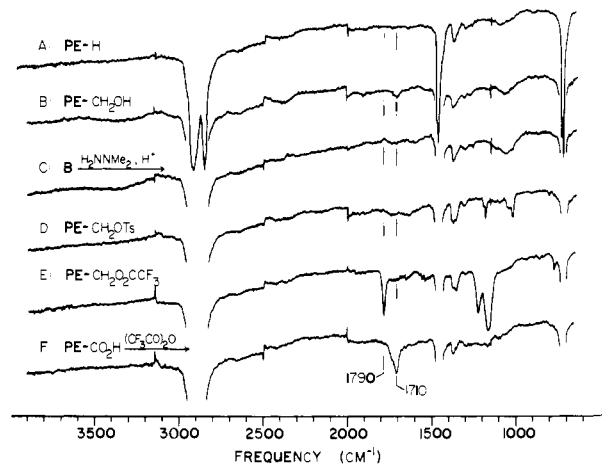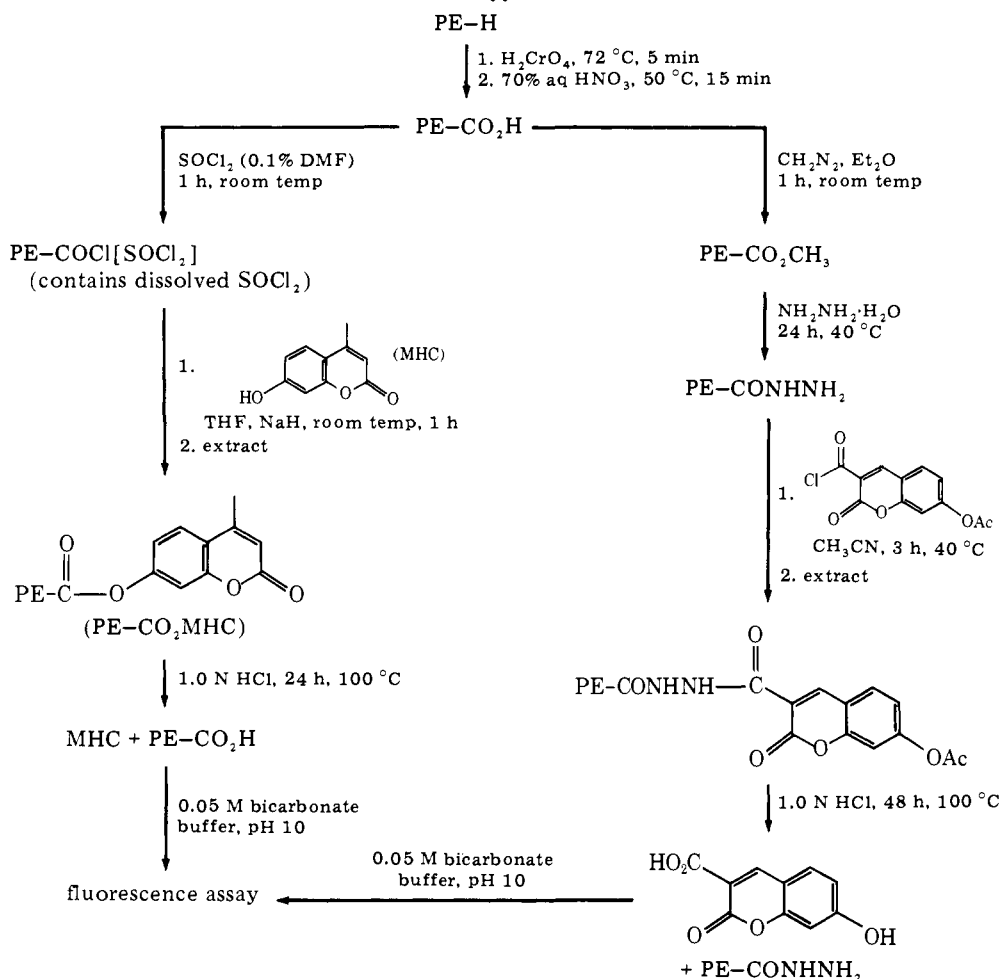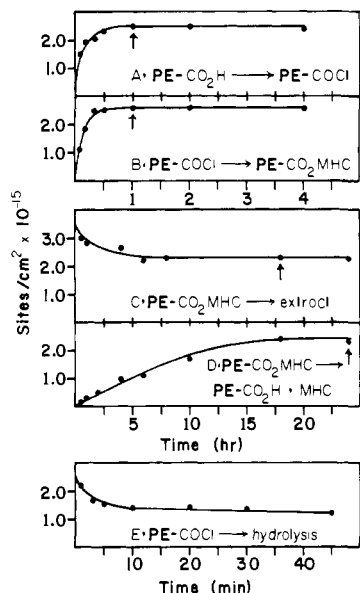
Figure 5. Conditions which optimize the reaction sequence used in the fluorometric assay for the carboxylic acid groups of PE-CO$_2$H were developed by varying the times used in each of these transformations: A, conversion of PE-CO$_2$H to PE-COCl[SOCl$_2$] with thionyl chloride; B, preparation of PE-CO$_2$MHC by reaction of PE-COCl with 4-methyl-7-hydroxycoumarin; C, extraction of PE-CO$_2$MHC with hot 2-propanol to remove absorbed and weakly covalently linked material; D, hydrolysis of PE-CO$_2$MHC to release 4-methyl-7-hydroxycoumarin for fluorometric assay; E describes the spontaneous hydrolysis of PE-COCl[SOCl$_2$] on exposure to laboratory air. The vertical axis in all the plots is the number of CO$_2$H groups (sites) calculated to be present per centimeter^2 of geometrical film area, based on the amount of 4-methyl-7-hydroxycoumarin detected after hydrolysis of PE-CO$_2$MHC. Experimental conditions were the same for each of these experiments with the exception of the single variable being explored: the standard conditions are summarized in Scheme 1, and indicated on the individual plots by arrows.

Figure 6. ATR IR spectra confirm that the fluorescence assay of PE-CO$_2$H based on 4-methyl-7-hydroxycoumarin detects the large majority of acid sites: A, PE-CO$_2$H; B, PE-CO$_2$MHC; C, PE-CO$_2$H recovered following hydrolysis of PE-CO$_2$MHC (B); D is a transmission IR spectrum of PE-H coated with 4-methyl-7-hydroxycoumaryl laurate. The absorbance at 1760 cm^{-1} in B and D is produced by the lactone moiety of the coumarin group.

nitric acid at >80 °C or with fuming nitric acid. Olefinic absorption is weak, and might go undetected. Olefinic groups are not likely to complicate studies of polar surface functionality, however, and were therefore ignored.

The density of surface carbonyl groups on PE-CO$_2$H can be determined by a fluorescence assay. The principal problem in developing a quantitative assay for surface functionality is sensitivity. If carbonyl groups are distributed on the PE-CO$_2$H surface with the same density as they are in compressed oriented fatty acid monolayers—5 × 10^{14} molecules/cm^2 [36]—fluorescence spectroscopy is one of the few techniques having the sensitivity and accuracy to provide reliable estimates of the small number of functional groups present on conveniently handled films.[37] Two different fluorescence assays, outlined in Scheme I, were developed to measure acid groups. Both assay procedures measure the fluorescence of a solution rather than that of a derivatized surface because measurements of a fluorophore attached to a surface are less sensitive and accurate than measurements on the same species in solution: the surface scatters light, and the fluorescence quantum yields of species immobilized on surfaces are difficult to estimate.[38] Derivatives of 7-hydroxycoumarin were used in the assays because they are intensely fluorescent in aqueous pH 10 buffer, insensitive to oxygen quenching, and stable to acidic hydrolysis conditions.[39]

The reaction sequence summarized in Scheme I that involves conversion of the carbonyl groups of PE-CO$_2$H to acid chloride moieties using thionyl chloride is the shorter and more direct. This sequence suffers from the fact that exposure of unoxidized polyethylene film PE-H to thionyl chloride, followed by treatment with a strong nucleophile, can result in binding of the nucleophile to the film. This phenomenon is
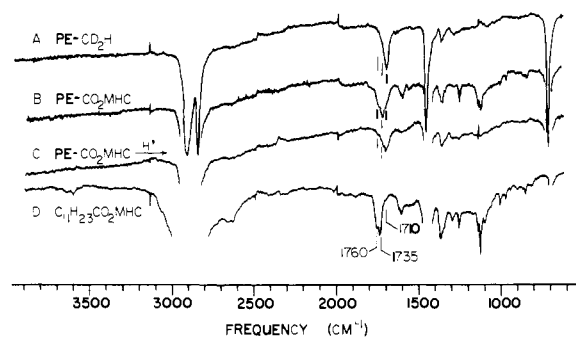
examined in detail in the following paper.[12] Briefly, it appears that thionyl chloride (and, probably, reactive impurities in the thionyl chloride such as sulfuryl chloride) dissolves in polyethylene, and reacts with nucleophiles, whether within the bulk polymer or at the polymer surface. Control experiments established that the amount of 4-methyl-7-hydroxycoumarin bound to thionyl chloride treated, unoxidized, PE-H after extraction with 2-propanol was negligible; when a strong nucleophile such as a primary alkyl amine was employed, however, the amount of material bound due to the thionyl chloride in PE-H[SOCl$_2$] (and presumably also in PE-COCl[SOCl$_2$]) before extraction was approximately the same as that released from extracted PE-CO$_2$MHC in the final step of the assay sequence. Thus, the material designated PE-COCl[SOCl$_2$] in Scheme I is not simply a film having surface acid chloride groups as the only reactive functionality: the dissolved or adsorbed thionyl chloride is actually a major reactive species, and any material bound due to it must be completely removed by extraction for a surface assay based on PE-COCl to be useful. An alternative assay for functional sites was developed in order to check the site densities from the assay employing thionyl chloride.

The assay sequence based on PE-CONHNH$_2$ in Scheme I is longer than that involving PE-COCl[SOCl$_2$], but serves two important functions. First, there are no ambiguities concerning reactive, dissolved species in the sequence proceeding through PE-CONHNH$_2$: PE-H carried through the sequence shows no more bound or adsorbed coumarin than does PE-H that has been exposed only to 3-chlorocarbonyl-7-acetoxycoumarin. Second, reaction sequences based on PE-CONHNH$_2$ provide an alternative method of attaching groups covalently to polyethylene, and an assay for carbonyl hydrazide moieties is important in its own right.

Optimization of the steps in the assay based on PE-COCl[SOCl$_2$] was carried out separately (Figure 5). The starting material for these experiments was PE-CO$_2$H that had not been extracted with 2-propanol after nitric acid oxidation: since the polyethylene–coumarin ester was carefully extracted, it seemed unnecessary to remove low molecular weight materials from the starting material. Further, control experiments indicated no significant difference in assays carried out using extracted and unextracted materials. In each experiment the fluorescence intensity of the final, buffered, aqueous solution of coumarin was converted to units of "sites/cm^2": that is, the number of molecules of coumarin bound (presumably at carboxylic acid sites) on one side of a 1 × 1 cm square of polyethylene film. The dimensions of the film give only a lower limit to its true surface area, since the film surface is rough. The functional group surface densities are thus upper limits.
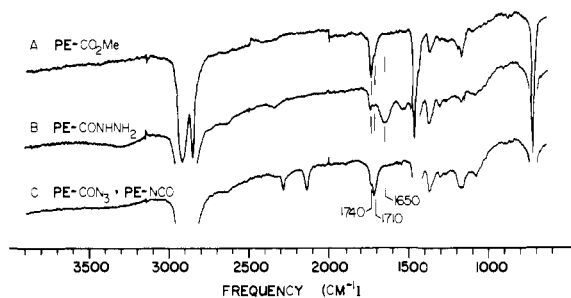
Figure 7. Conversion of PE-CO₂CH₃ to PE-CONHNH₂ proceeds in high yield; diacyl hydrazides are not produced: A, PE-CO₂CH₃ generated by treating PE-CO₂H with diazomethane. Peaks at 1740 and 1170 cm⁻¹ are characteristic ester absorptions. B, PE-CONHNH₂, obtained by reaction of PE-CO₂CH₃ with hydrazine hydrate, exhibits -NH- (3300 cm⁻¹) and carbonyl (1650 cm⁻¹) peaks. Residual ester absorption is clearly visible at 1170 cm⁻¹. C, A mixture of PE-CON₃ (2140, 1720 cm⁻¹) and PE-NCO (2290 cm⁻¹) generated from PE-CONHNH₂ by treatment with nitrous acid. Little residual acyl hydrazide absorption appears at 1650 cm⁻¹.
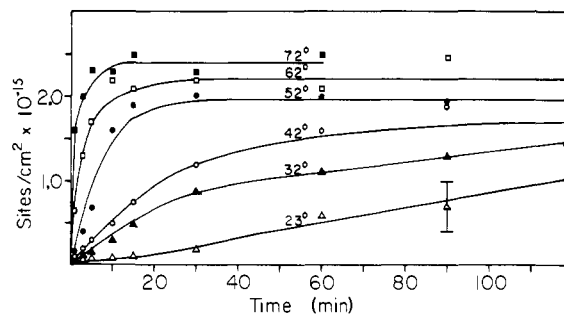

Figure 8. The density of carboxylic acid groups generated by oxidation of polyethylene film reaches stable values after sufficiently prolonged oxidation. This limiting value increases with temperature. The reproducibility of values is indicated by the error bar on the 23 °C oxidation line at 90 min.

verts 80–85% of the ester groups to carbonyl hydrazide moieties. The hydrazinolysis is conveniently monitored by following the disappearance of the ester absorbances (1740, 1170 cm⁻¹) and the appearance of carbonyl hydrazide peaks (3300, 1650 cm⁻¹) in the ATR IR spectrum. Immersion of PE-CONHNH₂ in cold, aqueous nitrous acid for 5 min converted the surface hydrazide to an acyl azide, PE-CON₃ (which rearranged to an isocyanate, PE-NCO, on warming)

The conversion of PE-CO₂H to PE-COCl[SOCl₂] is complete in 1 h. During this work we have not observed any IR absorbances which can be attributed to anhydrides at the surface. The acid chloride functionalities of PE-COCl[SOCl₂] are susceptible to hydrolysis by atmospheric water vapor (Figure 5E) and exposure of the film to air after treatment with thionyl chloride was minimized. Reaction of PE-CO-Cl[SOCl₂] with 4-methyl-7-hydroxycoumarin (MHC) (10 mg/mL) in THF containing sodium hydride is complete after 1 h. Since it was possible that even optimized conditions might leave a significant number of unreacted acid sites, the ATR IR spectrum of PE-CO₂MHC was examined (Figure 6B). The large reduction in intensity of the carbonyl absorption band at 1710 cm⁻¹ and the appearance of the coumarin ester band at 1735 cm⁻¹ confirm that the majority of acid groups have been esterified.

Figure 5C indicates that extraction of noncovalently bound and weakly bound coumarin and coumarin esters is complete after 8 h. The amount of adsorbed coumarin not removed by extraction with 2-propanol was determined by omitting the thionyl chloride treatment from Scheme I. The fluorescence observed at the conclusion of this experiment corresponds to 5 × 10¹² molecules/cm² (ca. 0.2% of the value when thionyl chloride was included), and this value was taken as the blank value for the assay.

Figure 5D establishes that hydrolysis for ca. 24 h is required to complete the cleavage of the PE-CO₂MHC. An ATR IR spectrum of the PE-CO₂H recovered from this hydrolysis was similar to the IR spectrum of the starting PE-CO₂H, and showed no absorption attributable to unhydrolyzed ester (Figure 6C).

Optimization of the assay in Scheme I based on PE-CONHNH₂ proceeded in a similar manner. The ATR IR spectra reproduced in Figure 7 indicate that the reaction sequence which converts PE-CO₂H to PE-CONHNH₂ takes place in an overall yield of approximately 80%. Treatment of the PE-CO₂H with diazomethane gives PE-CO₂CH₃ in ∼95% yield (see also Figure 3 and discussion in the text). Immersion of PE-CO₂CH₃ in hydrazine hydrate at 40 °C for 24 h con-

in high yield. The completeness of the chemical transformation of the acyl hydrazide moiety to acyl azide (and isocyanate) suggests that little diacyl hydrazide was present. The ATR IR spectrum reproduced in Figure 7C shows both acyl azide (2140, 1720 cm⁻¹) and isocyanate (2290 cm⁻¹) absorbances and no residual carbonyl hydrazide peak (1650 cm⁻¹).

The assay for carbonyl hydrazide moieties required the attachment of the acid chloride of 3-carboxy-7-acetylcoumarin to PE-CONHNH₂, extraction with hot 2-propanol, and hydrolysis of the coumarin-hydrazide linkage. The fluorescence observed when the optimized conditions listed in Scheme I were employed corresponds to 1.1 × 10¹⁵ molecules/cm². When a control film, PE-H, was subjected to an identical assay (beginning with diazomethane treatment), the fluorescence measured was equivalent to 5.0 × 10¹³ molecules/cm².

The number of hydrazide moieties detected by this assay is about 50% lower than the number of acid chloride sites estimated by the previously described procedure. Since conversion of PE-CO₂H to PE-CONHNH₂ only proceeds to the extent of 80–85% conversion, these assays are in good overall agreement.

The maximum density of carboxylic acid groups on PE-CO₂H is approximately 2.5 × 10¹⁵/cm². With reliable assays available, it was possible to establish conditions for the initial chromic acid oxidation that generated the maximum density of carboxyl groups on the polyethylene surface, and to define this density quantitatively. All carboxyl group densities discussed in the remainder of this paper are based on assays involving PE-CO₂MHC, prepared from PE-COCl[SOCl₂] unless otherwise specified. All site densities reported are the average of at least two, but normally three, samples whose deviation from the mean value was often less but never in excess of ±15%.

Figure 8 demonstrates that oxidation of polyethylene film using sufficiently long reaction times generates carboxyl group densities which do not further increase. This plateau increases slightly with increasing temperature. At the plateau, oxidation continues if the film is left exposed to the oxidizing medium, even though the carboxyl group density on the surface does not increase (Figure 9). A similar observation has been reported by Blais et al.²⁴ Thus, it appears that when the maximum carboxylic acid density (at a particular temperature) has been reached, the rate of formation of new groups is balanced by the rate of destruction or loss to solution of those already formed. This suggestion is supported by the observation that the loss of weight of a sample of polyethylene continues during oxidation after the limiting number of carboxylic acid groups has been reached (Figure 9).

When the oxidation of PE-H with chromic acid is carried out at 72 °C, the maximum surface density of carboxylic acid groups is approximately 2.5 × 10¹⁵/cm². For comparison, the
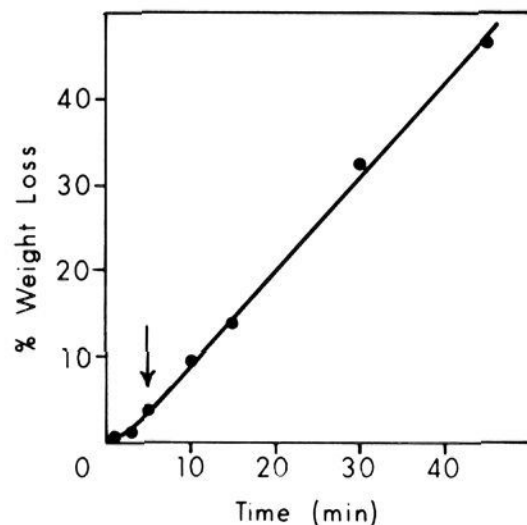
Figure 9. The loss of weight of polyethylene film on oxidation at 72 °C continues after the surface density of carboxylic acid groups has reached a constant value (Figure 8). The arrow indicates the time after which the density of CO_2H groups of PE–CO_2H no longer increases.

density of carboxyl groups indicated by this assay to be present on the surface of unoxidized polyethylene film is $2.5 \times 10^{12}/cm^2$,[40] and that on the surface of polyethylene that has been exposed only to the nitric acid oxidation is ca. $2.2 \times 10^{12}/cm^2$. These values include a correction for adsorbed coumarin that is not removed by 2-propanol extraction ($5.5 \times 10^{12}/cm^2$, see above): because this correction is larger than the values themselves, their accuracy is low. We have not established the origin of the difference in the surface carboxylic acid densities reached at different temperatures, although both variations in surface roughness and changes in the ratio of carboxylic acid to ketone and aldehyde groups at the surface could contribute.

Since the maximum packing density for stearic acid units in a monolayer is 5×10^{14} molecules/cm^2,[36] and the polyethylene films oxidized at high temperatures and long reaction times have site densities of carboxylic acids in excess of 2.0×10^{15} molecules/cm^2, it is clear that these surfaces cannot be pictured as a simple monolayer of acid groups on a flat polyethylene film. The degradation of bulk polyethylene by oxidants normally occurs by preferential attack at the amorphous regions of the polymer and thus PE–CO_2H would be expected to possess an uneven surface.[17]

The surface roughness of the oxidized polyethylene samples prepared in this work depends qualitatively on the conditions used. Films oxidized at 72 °C for a time sufficient to generate the maximum density of carboxylic acid groups are visibly etched: the surface is "frosted", and partially opaque. Examination of these films by scanning electron microscopy (SEM) reveals a pitted surface (Figure 10). Similar results have been reported by others.[24] Films oxidized at lower temperatures or for shorter times are less pitted. For example, a hydrophilic film is obtained by oxidation for 2 min at 50 °C (carboxylic acid surface density ca. $1 \times 10^{15}/cm^2$): this film shows little visible etching. All films that have been oxidized for sufficiently long times to reach their maximum carboxylic acid surface densities ($\geq 2 \times 10^{15}/cm^2$) are pitted.

We have attempted to compare the surface areas of unoxidized and heavily oxidized polyethylene film quantitatively using BET measurements.[41] The absolute accuracy of these results was not high, in part because the physical problems of oxidizing and manipulating the film restricted measurements to samples having surface areas of ca. 1 m^2, and BET measurements on small surface areas are difficult and inaccurate. Nonetheless, the measured areas give some estimation of the *increase* in surface area that accompanies oxidation. An unoxidized piece of film having a nominal geometrical surface area of 10 000 cm^2 (determined from its dimensions with the assumption that the film surface was perfectly flat) was esti-
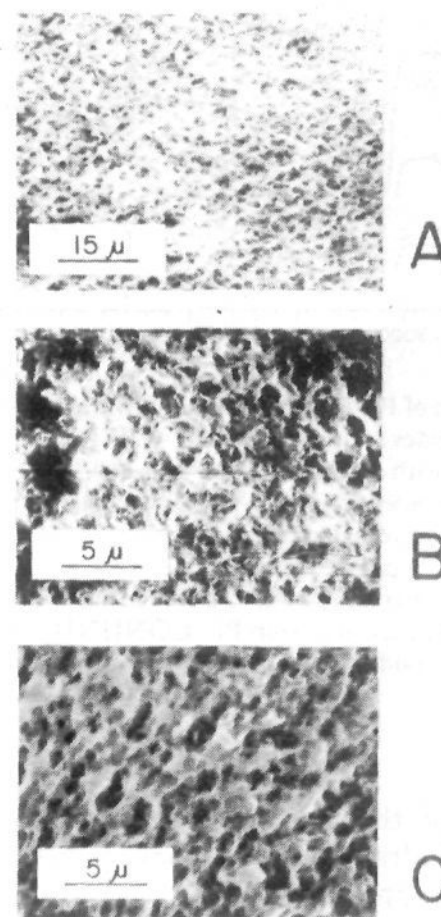

Figure 10. SEM photomicrographs of polyethylene films etched with "concentrated" chromic acid solution at 75 °C for 10 min: A, 1000× magnification; B, 3000× magnification; C, after immersion in hot solvents (in this instance, 70% nitric acid, 100 °C), oxidized films appear to be partly annealed (3000× magnification).

mated by BET measurements to have an area of 8000 cm^2. A piece of oxidized film (carboxylic acid surface density = 2.5×10^{15} molecules/cm^2) having the same nominal area exhibited a BET area of 14 000 cm^2. If we assume the same relative error in the two measurements, oxidation increases the surface area by 75%. This estimate is probably too conservative, since chromic acid oxidation produces extensive pitting in the film (Figure 10). Using the most conservative values for true surface area—that the geometrical and true surface of PE–H are identical (10 000 cm^2), and that oxidation increases the surface area by 75%, the upper value for the site density is recalculated to be 1.3×10^{15} sites/cm^2. This value is more than twice the value possible for a closely packed stearic acid monolayer, suggesting that the true surface is underestimated. Thus, at the present time, we are unable to determine with assurance the "true" site density. The site density measurements, the very hydrophilic nature of the surface, and the fact that the acid groups exist as dimers (1710 cm^{-1}) rather than monomers (1760 cm^{-1})[42] suggest, however, that the acid groups are closely packed on the surface.

Conclusions

Oxidation of low-density polyethylene film with chromic acid solution generates a surface containing a mixture of polar functions and adsorbed chromium species. Treatment of this film with nitric acid removes the inorganic compounds, and leaves a material (PE–CO_2H) whose surface contains carboxylic acid (~60%) and ketone or aldehyde (~40%) moieties as the only significant functional groups. This surface is highly hydrophilic.

Several techniques have proved valuable for characterization of the surface functionality on polyethylene film. ATR IR spectroscopy is a convenient qualitative method of identifying certain types of functional groups at the surface. It is particularly useful for studies of polyethylene surface chemistry, since the polymer itself is transparent in the regions of greatest interest in characterizing polar organic functional groups.

Fluorescence spectroscopy can be employed to estimate with high accuracy the numbers of molecules of appropriate derivatives attached to the functionalized surface.

Two useful procedures for attaching derivatives covalently to the carboxyl groups of PE–CO$_2$H emerge from this work. In one, treatment of PE–CO$_2$H with thionyl chloride generates reactive carbonyl chloride groups (PE–COCl[SOCl$_2$]) which react with alcohol and amine nucleophiles and generate esters and amides in high yield. This procedure is experimentally very simple; it suffers, however, from the complicating deficiency that thionyl chloride apparently dissolves in the polyethylene, and reaction of the dissolved thionyl chloride (or impurities introduced with it) with nucleophiles can generate derivatives at or close to the polymer surface which are not easily removed by superficial washing. In the second procedure, the carboxyl groups of PE–CO$_2$H are converted to methyl esters (PE–CO$_2$CH$_3$) by reaction with diazomethane. Treatment of PE–CO$_2$CH$_3$ with hydrazine generates acyl hydrazides (PE–CONHNH$_2$) in useful yield (~85% based on starting ester moieties). The hydrazides couple readily with acid chlorides.

These two procedures for forming derivatives of PE–CO$_2$H have been used to provide a spectrofluorometric assay for the number of carboxyl groups on the film surface, and give results in good agreement: ~2 × 10^{15} CO$_2$H groups/cm^2 of geometric film surface. Until we are able to measure the true surface area of the film, it is not possible to calculate the actual surface density of carbonyl groups. The number measured based on geometric surface area is, however, more than twice that of an oriented fatty acid monolayer, and, even after correction for surface roughness, the surface carbonyl group density will probably be high.

These studies, and those reported in the accompanying paper,[12] indicate that "PE–CO$_2$H" has the chemical and physical characteristics required to serve as the foundation for more elaborate surface functionality, and as a system with which to develop and test procedures for characterizing the functional group chemistry of organic surfaces.

Experimental Section

General Methods. All solvents were reagent grade; THF was distilled under argon from a dark purple solution of benzophenone dianion before use; diethyl ether was distilled from lithium aluminum hydride; pyridine was distilled from calcium hydride. Sodium hydride (99%, dry) was purchased from Alfa Inorganics, Inc. Polyethylene film was a low-density, 2-mil, commercial grade prepared from PE-TROTHENE NA 144 resin (0.919 density, 2.0 melt index), and was a gift of U.S. Industrial Chemicals. 1,1-Dimethylhydrazine was purchased from Eastman Chemicals. Trifluoroacetic anhydride was obtained from Matheson, Coleman, and Bell. Thionyl chloride (98%), N-methyl-N-nitroso-p-toluenesulfonamide (Diazald), diborane (1 M in THF), and 4-methyl-7-hydroxycoumarin were purchased in reagent quality from Aldrich and were not purified further. ATR IR spectra were measured on a Perkin-Elmer 521 grating spectrophotometer. Films were mounted in a Wilks MIR-2 solid sample holder against a KRS-5 plate (45 °, 50 × 2 mm). A Wilks Model 9 internal reflection attachment was used to position the sample. Fluorescent measurements were recorded on a Perkin-Elmer MPF-4 fluorescence spectrophotometer. SEM photomicrographs were obtained with a Jeolco JSM-U3 scanning electron microscope. The samples pictured in Figure 10 were sufficiently conductive to permit direct observation of the oxidized surface. Reactions performed on polyethylene films were normally with pieces 2 × 5 cm. The reaction vessel was usually a 100-mL vial which could be sealed with a plastic cover. Typically 50 mL of a reaction solution was added. When strictly anhydrous or reflux conditions were required, a 50-mL tube fitted with a 34/45 glass joint (prepared by sealing the end of a 34/45 outer joint) was employed. Except for the initial oxidation reaction, agitation was accomplished manually by swirling the flask occasionally because magnetic stirring often trapped the film beneath the stirring bar and resulted in excessive folding and abrasion of the film. In most organic

solvents, the film resided near the bottom without adhering to the walls of the reaction vessel. In aqueous solutions, the oxidized films were sufficiently hydrophilic and their surface free energies sufficiently low that even though the films were near the surface, they normally remained completely wetted with solvent. To prevent contamination of the surface, all films were handled with stainless steel forceps. Films were washed by immersing them in a vial of the wash solvent (ca. 100 mL) and gently agitating the film in and out of the wash six or seven times. Multiple washes were done with fresh solvent for each wash. Following the final wash, the film was dried in air ca. 120 s, and then dried in vacuo (0.005 Torr) for 12 h. During all manipulations exposure to the air was minimized.

ATR IR Spectroscopy. Films were cut to cover the entire KRS-5 sample faces. Following the final chemical manipulation performed on a film, it was thoroughly washed with the appropriate solvent(s) and then dried for 12 h in vacuo (0.005 Torr). Films were mounted in a MIR-2 stainless steel sample holder with thin rubber pads (18 × 45 mm) placed between the holder and film to improve contact between the sample and the KRS-5 reflection element. The retaining screws of the holder were tightened to a pressure of 80 in.-oz with an Allen torque wrench. The methylene absorption peak (1462 cm^{-1}) of film prepared in this manner usually transmitted 15–25% of the incident light. KRS-5 elements were used which had transmission levels of 25–35% at 4000 cm^{-1}. Frequent spectra of the element alone were taken (in a MIR-1 Teflon internal reflector plate holder) to ensure the absence of adsorbed polymer material. When necessary, the plates were cleaned with chloroform. The sample chamber of the Perkin-Elmer 521 spectrometer was flushed with nitrogen to reduce atmospheric absorptions. With the exception of minor gain and balance variations, all spectra were obtained under identical instrumental operating conditions.

PE–H. In order to remove surface additives prior to oxidation, polyethylene films, precut to the appropriate size, were enclosed in filter paper envelopes and extracted in a Soxhlet extraction apparatus with hot 2-propanol (72–76 °C in thimble) for 18 h. After extraction, the films were removed from the envelopes, air dried, and dried in vacuo (0.005 Torr) at 65 °C for 12 h. Control experiments showed that the ATR IR spectra and site density measurements of standard oxidized films which had been extracted prior to oxidation were indistinguishable from films which had not been extracted. However, since certain experiments were performed under conditions for which the effect of the additives might become significant, all samples were extracted and dried before use.

Polyethylene Carboxylic Acid. In the standard oxidation procedure that formed the basis for most of this work, PE–H was immersed manually with forceps in a chromic acid solution (CrO$_3$/H$_2$O/H$_2$SO$_4$ = 29:42:29 by weight)[26] at 72 °C for 1 min. After this time, oxidation had sufficiently progressed that the oxidizing medium wetted the surface uniformly. Magnetic stirring was begun (sufficiently fast to hold the PE below the surface) and continued for an additional 4 min. The conditions were varied only when specific effects of oxidation time or temperature were under investigation. Following oxidation films were washed three times with water. Films treated in this manner were visibly etched and slightly opaque, and very hydrophilic. Normally the oxidized films were treated with nitric acid (70%).

Treatment of Polyethylene Carboxylic Acid with Nitric Acid (PE–CO$_2$H). Films oxidized with chromic acid were placed in concentrated nitric acid (70%) at 50 °C for 15 min. At the end of this time, the films were washed three times with distilled water (50 °C), once with acetone, and dried. The standard chromic acid–nitric acid oxidation sequence described here produces PE–CO$_2$H, which was used for all experimental studies unless indicated otherwise. The surface of PE–CO$_2$H was visibly etched, colorless, and hydrophilic. Oxidized films were stored in a sealed vial. Although a sample stored for 3 months in this manner remained hydrophilic, PE–CO$_2$H was normally prepared immediately prior to use to reduce the possibility of complications due to contamination or surface rearrangement.

Formation of the Carboxylate Ion of PE–CO$_2$H. A. Potassium Salt. PE–CO$_2$H was immersed for several hours in alcoholic or aqueous 1 N potassium hydroxide. The film was removed and washed twice with water (pH adjusted to 11 with 0.001 M Na$_3$PO$_4$) and twice with acetone. **B. Trimethylamine Salt.** PE–CO$_2$H was immersed in a 25% aqueous solution of trimethylamine for the desired time (10 h for maximum reaction). The film was removed and washed twice with acetone.

Reaction of PE–CO$_2$H with 1,1-Dimethylhydrazine. PE–CO$_2$H was

immersed in 50 mL of 5% methanolic 1,1-dimethylhydrazine containing two drops of concentrated H_2SO_4, and the solution was gently refluxed for 18 h. The film was removed and washed three times with methanol.

PE-COCl[SOCl$_2$]. Polyethylene acid chloride was prepared by immersing $PE-CO_2H$ in 40 mL of neat thionyl chloride containing 0.1% dimethylformamide[43] for 1 h at room temperature. To minimize hydrolysis, the normal wash procedure was altered slightly. Most of the $SOCl_2$ was decanted and 30 mL of dry THF added, briefly agitated, and decanted. A second 30-mL portion of THF was added and agitated. The film was removed by forceps and transferred while still wet with THF to the subsequent reaction solution.

PE-CO$_2$CH$_3$. A. Reaction of Diazomethane with PE-CO$_2$H. PE-CO_2H was immersed in 75 mL of an ethereal solution of diazomethane generated by standard procedures from 5.4 g of N-methyl-N-nitroso-p-toluenesulfonamide (Diazald). After 1 h the film was removed and washed with ether. **B. Reaction of Methanol with PE-CO-Cl[SOCl$_2$].** Freshly prepared PE-COCl[SOCl$_2$] was immersed in 50 mL of absolute methanol for 1 h at room temperature. The film was removed and washed with methanol. These two preparations yielded films indistinguishable by ATR IR. $PE-CO_2CH_3$ prepared by the diazomethane procedure is preferred because it avoids the problems which accompany the use of thionyl chloride.

PE-CH$_2$OH. $PE-CO_2H$ was stirred under N_2 at room temperature in 50 mL of a 1 M diborane solution in THF for 18 h. The film was removed and washed sequentially with THF (twice), methanol, 4 N H_2SO_4 (50 °C, twice), water (twice), and acetone. Alternatively, $PE-CH_2OH$ could be produced by reaction of $PE-CO_2CH_3$ with 40 mL of a refluxing, ethereal solution of lithium aluminum hydride (2 g/100 mL).

PE-CH$_2$O$_2$CCF$_3$. $PE-CH_2OH$ was immersed at room temperature in 50 mL of ethyl ether containing 3 mL of trifluoroacetic anhydride. After 2 h the film was removed and washed with ether and acetone.

PE-CH$_2$OTS. $PE-CH_2OH$ was stirred at room temperature with 3 g of toluenesulfonyl chloride in 40 mL of anhydrous pyridine for 24 h. The film was removed and washed once with benzene and dioxane, and three times with ethyl ether.

PE-CO$_2$MHC. A slurry of the sodium salt of 4-methyl-7-hydroxycoumarin was prepared by dissolving the coumarin in dry THF (10 mg/mL) and adding excess sodium hydride. The coumarin salt was an intense yellow color. Freshly prepared PE-COCl[SOCl$_2$] was immersed in the resulting slurry. After 1 h the film was removed and washed with THF, water, 1 N HCl, water, THF, water, and acetone.

Hydrolysis of PE-CO$_2$MHC. $PE-CO_2MHC$ was sealed in a test tube containing 1 N HCl and heated at 100 °C for 24 h. After cooling the tube was opened and the film washed once with water and twice with THF.

PE-CONHNH$_2$. $PE-CO_2CH_3$ was immersed in 40 mL of hydrazine hydrate in a nitrogen atmosphere and the reaction vessel maintained at 40 °C for 24 h. The film was removed and washed three times with water, twice with ethanol, and twice with ethyl ether.

PE-CON$_3$. $PE-CONHNH_2$ was immersed in 35 mL of cold, 4.3 N HCl, and 1 mL of 3.0 M aqueous $NaNO_2$ added. The reaction mixture was swirled for several seconds and the film was allowed to stand for 5 min. The film was removed and washed with cold water (twice) and acetone. The sample was dried overnight in vacuo (0.005 Torr). The film was protected from exposure to light during these manipulations. Upon prolonged standing or warming, the acyl azide (2140, 1720 cm^{-1}) rearranged to the isocyanate, PE-NCO (2290 cm^{-1}).

3-Carboxy-7-hydroxycoumarin.[44] 2,4-Dihydroxybenzaldehyde[45] (6.9 g, 50 mmol), diethyl malonate (8.8 g, 55 mmol), and 20 mL of absolute ethanol were combined in a 50-mL round-bottomed flask. Following addition of piperidine (0.5 mL) and acetic acid (50 μL), the solution was refluxed for 3 h. After neutralizing the hot product mixture with 1 mL of glacial acetic acid, 40 mL of hot water (60 °C) was added. Upon standing at 0 °C, long, nearly colorless needles of 3-carbethoxy-7-hydroxycoumarin precipitated (mp 168–169.5 °C). A second recrystallization from 80 mL of EtOH/H$_2$O (5:3 by volume) yielded 4.2 g (18 mmol, 36%) of nearly colorless plates, mp 171.0–171.5 °C (lit. mp[44] 165–170 °C). Hydrolysis of the coumarin ester was effected by briefly warming the ester (11.7 g, 50 mmol) with 300 mL of 0.5 N NaOH. After cooling, this solution was added to 200 mL of vigorously stirred 1.0 N HCl. The amorphous yellow precipitate

was filtered and washed with three 100-mL portions of water. Recrystallization from 350 mL of 95% EtOH at −20 °C produced 8.0 g (39 mmol, 78%) of light yellow crystals of 3-carboxy-7-hydroxycoumarin having mp 269 °C (with decomposition and gas evolution; lit. mp[44] 262 °C): IR (KBr pellet) 3340, 3100, 1740, 1680, 1220 cm^{-1}; NMR (Me$_2$SO-d_6) δ 11.7 (br s, 2 H), 8.4 (s, 1 H), 7.4 (d, 1 H), 6.4–6.8 (m, 2 H).

3-Carboxy-7-acetylcoumarin. Treatment of 3-carboxy-7-hydroxycoumarin (7.6 g, 37 mmol) in 150 mL of THF with pyridine (25.4 mL, 300 mmol) and acetic anhydride (15 g, 150 mmol) produced a colorless solution after 1 h (unreacted phenoxide is an intense yellow color). The solution was filtered and made acidic with 15 mL of glacial acetic acid. The product precipitated as an amorphous, white solid on addition of 400 mL of petroleum ether. The product was collected by filtration and washed with three 75-mL portions of diethyl ether. Recrystallization from ethyl acetate yielded 6.5 g (26 mmol, 70%) of product having mp 209 °C (sharp): NMR (Me$_2$SO-d_6) δ 13.2 (br s, 1 H), 8.75 (s, 1 H), 7.93 (d, 1 H), 7.3 (s, 1 H), 7.25 (m, 1 H), 2.4 (s, 3 H).

3-Carbonylchloride-7-acetylcoumarin. Thionyl chloride (4 mL, 56 mmol) and 3-carboxy-7-acetylcoumarin (400 mg, 1.6 mmol) were refluxed for 20 min in a 10-mL round-bottomed flask protected from air with a drying tube. The reflux condenser was exchanged for a distilling head and excess thionyl chloride was removed by distillation at 1 atm. Residual traces of thionyl chloride were removed in vacuo (0.1 Torr) over KOH to yield the solid acid chloride, mp 191.5–192.0 °C: IR (KBr pellet) 1770 cm^{-1}. The acid chloride was normally used without further purification. (Recrystallization can be accomplished from tetrahydrofuran.)

Fluorescent Assays for Measuring Acid Chloride and Carbonyl Hydrazide Site Densities. The fluorescent properties of 4-methyl-7-hydroxycoumarin (MHC) and 3-carboxy-7-hydroxycoumarin (CHC) have been described elsewhere.[39] Fluorescent measurements were made with the MPF-4 spectrophotometer set in the ratio operation mode and with a dynode voltage setting of 750 V. Both excitation and emission slits were set at 6 nm; λ_{ex} was 360 nm and λ_{em} was measured at 447 nm for MHC and λ_{ex} 385 nm, λ_{em} 445 nm for CHC. Fluorescent measurements were made in pH 10 buffer which was prepared by dilution of 50 mL of 0.05 M sodium bicarbonate and 10.7 mL of 0.1 M sodium hydroxide to 100 mL with doubly distilled water. The fluorescence of the buffer was <0.1% of typical values obtained from the assay. Solutions of MHC and CHC (1.6 × 10^{-5} M) were stable at room temperature for several months and were used as primary standards. Fresh solutions were prepared monthly to insure there was no decrease in the fluorescence of the standard. The calibration curves of MHC and CHC were linear in the range 3 × 10^{12}–1 × 10^{15} molecules/mL (1.6 × 10^{-5}–5 × 10^{-9} M). The fluorescent intensity and emission spectra of the coumarins were uneffected by heating a sample in 1.0 N HCl at 100 °C for 24 h.

A. Measurement of Acid Site Densities of PE-CO$_2$H. A circle (1.1-cm diameter) was cut with a cork borer from a 2-cm × 5-cm piece of PE-CO$_2$H and allowed to react with 5 ml of thionyl chloride containing 0.1% DMF for 1 h to produce PE-COCl[SOCl$_2$]. The PE-COCl[SOCl$_2$] was washed and allowed to react to produce PE-CO$_2$MHC as previously described. Following the washing procedure, the film was placed in a filter paper envelope and extracted in a Soxhlet apparatus with hot 2-propanol for 18 h. After air drying, the film was sealed in a 5-mL breakseal ampule with 0.5 mL of 1.0 N HCl and hydrolyzed at 100 °C for 24 h. When cool, the ampule was opened and the contents neutralized with 0.5 mL of 1.0 N NaOH. This solution was transferred with washing to a 10-mL volumetric flask and brought to volume with pH 10 buffer. Fluorescent readings were taken immediately following completion of the final dilution. All values in this paper are the mean of at least two samples whose deviation from the mean was often less, but never in excess of ±15%. In cases where the values did not agree to within ±15% (<5% of the total measurements), the assay was repeated.

B. Measurement of Carbonyl Hydrazide Site Densities of PE-CONHNH$_2$. A circle (1.1-cm diameter) of PE-CONHNH$_2$ was placed in 5 mL of a solution of 3-carbonylchloride 7-acetylcoumarin (12 mg/mL) in warm acetonitrile (45 °C). A drop of triethylamine was added, and the reaction mixture maintained at 45 °C for 3 h. The film was removed and washed with acetonitrile (three times) and diethyl ether (three times). Extraction, hydrolysis, and fluorescent measurements were performed in the manner described for the assay of PE-CO$_2$H except the hydrolysis time was 48 h.

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