Location and Mobility of Functional Groups at the Surface of Oxidized, Low-Density Polyethylene Film

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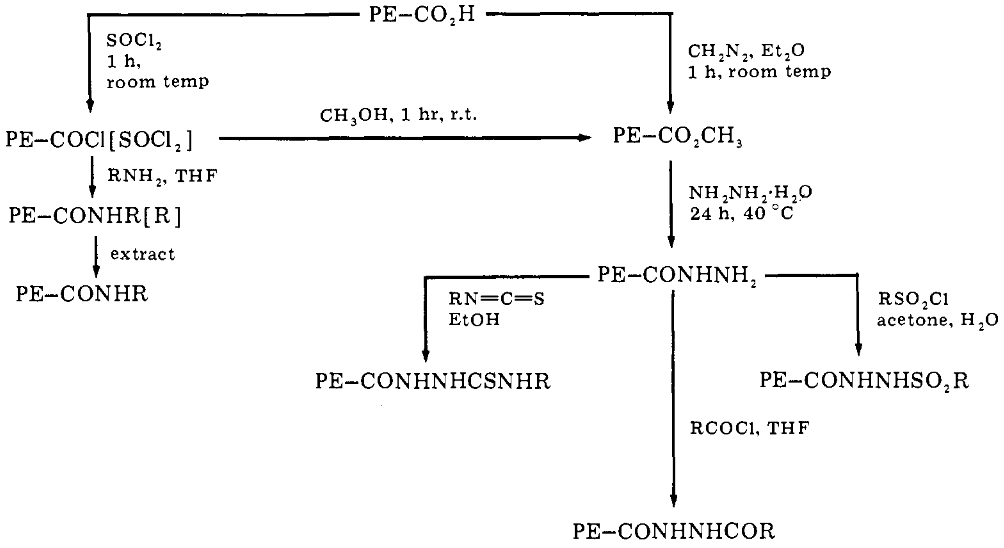
Abstract: Samples of low-density polyethylene film modified by introduction of surface carbonyl hydrazide groups (PE-$CONHNH_2$) react with 4-thiocyanato-2,2,6,6-tetramethylpiperidin-1-oxyl and 5-dimethylamino-1-naphthalenesulfonyl chloride to yield spin-labeled (PE-CONHNHCSNH-TMPO) and fluorescence-labeled (PE-CONHNH-DANS) films, respectively. Polyethylene acid chloride (PE-COCl[$SOCl_2$]), prepared by treatment of PE-CO_2H with thionyl chloride, reacts with 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl in high yield. Films prepared by this method (PE-CONH-TMPO[TMPO]) are contaminated with material not covalently bonded to the surface via an amide linkage, and, apparently, generated by reaction of thionyl chloride (or an impurity in the thionyl chloride) dissolved in the polyethylene with the primary amine. Extensive washing of the surface of films prepared by reaction of amines with polyethylene containing thionyl chloride using common organic solvents removes little of the contaminating material; extraction of the film with hot 2-propanol removes most but not all of it. Several experiments demonstrate that groups attached to these PE-$CONHNH_2$ films via carbonyl hydrazide moieties react with aqueous reagents which are insoluble in polyethylene, and establish that the labeling groups are located predominantly at the polyethylene film surface. Immersion of nitroxide-labeled film in 0.1 M aqueous sodium ascorbate solution (pH 6.8) for 5 h reduces the intensity of the ESR signal of the film by >85%; treatment of the film with 3.0 N aqueous HCl reduces its ESR signal intensity by 70–95%. The fluorescence emission maximum of PE-CONHNH-DANS falls at 468 nm when the film is dry; in contact with water, it shifts to 510 nm. Aqueous 1.0 N HCl quenches the fluorescence almost completely. Both observations are compatible with localization of the dansyl groups at the polyethylene–water interface. Treatment of PE-$CONHNH_2$ with cold, aqueous nitrous acid rapidly generates the corresponding acyl azide (PE-CON_3). This material, in turn, is rapidly hydrolyzed by aqueous 1.0 N HCl. In contrast to PE-CONHNHCSNH-TMPO, the nitroxyl groups of PE-H[TMPO] (prepared by reaction of polyethylene containing dissolved thionyl chloride, PE-H[$SOCl_2$], with H_2N-TMPO) are not reduced by 0.1 M aqueous sodium ascorbate or 3 N aqueous HCl. The effects of temperature and organic solvents upon the mobility of nitroxyl radicals bonded to surface-functionalized polyethylene indicate that the nitroxyl groups experience little restriction to free rotation when the films are in contact with organic liquids. Rotation of the nitroxyl groups of dry film is more hindered.

The preceding paper describes a method for generating carboxylic acid groups at or near the surface of low-density polyethylene film by oxidation.[2] The present paper provides evidence that the carboxylic acid moieties of the functionalized film (referred to as PE-CO_2H although ketones and aldehydes are also present) are located at the surface and are accessible to reagents in a solution in contact with the film. In addition, the mobility of derivatives of these functional groups, both on dry film and on film in contact with liquids, is examined. These studies required reliable techniques for attaching functional groups to PE-CO_2H. The procedure that initially seemed most direct for coupling nucleophiles to the carbonyl moieties of PE-CO_2H converted carboxyl groups first to carbonyl chloride moieties with thionyl chloride, and then to amides by reaction with amines. These transformations do in fact take place in good overall yield, as judged by ATR spectra which demonstrate high conversions of -CO_2H to -CONHR groups. This coupling sequence is, however, complicated by a second, nonspecific, thionyl chloride dependent process, which does not involve the carboxyl groups and which binds the amine in the polyethylene. Evidence that this nonspecific binding of amines to polyethylene is caused by thionyl chloride dissolved in the film is discussed later in this paper. Since we refer to reactions of polyethylene containing dissolved thionyl chloride frequently in what follows, we indicate the presence of dissolved material with square brackets: e.g., PE-H[$SOCl_2$] (or PE-COCl[$SOCl_2$], if appropriate). The material obtained by treating PE-H[$SOCl_2$] with 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl (H_2N-TMPO) will be referred to as PE-H[TMPO], and that from PE-COCl[$SOCl_2$] with H_2N-TMPO as PE-CONH-TMPO[TMPO]. PE-CONH-TMPO[TMPO] extracted with 2-propanol to remove noncovalently bound TMPO species is designated PE-CONH-TMPO. The occurrence of this binding diminishes, but does not nullify the value of the coupling of surface -COCl groups with amines as a method of coupling organic groups to polyethylene: in many applications the noncovalently bound material may not interfere, particularly since most of it seems to lie beneath the surface of the polymer (vide infra); if it does interfere, much of it can be removed by extraction. The nonspecific binding does, however, sufficiently complicate both the execution and interpretation of experiments based on reactions of thionyl chloride treated PE-CO_2H with amines that it was desirable to have a second, independent method for covalently binding molecules to PE-CO_2H, and important that applications of this method to unoxidized polyethylene produce no bonding. The route developed for this purpose relies on the coupling of the nucleophilic nitrogen of an acylhydrazide (in this instance, of PE-$CONHNH_2$) with an acid chloride or other reactive nucleophile (Scheme I).

To use polyethylene films whose surfaces have been modified by synthetic sequences of the type outlined in Scheme I for studies of the effect of the surface chemistry of this polymer on its properties, it is first necessary to establish the location of the carboxylic acid groups relative to the surface: are these functional groups localized at the surface, or are they distributed between the surface and the bulk of the polymer? An answer to this question requires a definition of the word "surface". We have adopted an operational approach to determine the distribution of functional groups between the "surface" and "interior" of the polyethylene: *if the functional groups interacts with a reagent which would be expected to be insoluble in bulk polyethylene, and which is dissolved in a solvent (e.g., water) that does not swell polyethylene, we consider it to be a "surface" group.*

No instrumental techniques now available can determine directly whether the functional groups of PE-CO_2H and its derivatives are fully exposed at the surface or buried in the polymer. ATR IR spectroscopy can provide an estimate of the limiting depth of a functional group in a film,[3,4] but since the infrared radiation penetrates approximately one-quarter the wavelength of the observing light (~1200 nm at 1700 cm^{-1})[5]

Scheme I. Procedures Used to Couple Organic Groups to PE–CO_2H. In This Scheme, "Extract" Indicates That the Film Is Treated for 18 h in a Soxhlet Apparatus with 2-Propanol (72–76 °C in extraction thimble)



into the film, it is not possible to localize a species at the surface with this technique. ESCA[6] samples approximately the outermost 10 nm of the polymer and Auger spectroscopy[7,8] somewhat less (usually 1–2 nm depending on the kinetic energy of the exciting electrons). These sample depths would also include both surface and buried functional groups. Further, surface charging, damage to the surface from the exciting radiation and from local heating, and difficulties in quantitative analysis limit the value of these techniques for polymers.[8] Electrochemical techniques are not applicable, since polyethylene is an insulator. LEED cannot be used because the surface does not have the required crystalline order.

This paper describes several indirect chemical and spectroscopic procedures for discriminating between groups located at the surface and in the bulk of the polyethylene film. These procedures are based on the premise that if a polyethylene film is brought into contact with an aqueous solution of a water-soluble, hydrocarbon-insoluble reagent, reaction (or interaction) of this reagent with polyethylene functional groups will involve only those groups located at the surface of the polymer. Thus, the terms "surface" and "polyethylene-water interface" are used interchangeably.

The techniques used to establish the location of the functional groups of derivatives of PE-CO_2H also serve to explore the mobility and accessibility to solvents of these functional groups. These characteristics are important for two reasons. First, the stability of a functionalized surface depends (inter alia) on the rate at which the thermal movements of the polymer chains transport surface groups into the bulk of the polymer. Second, the chemical reactivity of functional groups on polymers depends on their solvation by the reaction medium. The stability and reactivity of functionalized surfaces thus are influenced by, and reflect, functional groups' solvation and mobility.[9–11] It was possible to derive information about both solvation and mobility from the study of spin and fluorescence labels attached to the surface groups.

Results and Discussion

Reaction of polyethylene containing adsorbed or dissolved thionyl chloride with an amine results in firm, but not covalent, binding of the amine in the polymer. Initial studies designed to develop a reaction which would couple primary amines to PE-CO_2H used the stable radical 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl (H_2N-TMPO) as reactant. PE-CO_2H was treated with thionyl chloride, washed with THF, treated with H_2N-TMPO, and washed with THF, water, and acetone. The resulting film exhibited an easily detectable ESR signal; covalent binding of H_2N-TMPO to the film was confirmed by the presence of an amide linkage in the ATR IR signal (Figure 1). When the sequence of manipulations was repeated using unoxidized polyethylene film (PE-H) rather than PE-CO_2H, an ESR spectrum having indistinguishable shape and ~60% of the intensity of PE-CONH-TMPO[TMPO] was obtained (Figure 1). The spin label retained in PE-H (and presumably a significant portion of that retained in PE-CO_2H) following this reaction sequence is not specifically bonded to carboxyl groups by covalent amide linkages. The species and reactions responsible for the incorporation of amine moieties into PE-H[$SOCl_2$] have not been established. Several observations are, however, central to the use of thionyl chloride as a method for converting carboxyl groups on PE-CO_2H to acid chloride moieties.

(1) If PE-H is treated with H_2N-TMPO without prior exposure to thionyl chloride, the quantity of spin label retained on the film is $\leq 5\%$ that detected when it has first been treated with thionyl chloride. Adsorption of H_2N-TMPO in the absence of thionyl chloride is thus only a minor problem.

(2) The major part (80–90%) of the spin label in PE-H[TMPO] and presumably of that included nonspecifically in PE-CONH-TMPO[TMPO] can be removed by extraction with 2-propanol (however, see below). Extraction of PE-CONH-TMPO[TMPO] also results in the loss of covalently bound material, since a decrease (20–30%) in the intensity of the amide absorption is detectable by ATR IR.

(3) PE-H retains dissolved thionyl chloride tenaciously. Film which has been treated with liquid thionyl chloride for 60 min at room temperature, and then exposed to vacuum (0.005 Torr) for 24 h at 70 °C still binds appreciable H_2N-TMPO (Figure 1). The ESR signal intensity of polyethylene film obtained by allowing H_2N-TMPO to react with PE-H[$SOCl_2$] that has been soaked in water for 1 h at room temperature is 50% that of PE-H[TMPO]. Extraction of PE-H[$SOCl_2$] with hot 2-propanol for several hours does, however, eliminate its reactivity toward H_2N-TMPO.

(4) The species resulting from reaction of dissolved thionyl chloride with H_2N-TMPO seem to be trapped beneath the surface of the polymer: PE-H[TMPO] is strongly hydrophobic, and the TMPO-containing substances do not react with reagents which reduce TMPO moieties covalently bonded at the surface (vide infra).

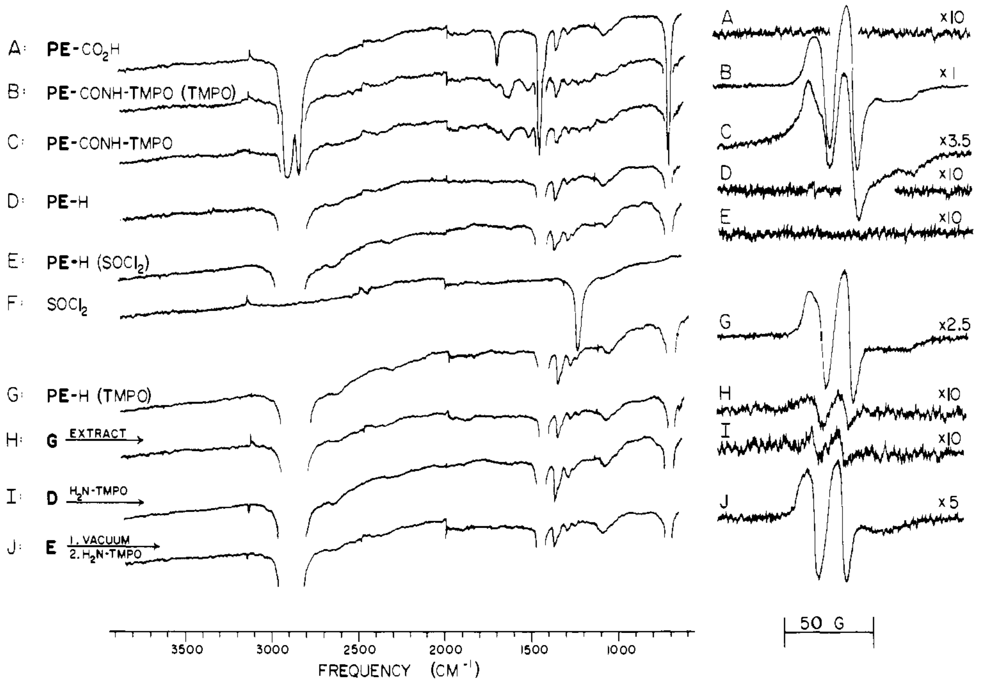


Figure 1. ATR IR and ESR spectra indicate that reaction of PE-COCl[$SOCl_2$] and H_2N-TMPO proceeds in high yield, but dissolved thionyl chloride (or impurities in the thionyl chloride) cause nonspecific binding of H_2N-TMPO to this and to unoxidized polyethylene film: A, reference spectra of PE-CO_2H; B, PE-CONH-TMPO[TMPO]; C, PE-CONH-TMPO (B extracted for 18 h with 2-propanol); D, reference spectra of PE-H; E, PE-H[$SOCl_2$]; F, transmission IR spectrum of thionyl chloride; G, PE-H[TMPO]; H, PE-H[TMPO] extracted for 18 h with hot 2-propanol; I, PE-H immersed for 1 h in 0.05 M H_2N-TMPO in THF, and then washed with THF; J, PE-H[$SOCl_2$] exposed to vacuum (0.05 Torr) at 70 °C for 24 h and then treated with 0.05 M H_2N-TMPO in THF and washed with THF.

(5) Thionyl chloride samples obtained from different suppliers promote the binding of amines to PE-H[$SOCl_2$] to different degrees. PE-H[TMPO] films which have adsorbed relatively large amounts of TMPO moieties release approximately the same quantity of nitroxide when extracted as do PE-H[TMPO] films containing far fewer TMPO groups; consequently, they retain more nitroxide after extraction. This behavior suggests that at least two distinct processes are responsible for the binding of amines to PE-H[$SOCl_2$]. First, in all films, dissolved thionyl chloride and/or a hydrolysis product (e.g., HCl) reacts with H_2N-TMPO to produce a *noncovalently* attached nitroxide species that is uneffected by superficial washings, but that can be removed by vigorous extraction. Two such possible species are the amine hydrochloride and the sulfinimide derivatives of H_2N-TMPO.[12] Second, an impurity in the thionyl chloride may oxidize the polyethylene and produce a reactive species that is capable of *covalently* binding H_2N-TMPO to the film.[13] For example, sulfuryl chloride, a common impurity in commercial thionyl chloride[14] is known to sulfochlorinate alkanes.[15] TMPO moieties bound to polyethylene via a sulfonamide linkage would not be easily extracted.

The actual identity of the compound(s) which traps amines in polyethylene and the nature of the adsorbed TMPO derivatives are not known. The ATR IR spectra of PE-H[$SOCl_2$] and PE-H[TMPO] have no absorbances not observed in PE-H: no peaks characteristic of thionyl chloride (1235 cm^{-1}), sulfinimides (1230, 1110 cm^{-1}), amine hydrochlorides (3100-2600 cm^{-1}), or sulfonamides (1340, 1150 cm^{-1}) can be detected.

We conclude from these observations that thionyl chloride does convert the carboxylic acid moieties of PE-CO_2H to acid chlorides, but that thionyl chloride or a contaminant in it also dissolves in or reacts with polyethylene to a significant extent. When PE-COCl[$SOCl_2$] is allowed to react with an amine, the product of reaction of the amine with thionyl chloride is present in a quantity comparable to that formed by reaction with -COCl moieties. If solutions of thionyl chloride which minimize amine binding are used to prepare PE-H[$SOCl_2$], the adsorbed nucleophile can be removed almost completely by extraction with 2-propanol. This procedure still provides a useful method of derivatizing the carboxyl groups of PE-CO_2H. Nonetheless, the uncertainty concerning the composition and location of the product(s) of reaction of dissolved thionyl chloride with the nucleophile and the need for extensive extraction at elevated temperatures to remove the large amount of noncovalently bound material (with attendant uncertainties concerning the stability of the polymer surface), all indicate that it is important to have another, better defined, procedure with which to form derivatives of the surface carboxyl moieties of PE-CO_2H.

Carbonyl hydrazides (PE-$CONHNH_2$) provide the basis of a useful method for covalent derivatization of PE-CO_2H. Of the several approaches[16] explored to circumvent the difficulties apparent in using thionyl chloride to activate the carboxyl groups of PE-CO_2H, the most successful involved preparation of polyethylene having surface carbonyl hydrazide moieties (PE-$CONHNH_2$) by treatment of PE-CO_2H with diazomethane in ether, followed by hydrazinolysis of the resulting ester groups with hydrazine hydrate (Scheme I). Although PE-CO_2CH_3 obtained by treatment of PE-COCl[$SOCl_2$] with methanol was superficially indistinguishable (as judged by ATR IR spectra) from PE-CO_2CH_3 generated by the diazomethane procedure, the latter reaction sequence was employed because it uses a chemically simple, high-yield reaction and is not complicated by the presence of dissolved thionyl chloride. Hydrazine hydrate, unlike thionyl chloride, is immiscible with hydrocarbon solvents and should not swell or dissolve in polyethylene film. Support for this argument is derived from the observation that a small population of the ester groups (10-20%) of PE-CO_2CH_3 appears to be inaccessible to the hydrazine since they do not react with it (Figure 2).

PE-$CONHNH_2$ is a useful starting material for modifi-

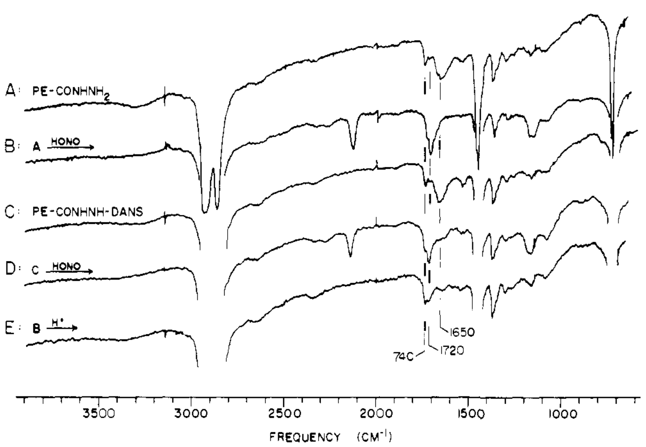


Figure 2. The extent of conversion of the carbonyl hydrazide groups of PE-CONHNH$_2$ to derivatives is determined by treating the derivatized film with nitrous acid and by comparing the remaining intensity of the carbonyl hydrazide absorbance with that of unreacted PE-CONHNH$_2$. ATR IR spectra of: A, PE-CONHNH$_2$; B, PE-CONHNH$_2$ treated for 5 min with cold, aqueous nitrous acid; C, PE-CONHNH-DANS; D, PE-CONHNH-DANS treated for 5 min with cold, aqueous nitrous acid; E, B hydrolyzed with 1 N HCl at 35 °C for 1 h.

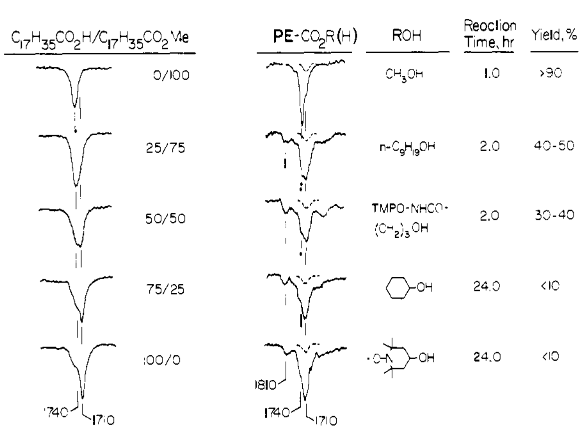


Figure 3. The extent of reaction between an alcohol and PE-COCl depends on the steric bulk of the alcohol. The ATR IR spectra are of films obtained by allowing PE-COCl to react with alcohols (ROH) at room temperature for the indicated times. The reaction yields were estimated by comparing the relative intensities of the ester (1740 cm^{-1}) and acid (1710 cm^{-1}) carbonyl peaks with those obtained from transmission IR spectra of known mixtures of stearic acid and methyl stearate. (Allowance was made for the absorbance from the ketone carbonyls ---, present in PE-CO$_2$H.) The IR spectrum of stearic acid contains a shoulder at 1750 cm^{-1} which is due to acid present as the monomer.

cation of the polymer surface, since hydrazine moieties react readily with electrophilic reagents. For example, PE-CONHNH$_2$ immersed in an 0.1 M ethanolic solution of 4-thiocyanato-2,2,6,6-tetramethylpiperidin-1-oxyl (SCN-TMPO) produced the nitroxide-labeled film, PE-CONHNHCSNH-TMPO. Maximum covalent labeling was obtained after 1 h at 35 °C; longer reaction times or higher reaction temperatures (70 °C, 1 h) increased the intensity of the nitroxide ESR signal of the film only slightly, and this increase could be accounted for by adsorption of SCN-TMPO into the film. Extraction of PE-CONHNHCSNH-TMPO with 2-propanol for 8 h produced an approximately 30% decrease in ESR signal intensity. The extractable TMPO moieties could be either noncovalently adsorbed in the film or attached to short-chain polyethylene chains which are soluble in hot 2-propanol. The latter possibility appears more likely: if PE-CO$_2$CH$_3$ is extracted with 2-propanol prior to conversion to PE-CONHNHCSNH-TMPO (Scheme I), <10% of the TMPO moieties of the product are removed by extraction with 2-propanol for 8 h.[17] The nitroxide groups of PE-CONHNHCSNH-TMPO which are not removed by extraction appear to be covalently bonded to the film. The conclusion that extraction removes TMPO groups attached to short polyethylene chains was supported by control experiments using PE-H: the ESR signal intensity of PE-H which had undergone the same reaction sequence was $\leq$5% the intensity of the signal from PE-CONHNHCSNH-TMPO and <1% the intensity of the signal obtained from PE-H[TMPO].

Treatment of PE-CONHNH$_2$ with dansyl chloride yielded a film (PE-CONHNH-DANS) having covalently attached dansyl moieties. Extraction of the film with hot 2-propanol produced approximately a 40% decrease in the number of attached dansyl moieties (as measured semiquantitatively by the intensity of fluorescence emission from the film). As a control, PE-H was exposed to dansyl chloride using reaction conditions analogous to those developed for PE-CONHNH$_2$. The resulting material showed 5-10% of the fluorescence observed for unextracted PE-CONHNH-DANS. After extraction with hot 2-propanol, no appreciable fluorescence remained.

It was difficult to assay for the completeness of the reactions leading to dansyl and TMPO derivatives of PE-CONHNH$_2$ by direct spectroscopic examination of the film, since the ATR IR frequencies of the newly introduced groups were not sufficiently intense to be useful. Instead, PE-CONHNH-TMPO and PE-CONHNH-DANS were treated with nitrous acid under conditions which generate PE-CON$_3$ (and PE-NCO) from PE-CONHNH$_2$.[2] These conditions appear to consume the carbonyl hydrazide moieties of PE-CONHNH$_2$ quantitatively as judged by the disappearance of the carbonyl hydrazide absorption at 1650 cm^{-1} from the ATR IR spectrum (Figure 2B). The carbonyl hydrazide groups of PE-CONHNHCSNH-TMPO and PE-CONHNH-DANS which give rise to an absorption at 1650 cm^{-1} after treatment of the film with nitrous acid are assumed to be covalently bonded to a TMPO (DANS) moiety. Comparison of the intensity of the 1650-cm^{-1} carbonyl hydrazide absorption from nitrous acid treated PE-CONHNH-TMPO and PE-CONHNH-DANS with that from PE-CONHNH$_2$ suggests that approximately 20-30% of the carbonyl hydrazide groups of PE-CONHNH$_2$ react and form derivatives with SCN-TMPO and dansyl chloride.

A systematic investigation of the factors which determine the yields of derivatives of functional groups on the surface of polyethylene has not been conducted. A series of observations suggest, however, that incomplete reaction is attributable in part to steric requirements around the surface functionality on polyethylene films. Methanol converts PE-COCl to the ester derivative in 1 h in >90% yield (Figure 3). Larger alcohols react with increasing difficulty, and very bulky alcohols such as cyclohexanol give <10% of the ester product after a 24-h reaction. Unreacted acid chloride moieties (1810 cm^{-1}) are visible in the ATR IR spectra of these films (Figure 3). Strong nucleophiles can overcome the steric difficulties: H$_2$N-TMPO converts >90% of the acid chloride groups of PE-COCl to product (Figure 1), while HO-TMPO is unreactive under similar conditions.

The incomplete conversion of carbonyl hydrazide groups to product observed on reaction of PE-CONHNH$_2$ with electrophiles restricts this surface modification procedure to applications in which quantitative reaction is not essential. Despite this limitation, this coupling has the important advantage relative to reaction of PE-COCl[SOCl$_2$] with nucleophiles that little material is nonspecifically included or adsorbed. Extraction to remove noncovalently bound species is therefore not necessary for films prepared using PE-conhnh$_2$ as starting material.

With PE-CONHNHCSNH-TMPO and PE-

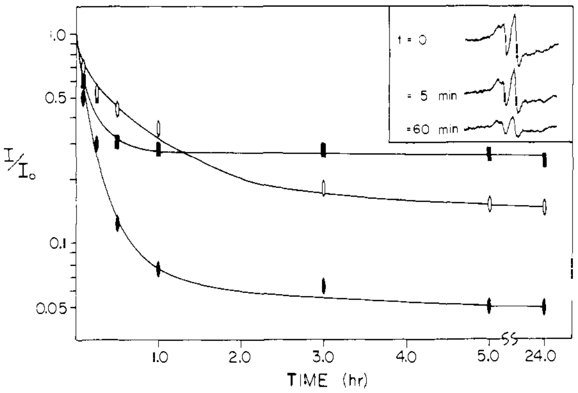


Figure 4. Reduction of the nitroxyl moieties of PE-CONHNHCSNH-TMPO on exposure to: 0.1 M aqueous sodium ascorbate, film dried 36 h (○) and film dried 1 h (●); 3 N aqueous HCl, film dried 36 h (■). The inset shows representative ESR spectra for the first of these films at the times indicated. The vertical axis, I/I_0, is the normalized amplitude of the largest peak of the ESR spectrum. Values are reproducible to ±20%.

CONHNH-DANS in hand, we wished to establish whether these spin and fluorescence labels were located at or beneath the surface of the films using as a criterion their reactivity toward, or accessibility to, polar, nonswelling solvents, or hydrophilic reagents dissolved in these solvents. Several independent experiments indicate that the TMPO and DANS groups of these derivatized films lie at the film surface.

Aqueous sodium ascorbate reduces the nitroxyl groups of PE-CONHNHCSNH-TMPO. Kornberg and McConnell have reported that aqueous sodium ascorbate cannot reach the interior of phospholipid vesicles, but that it rapidly reduces nitroxide derivatives at the outside of the vesicles.[18] If the nitroxide groups of PE-CONHNHCSNH-TMPO are at the interface formed by the polymer surface and water, they should be reduced by aqueous sodium ascorbate. Figure 4 shows the change in intensity of the ESR signal of PE-CONHNHCSNH-TMPO as a function of the time for which it is immersed in 0.1 M aqueous sodium ascorbate solution (pH 6.8). The rate and extent of reduction of PE-CONHNHCSNH-TMPO depended on the history of the film. A film subjected to reduction by the ascorbate solution immediately following reaction between PE-$CONHNH_2$ and ethanolic SCN-TMPO retained no detectable ESR signal after 3 h; however, a film dried in vacuo for 36 h prior to reduction contained an appreciable amount of nitroxide (10-15%) which resisted reduction even after 24 h (Figure 4). The presence of a nonreducing TMPO population suggests the presence of at least two different species in PE-CONHNHCSNH-TMPO. The ESR spectra of PE-CONHNHCSNH-TMPO films (dry) also indicate that more than one type of nitroxyl group is present (vide infra). The use of ethanol as a solvent for the preparation of PE-CONHNHSCNH-TMPO undoubtedly results in the generation of a surface layer in a partially or completely swollen form. The dependence of the accessibility of the nitroxyl groups to reagents in water on the sample history can be rationalized if loss of ethanol from the swollen surface is accompanied by diffusion of spin labels from the surface toward the interior of the polymer, or if this loss collapses a thin swollen surface layer containing nitroxyl groups in a form which is not readily hydrated. Evidence from ESR studies of the mobility of the nitroxyl labels (presented in detail below) indicates that swelling of the polymer at the surface on exposure of dry film to solvent, and collapse of the swollen film when the solvent is removed, can both require hours to go to (apparent) completion. It is not, in fact, certain that the nonreducible nitroxyl groups of the dried film are all actually covalently bonded to the polyethylene carbonyl hydrazide moieties. If the amount of SCN-TMPO adsorbed into PE-CONHNHCSNH-TMPO is equal to that adsorbed in a control film (PE-H treated with SCN-TMPO), up to 50% of the residual signal may be from noncovalently attached nitroxyl groups.

In any case, it appears that the large majority of nitroxyls present in PE-CONHNHCSNH-TMPO are accessible to aqueous ascorbate solution, and thus located at the polyethylene-water interface. In direct contrast, exposure of PE-H[TMPO] or PE-CO_2CH_3[TMPO] (obtained by treatment of PE-CO_2CH_3 with thionyl chloride and H_2N-TMPO in succession) to aqueous sodium ascorbate solution (pH 6.8) for 24 h at room temperature did not change the ESR signal intensity of these samples. This observation supports our assumption that aqueous, hydrophilic reagents are excluded from the interior of the polymer, and emphasizes that the nitroxyl species of PE-H[TMPO] are not at the polymer surface.

Aqueous 3 N hydrochloric acid catalyzes the disproportionation of the nitroxyl groups of PE-CONHNHCSNH-TMPO. Aqueous mineral acid catalyzes a bimolecular disproportionation of nitroxyl radicals.[19] Two conditions must be met if an acid solution is to promote the disproportionation of the nitroxyl radicals of PE-CONHNHCSNH-TMPO. First, the protons must have access to the nitroxyl groups; second, the spin labels must have a means to interact with one another. Figure 4 indicates that immersion of a dried (36 h) PE-CONHNHCSNH-TMPO film in 3 N aqueous HCl reduces the intensity of the ESR signal. As was the case with the ascorbate reduction, no residual ESR signal remains if freshly prepared films are employed. Since we have not established conclusively that the HCl-promoted reaction proceeds entirely on the polymer, rather than between nitroxyl groups hydrolytically cleaved from the polymer, it is premature to infer the proximity of surface nitroxyl groups from the course of the reaction. Nonetheless, indirect evidence suggests that the disproportionation may indeed occur at the surface: fluorescein isothiocyanate (FITC) reacts with PE-$CONHNH_2$ to produce PE-CONHNH-FITC, a film containing a fluorescent moiety bonded to the film surface in the same manner that the TMPO groups are bonded to PE-CONHNHCSNH-TMPO. The fluorescence intensity of PE-CONHNH-FITC was uneffected by a 3-h immersion in 3 N HCl,[20] indicating that, for this derivative at least, hydrolytic cleavage is slow compared with the time for reduction of the nitroxyl groups. In any case, these results do indicate that the majority of nitroxyl groups bonded to PE-CONHNHCSNH-TMPO are able to interact with aqueous acid, and suggest that they are present at the polyethylene-water interface. As anticipated by the analogous sodium ascorbate experiments, the ESR signal of the nitroxyl groups of PE-H[TMPO] was unaffected by a 24-h immersion in 3 N HCl. Approximately 95% of these nitroxyl groups are destroyed within 2 h when a solution containing a cosolvent which swells polyethylene is used (i.e., 3 N HCl in H_2O/THF 1/1 v/v).

Aqueous nitrous acid rapidly converts PE-$CONHNH_2$ to PE-CON_3. Treatment of PE-$CONHNH_2$ with aqueous nitrous acid (0 °C, 5 min) results in complete disappearance of the IR absorbance due to the carbonyl hydrazide moiety (1650 cm^{-1}) and appearance of peaks at 2140 and 1710 cm^{-1}, attributable to formation of an acyl azide group.[2] Hydrolysis of the acyl azide moieties is complete in <1 h on treatment with 1 N aqueous HCl at 35 °C (Figure 2). These reactions are compatible with the ready accessibility of the carbonyl hydrazide moieties of PE-$CONHNH_2$ to oleophobic reagents in aqueous solution.

The fluorescence emission of PE-CONHNH-DANS in contact with water suggests an environment for the dansyl group intermediate in polarity between water and polyethylene. The fluorescence is quenched by aqueous 1 N HCl. The fluorescence spectrum and intensity of dansyl derivatives is

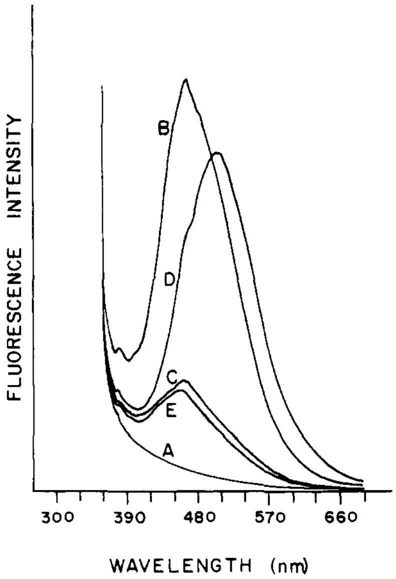


Figure 5. The fluorescence of PE-CONHNH-DANS is quenched by 1 N aqueous HCl: A, PE-CO_2H; B, PE-CONHNH-DANS, dry film; C, PE-H (dry film) carried through the procedure to prepare PE-CONHNH-DANS from PE-$CONHNH_2$ (the fluorescence is due to adsorbed dansyl moieties); D, PE-CONHNH-DANS in contact with water for 1 h; E, PE-CONHNH-DANS in contact with 1 N HCl. Instrumental settings were identical for all spectra.

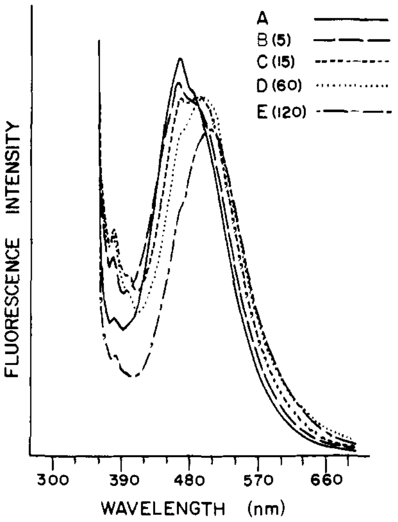


Figure 6. The wavelength of the fluorescence maximum of PE-CONHNH-DANS shows a time-dependent shift on contact with water: A, PE-CONHNH-DANS, dry film; B-E, PE-CONHNH-DANS, in contact with water for the indicated time (min). The instrument gain was adjusted to obtain spectra of equivalent intensity.

strongly influenced by the polarity of the surrounding solvent. For example, the fluorescence maximum of *N*-dansylglycine shifts from ca. 575 nm in water to 468 nm in cyclohexane, and its quantum yield increases tenfold.[21] The fluorescence of surface-dansylated polyethylene in contact with polar solvents can thus be used to probe the polarity of the interfacial region. Treatment of PE-$CONHNH_2$ with dansyl chloride in an acetone-water solution buffered with sodium bicarbonate yielded PE-CONHNH-DANS (Figure 5). A control, prepared by subjecting PE-H to the same sequence of reactions, had a fluorescence intensity approximately 10% that of the PE-CONHNH-DANS. This fluorescence presumably is produced by dansyl moieties noncovalently adsorbed in the film. As expected, the emission maximum of PE-CONHNH-DANS as a dry film or in contact with a hydrocarbon solvent (*n*-decane) is at 468 nm, indicating that the dansyl groups are in a nonpolar environment. This film is slightly hydrophilic. When it is wetted with water, a time-dependent shift in the emission maximum to 510 nm occurs (Figure 6). After 1 h in contact with water, only a small shoulder remains at 468 nm. The width of the peak at 510 nm is, however, approximately 20% wider than the solution spectrum observed from the model compound $CH_3CONHNH$-DANS and may imply that the dansyl groups attached to the films are not equally solvated. The final position of the fluorescence maximum of PE-CONHNH-DANS in contact with water is consistent with a location for the groups at the interface between polyethylene and water.

Additional evidence that the dansyl groups of PE-CONHNH-DANS are located at the film surface comes from observing the effect of acid on the fluorescence of the sample. After the film is immersed for 1 min in aqueous 1 N HCl, the emission at 510 nm is quenched, and only a small peak remains at 468 nm (Figure 5). The residual fluorescence is approximately equal in intensity to that observed for the control film PE-H[DANS], which has only adsorbed dansyl groups. The fluorescence quenching by the acid is completely and rapidly reversed by washing the film with 0.1 N aqueous sodium bicarbonate solution.[22]

These results demonstrate that the dansyl groups of PE-CONHNH-DANS are strongly influenced by the medium in which the film is immersed: both general dielectric strength and specific proton donating ability have the effect on fluorescence intensity and position expected if the dansyl groups are localized at the polymer-solution interface. The surface dansyl groups do not appear to constitute a homogeneous population: different groups of dansyl moieties respond at different rates to medium effects (and a small fraction of groups—possibly dissolved in the polyethylene in noncovalently bonded form—does not interact with the medium at all). The exact nature of the heterogeneity in local environment suggested by the differential response to water solvation is undetermined.

The fluorescence from dansyl groups of films prepared by reaction of PE-H[$SOCl_2$] with ethylenediamine followed by treatment with an acetone/water solution of dansyl chloride is insensitive to polar solvents.[23] The fluorescence is not quenched by aqueous acid, and the wavelength of the fluorescence emission maximum (468 nm) is the same for the dry film and for film immersed in water. Solvents which swell polyethylene do, however, interact with these dansyl groups. These groups thus appear to be localized beneath the surface of the polyethylene and to be inaccessible to aqueous reagents.

The nitroxyl groups of dry PE-CONHNHCSNH-TMPO have ESR line shapes indicating intermediate rotational mobility ($\tau_R \simeq 10^{-8}$ s). Exposing the film to polar and nonpolar liquids increases the mobility of at least some of the nitroxyls sufficiently that they seem to be rotating freely ($\tau_R \simeq 10^{-11}$ s). The ESR spectrum of freshly-prepared PE-CONHNHCSNH-TMPO consists of at least two components: a mobile component showing the sharp three-line spectrum characteristic of a freely rotating species, and a broader spectrum due to a species experiencing slower rotation (Figure 7).[24,25] As the sample is dried, the mobile species gradually disappear. When samples of dry PE-CONHNHCSNH-TMPO are immersed in ethanol, rotational mobility is restored to a fraction of the nitroxyl groups whose magnitude depends on the extent to which the film has been dried. All of the nitroxyl groups of samples dried only briefly became mobile; films dried in vacuo for 36 h contained a population of nitroxyl groups which remained immobile even after immersion in ethanol for 24 h. All of the nitroxyl groups remain bound to the polymer during immersion: if the poly-

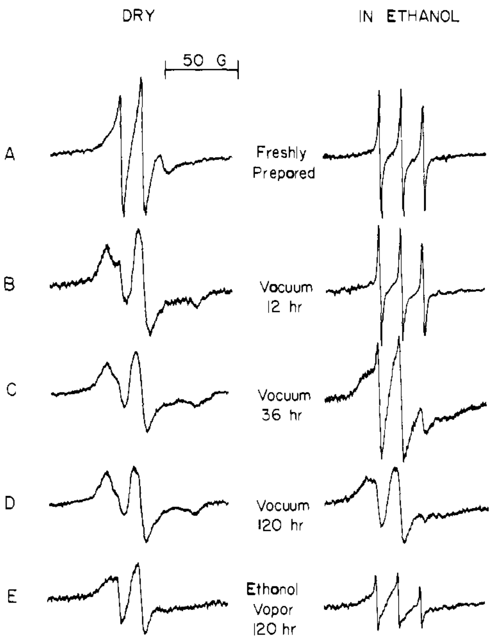


Figure 7. The nitroxyl moieties of PE-CONHNHCSNH-TMPO slowly lose mobility on drying. This immobilization proceeds more slowly if the sample is allowed to stand in contact with saturated ethanol vapor. It is rapidly reversed by immersion in liquid ethanol. Each pair of ESR spectra are of samples treated as indicated after preparation: one spectrum is taken with the film dry in air, the second with the film in ethanol after immersion for 10 min.

ethylene sample is removed from the liquid, no ESR signal is detected in the liquid.

The change which occurs in the surface during prolonged drying has not been identified. Evaporation of solvent from a swollen polyethylene surface layer might result in a collapse or reorganization of the surface. Alternatively, slow thermal movement of the polymer chains might transport surface nitroxyl groups into the interior of the polymer.[26] The observation that storing the nitroxyl-labeled polyethylene in a container saturated with ethanol vapor slows the formation of the immobile species (Figure 7) favors the first alternative.

Three structural characteristics of PE-CONHNHCSNH-TMPO emerge from these studies. First, the microscopic viscosity experienced by the TMPO moieties when the film is immersed in ethanol is low: the line shapes observed are similar to those of low molecular weight derivatives of TMPO in solvents such as glycerol,[24] in which the rotational correlation time, τ_R, is approximately 10^{-11} s.[27,28] Second, even in carefully dried film the nitroxyl groups retain some rotational freedom: the immobile TMPO groups appear to have $\tau_R \simeq 10^{-8}$ s. Third, the polymer surface seems to show behavior analogous to solvent swelling of a polymer gel. The rate of swelling seems to be rapid (<10 min). The rate of loss of solvent from a swollen surface can be slow (hours). Interconversion of dry and swollen forms is not fully reversible for all solvents: drying seems to be accompanied by trapping of a fraction of the nitroxyl groups beneath the polymer surface.

Since these ESR spectra depend on the way in which the sample is prepared, we have arbitrarily selected drying for 12 h in vacuo (0.005 Torr) as standard. This drying interval yields a sample which shows both mobile and immobile nitroxyl groups when immersed in ethanol. That is, changes in the mobility of the surface functionality are evident in the dry film, but these changes are apparently still reversible. The studies discussed in this section employ films dried under these conditions unless indicated otherwise.

A variety of solvents confer rotational mobility on the nitroxyl groups of PE-CONHNHCSNH-TMPO: Figure 8 shows representative ESR spectra of films immersed in methanol, acetone, and THF. These spectra are attributable to a homogeneous population of freely tumbling nitroxyl groups. Solvation of the surface groups is complete in the 5 min required to prepare the samples: no change in mobility is observed on more prolonged immersion. Spectra indistinguishable from those in THF were obtained in chloroform, methylene chloride, diethyl ether, and pentane. Perfluorokerosene, the only solvent investigated in which H_2N-TMPO is insoluble, does not increase the mobility of the surface TMPO groups (Figure 8). We were not able to obtain ESR in water due to high dielectric losses, and spectra obtained in liquid ammonia were complicated by aminolysis: the sharp spectrum observed in this solvent persisted when the film was removed from the ammonia. No ESR signal was detected in any other solvent following removal of the PE-CONHNHCSNH-TMPO films.

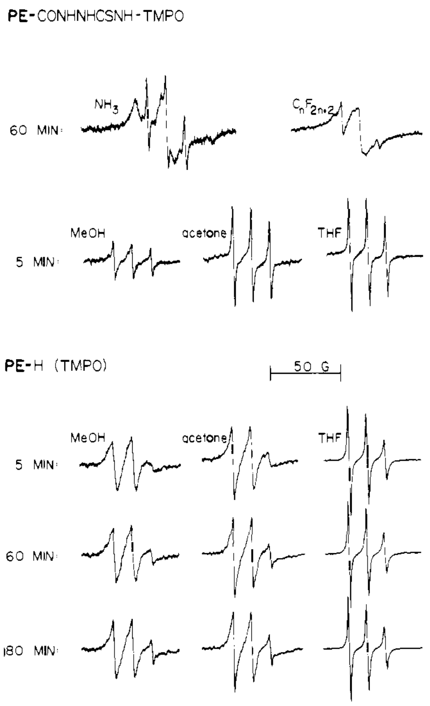


Figure 8. The nitroxyl groups of PE-CONHNHCSNH-TMPO (dried 12 h) rapidly regain rotational mobility on exposure to solvents. ESR spectra were recorded after a 5-min immersion in methanol, acetone, and THF, and after a 1-h immersion in perfluorokerosene. Spectra indistinguishable from those in THF were also observed in chloroform, methylene chloride, diethyl ether, and pentane. Liquid ammonia (−60 °C) releases TMPO moieties into the solvent by aminolysis. The nitroxyl moieties of PE-H[TMPO] regain mobility more slowly in polar solvents—methanol and acetone. Sequences of spectra indistinguishable from those in THF were also observed in chloroform, methylene chloride, diethyl ether, and pentane.

The ready accessibility of the nitroxyl groups of PE-CONHNHCSNH-TMPO to solvent, and the uniform response of the spectra to solvents which swell (e.g., THF, $CHCl_3$) and do not swell (methanol) bulk polyethylene,[29] support the contention that the functional groups are present at the polymer surface. The observations also suggest that the choice of solvents to influence the mobility or reactivity of surface functionalities of polyethylene should be based on the strength of their interactions with the functional groups rather than on their ability to swell polyethylene.

The interactions of solvents with the nitroxyl groups of PE-H[TMPO] differ significantly from their interactions with PE-CONHNHCSNH-TMPO (Figure 8). Polar solvents require several hours to swell the film to equilibrium (methanol solvates more slowly than ethanol, and ethanol more slowly than acetone); even at equilibrium, the nitroxyls are not freely mobile. Solvents which swell polyethylene film (e.g., THF and $CHCl_3$) rapidly solvate the nitroxyl groups. The behavior of the nitroxyl species in PE-H[TMPO] is consistent with the hypothesis that they are located beneath the surface of the polymer film.

The temperature dependence of the ESR spectra of dry films of PE-CONHNHCSNH-TMPO and PE-H[TMPO] (Figure 9) provides additional information about the mobility of the nitroxyls in each. The nitroxyl groups of PE-H[TMPO] appear to be of one type, and they obtain considerable mobility at elevated temperature. These spectra are similar to those of 2,2,6,6-tetramethyl-4-hydroxylpiperidin-1-oxyl benzoate ($PhCO_2$-TMPO) dissolved in low-density polyethylene film.[30] Since gases and liquids penetrate preferentially into the amorphous regions of a semicrystalline polymer,[31] the TMPO moieties are probably located in these regions of the polymer film and reflect the motion of the nonordered polymer chains. In contrast, the ESR spectrum of PE-CONHNHCSNH-TMPO is the superposition of signals from at least two, distinct, nitroxyl-containing species. A more mobile population exhibits a temperature dependence which resembles the behavior of TMPO derivatives incorporated noncovalently (e.g., PE-H[TMPO], $PhCO_2$-TMPO[30]) in polyethylene. A second, major portion of the spin label is immobile even at temperatures near the melting point of the film (probe temperature = 100 °C). It is possible (although not presently proved) that the mobile nitroxyl groups are attached to polyethylene chains in the amorphous regions, and the less mobile nitroxyl groups are bonded to polyethylene chains in the crystalline region.

The observation that a major part of the nitroxyl groups of PE-CONHNHCSNH-TMPO show low mobility even above room temperature may bear on the qualitative observation that we and others[32] have made that the surface of oxidized polyethylene film remains hydrophilic unless heated to 90-100 °C.

Summary and Conclusions

Two reaction sequences are sufficiently developed that they can be used to couple soluble molecules to the carbonyl groups of PE-CO_2H. The first (Scheme I) converts the carboxylic acids of PE-CO_2H to carbonyl chloride moieties with thionyl chloride, and then generates amides or esters by reaction with appropriate nucleophiles. This sequence proceeds in high yield using primary amines, methanol, or ethanol: >90% of the carboxyl groups are transformed to product. Yields of more hindered esters are lower. The coupling reaction between PE-COCl[$SOCl_2$] and amines has the advantages of simplicity, general applicability, and high yield. It has the disadvantage that thionyl chloride (or an impurity) dissolved in the polyethylene reacts with the amine and forms amine-derived products which, although apparently not covalently bound to the polymer, are difficult to remove completely by extraction. Further, it is not clear that functional groups on the surface survive the conditions required for extraction (hot 2-propanol) without some migration beneath the surface.

The second reaction sequence (Scheme I) is based on generation of surface carbonyl hydrazide groups from PE-CO_2H with diazomethane and hydrazine hydrate, and reaction of PE-$CONHNH_2$ with electrophiles. Its advantage is that it appears to be cleanly a surface sequence: no adsorbed or included by-products are generated, and extraction is not necessary. Its disadvantages are that yields for conversions from -CO_2H to -CONHNHR groups are only ca. 20-30%, and that several reactions are required to effect this transformation. Acid chlorides, sulfonyl chlorides, and isothiocyanates are useful electrophiles for reaction with the carbonyl hydrazides.

A large fraction of functional groups which are the products of these sequences are on the surface of the polyethylene. We hypothesize that only groups located at the polymer surface interact with reagents or solvents which are insoluble in bulk polyethylene. The fluorescence of the dansyl groups of PE-CONHNH-DANS shifts when the film is immersed in water, and is quenched when the film is treated with aqueous acid. Most of the nitroxyl groups of PE-CONHNHCSNH-TMPO are solvated on exposure to solvents that do not swell polyethylene. The carbonyl hydrazide groups of PE-$CONHNH_2$ are rapidly and quantitatively converted to carbonyl azides with aqueous nitrous acid. The conclusion from these observations—that the functional groups are at the polymer surface—is compatible with the observation that the wettability is dependent upon the nature of the attached moieties.

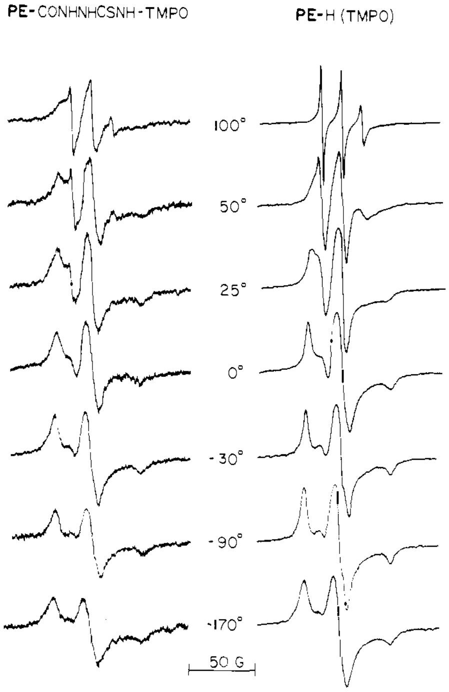


Figure 9. Variable temperature ESR spectra of dry films of PE-CONHNHCSNH-TMPO and PE-H[TMPO].

The spectroscopic studies of films labeled with dansyl and nitroxyl moieties show a small population of groups which behave as if their origin were not on the polymer surface. We do not know if these signals arise from small amounts of the label which dissolve in the polymer (that is, which is not covalently bound to the polymer) or whether a portion of the functional groups are initially generated below the surface or migrate below the surface subsequent to generation.[26] It is thus not possible at present to generate functionalized polymers in which *all* functional groups are unambiguously located at the surface. Nonetheless, the majority of the functional groups on these films appear to be at the surface.

Surface functional groups of films in liquids are solvated and show high rotational mobility. The rates of solvation and desolvation may be slow. The shift in fluorescence wavelength maximum observed when PE-CONHNH-DANS is transferred from a nonpolar to a polar medium, and the increase in mobility of the nitroxyl groups of PE-CONHNHCSNH-TMPO on its immersion in any of a number of solvents, establish that functional groups on the surface of these polyethylene films interact strongly with solvents. The fluorescence maximum of dansyl-labeled film in water occurs roughly halfway between the values characteristic of hydrocarbon and pure water, and suggests that the polarity of the environment experienced by the dansyl group is similar to solution in a solvent such as chloroform or THF (apparent dielectric constant approximately 5-10). The ESR signal of the nitroxyl-labeled film in solvents suggests that the restriction to rotation experienced by the TMPO group is not much different from that imposed on low molecular weight derivatives of TMPO in glycerol.

Both the position of the fluorescence maximum and the rotational correlation time can be used to examine qualitatively the rates at which the surface functional groups solvate and desolvate. Although solvation of the TMPO groups of newly prepared PE-CONHNHCSNH-TMPO is complete in <5 min, loss of solvent and reversion to the ESR spectrum of immobilized material takes hours under vacuum. Complete solvation of the dansyl groups of PE-CONHNH-DANS also takes several hours. We cannot explain why some of the processes require such long times to reach completion.

The surfaces are stable. The majority of the functional groups of PE-CO_2H and its derivatives do not extract into solution, and do not appear to migrate spontaneously from the surface to the interior of the polymer, over periods of days at room temperature. Exposure of the film to temperatures close to the melting point of the polymer and prolonged drying of an initially solvent-swollen surface do, however, result in apparently irreversible changes that appear to transport functional groups below the polymer surface. There is some qualitative evidence to suggest that contact of hydrophilic surface groups with water inhibits migration of these groups to the polymer interior. Thus, the surface of PE-CO_2H remains hydrophilic for extended periods at room temperature. PE-CO_2H heated in air at 90-100 °C rapidly becomes hydrophobic but, when heated in water, remains hydrophilic. The spatial stability of the surface groups to extraction with 2-propanol has not been studied in detail.

The surface functionality of derivatives of PE-CO_2H is probably not homogeneous and may be distributed between crystalline and amorphous regions of the polymer. The ESR spectra of dry PE-CONHNHCSNH-TMPO show two species of different rotational mobility. Although this observation is the only clear spectroscopic example of surface heterogeneity, the variable conversion of surface groups for several of the reactions carried out on the same films with different sample histories (destruction of nitroxyl groups by ascorbate and aqueous acid) suggests contributions from species with different reactivities. This heterogeneity may reflect attachment to amorphous and crystalline regions.

The species formed by reaction of PE-H[$SOCl_2$] with amines lie beneath the surface of the polymer. Polyethylene which has been treated with thionyl chloride reacts with amines, and generates a material which contains the amine in a form which requires exhaustive extraction to remove. The chemical details of this process are not clear, but this reaction is important in this work in three ways. First, it is an unavoidable side reaction in reactions of PE-COCl[$SOCl_2$] with amines, since thionyl chloride cannot be removed from the polymer before reaction. Second, it provides a simple method of incorporating reactive groups into polyethylene, and may have its own applications. Third, it generates materials in which the dansyl and nitroxyl labels are apparently *not* located at the polymer surface, since they interact weakly or not at all with liquids, or with reagents in solvents which do not swell polyethylene.

In conclusion, PE-CO_2H and its derivatives appear to be suitable materials to use as the basis for detailed studies of the relationship between polyethylene surface composition and structure and polyethylene surface properties. A number of important structural questions remain unanswered: the mean distance separating functional groups and details of the three-dimensional arrangement of functional groups at the surface are not known; the distribution of functionality between crystalline and noncrystalline regions is uncertain; the uniformity of the microscopic distribution of functional groups in different regions of the polymer has not been established. These questions will be the objects of further research. Nonetheless, the techniques outlined in this and the preceding paper[2] can be used reliably to introduce, and to assay, high densities of functional groups on the surface of polyethylene film by simple techniques, and the resulting functionalized surfaces appear to have good stability.

Experimental Section

General Methods. All solvents were reagent grade; THF was distilled under argon from a dark purple solution of benzophenone dianion; distilled water was passed through an ion-exchange resin and distilled in a Corning Model AG-1b glass distillation apparatus before use. Polyethylene film was a low-density, 2-mil commercial grade, prepared from PETROTHENE NA 144 resin (0.919 density, 2.0 melt index) and was a gift of U.S. Industrial Chemicals. 4-Amino-2,2,6,6-tetramethylpiperidin-1-oxyl, acetyl hydrazide, and thiophosgene were purchased from Aldrich and used without further purification. Dansyl chloride and fluorescein isothiocyanate were obtained from Sigma. Thionyl chloride from Matheson, Coleman, and Bell, Aldrich, or Eastman was employed, see below. ATR IR spectra were measured on a Perkin-Elmer 521 grating spectrophotometer using procedures described previously.[2] Fluorescence measurements were recorded on a Perkin-Elmer MPF-4 fluorescence spectrometer using a solid sample holder to mount the films. ESR spectra were measured on a Varian E-9 spectrometer. General procedures for manipulating the polyethylene films and the preparations of PE-CO_2H, PE-COCl[$SOCl_2$] PE-CO_2CH_3, and PE-CONHNH_2 are described elsewhere.[2]

4-Thiocyanato-2,2,6,6-tetramethylpiperidin-1-oxyl (SCN-TMPO). SCN-TMPO was prepared by the procedure of Gaffney.[35] H_2N-TMPO (3.94 g, 22.4 mmol) was dissolved in 90 mL of 5% aqueous NaOH and the solution cooled with an ice-salt bath. Thiophosgene (2.58 g, 22.4 mmol) was added dropwise over a 15-min period while vigorous stirring was maintained. After addition was complete, the reaction was stirred for an additional 10 min. The orange precipitate was filtered, washed with water, and dried to constant weight in vacuo over P_2O_5. Recrystallization of crude SCN-TMPO from 50 mL of absolute ethanol yielded 1.85 g (8.2 mmol, 36%) of the isothiocyanate as red plates: mp 126-127 °C (lit.[35] mp 126-127 °C); IR ($CHCl_3$) 2065 cm^{-1}.

PE-CONHNHCSNH-TMPO. A 1 × 5-cm piece of PE-CONHNH_2 (the most convenient size for ESR measurements, see below) was placed in a 5-mL vial filled with a 0.1 M solution of SCN-TMPO in ethanol. The vial was sealed with a Teflon-lined cap and placed in a 35 °C water bath for 1 h. At the end of this time the film was removed and washed twice with ethanol, twice with acetone, and twice with diethyl ether. The film was dried for 12 h in vacuo (0.005 Torr) prior to use in ESR measurements.

PE-H[$SOCl_2$]. Polyethylene film was extracted with hot 2-propanol as described previously[2] to remove any commercial additives. The extracted film, PE-H, was immersed in liquid thionyl chloride for 1 h, removed, and washed twice with THF. Normally this film was allowed to react further immediately. PE-H[$SOCl_2$] films prepared with thionyl chloride from different sources bound different amounts of amines. When Matheson, Coleman, and Bell reagent was employed, the smallest amount of nucleophile was adsorbed to PE-H[$SOCl_2$] during subsequent reaction, and >85% of this material could be extracted with hot 2-propanol. Thionyl chloride from Aldrich promoted much greater adsorption of nucleophilic reagents to PE-H[$SOCl_2$], and a significant quantity (40-50%) of the adsorbed species was not extractable. Purification of thionyl chloride by distillation from triphenyl phosphite did not reduce the adsorption problem.

PE-H[TMPO]. Freshly prepared PE-H[$SOCl_2$] was immersed in a 0.1 M solution of H_2N-TMPO in THF/pyridine (1:1 v/v) for 1 h. The sample was removed from the reaction mixture and washed with THF (twice), water (twice), and acetone (twice). This film was dried for 12 h in vacuo (0.005 Torr) before use in the ESR experiments.

PE-CONHNH-DANS. A 1 × 5-cm piece of PE-CONHNH_2 was placed in a 5-ml vial containing 2.2 mL of a 0.1 M solution of dansyl chloride in acetone, and 0.8 mL of 0.1 N aqueous $NaHCO_3$ added. The vial was sealed with a Teflon-lined cap and the reaction mixture agitated briefly with a Vortex stirrer. After a total reaction time of

5 min, the film was removed and washed three times with acetone, once with water, and again with acetone. Films were dried overnight in vacuo (0.005 Torr) prior to use in fluorescence experiments.

PE-H[DANS]. PE-H[$SOCl_2$] was placed in 30 mL of a 5% solution of ethylene diamine in THF. After 30 min the film was removed and washed with two 50-mL portions each of THF, water, and acetone. After brief air drying, the film was treated with dansyl chloride in the same manner that was employed during the preparation of PE-CONHNH-DANS.

PE-CONHNH-FITC. A 1 × 5-cm piece of PE-$CONHNH_2$ was immersed in a 5-mL vial containing ~5 mL of an ethanol solution saturated with fluorescein isothiocyanate. The vial was sealed with a Teflon-lined cap and placed in a 35 °C water bath for 1 h. At the end of this time the film was removed and washed with ethanol (twice), acetone (twice), and diethyl ether. The film was dried for 12 h in vacuo (0.005 Torr) before use. Prior to performing fluorescence measurements on these films, they were placed in 0.1 N aqueous sodium bicarbonate for 5 min, washed with water and acetone, and air dried.

N-Dansyl Acetyl Hydrazide. Acetyl hydrazide (250 mg, 3.25 mmol) and 5-dimethylamino-1-napthalenesulfonyl chloride (800 mg, 2.96 mmol) were dissolved in 10 mL of chloroform containing triethylamine (300 μL) and stirred for 2 h. At the end of this time the orange solution was concentrated under reduced pressure to a viscous oil. The oil was extracted with three 20-mL portions of acetone. The combined acetone extracts were concentrated to ~4 mL under reduced pressure and applied to two preparative TLC plates (Analtech silica gel, 2000-μm thickness). The plates were developed with $CHCl_3$/methanol (9:1 v/v). The yellow band with R_f 0.30-0.47 was scraped and eluted from the silica gel with 25 mL of acetone. Concentration of the acetone solution yielded *N*-dansyl acetyl hydrazide as an intensely yellow solid with mp 179-181 °C; IR ($CHCl_3$) 3260, 1690, 1340, 1160, 1140 cm^{-1}; NMR ($CDCl_3$) δ 8.6-6.7 (m, 6 H), 2.9 (s, 6 H), 2.2 (s, 3 H).

4-Hydroxylbutyramido-1-amino-2,2,6,6-tetramethylpiperidin-1-oxyl. γ-Butyric lactone (108 mg, 1.25 mmol) and H_2N-TMPO (200 mg, 1.14 mmol) were mixed in a 5-mL round-bottomed flask and heated on a steam bath for 4 h. After cooling, the residue was taken up in 2 mL of chloroform and applied to a preparative TLC plate (Analtech silica gel, 1000 μm thickness). The plate was scraped and the product eluted from the silica gel with methanol. The methanol solution was concentrated under reduced pressure to yield a thick red oil which solidified on standing to yield 130 mg (0.45 mmol, 40%) of product with mp 100.0-100.5 °C: IR ($CHCl_3$) 3440, 3350, 1650 cm^{-1}.

ESR Measurements. To prepare a nitroxyl film for ESR measurements, the film (1 × 5 cm) was rolled into a tight cylinder (height, 1 cm), and maneuvered into the bottom of the ESR tube. To ensure that a tube was positioned the same way for each of a series of measurements, a tightly fitting Teflon collar was placed around the tube in such a manner that it touched the top of the sample holder when the film was in the center of the sample cavity. To prevent saturation of the signal the microwave power applied to the sample was maintained at or below 1 mW. To prevent line shape distortion, the modulation amplitude setting never exceeded 1 g. In studies of solvent effects the film was covered with the desired solvent and the sample degassed with three freeze-thaw cycles.

Reduction of PE-CONHNHCSNH-TMPO by Aqueous Sodium Ascorbate. After the ESR spectrum of a PE-CONHNHCSNH-TMPO sample was recorded, the film was removed from the ESR tube and immersed in freshly prepared 0.1 M aqueous sodium ascorbate (pH adjusted to 6.8 with 0.1 N NaOH). At the proper time the film was removed, washed three times with water and twice with acetone, and air dried. The dry film was reinserted into the ESR tube and the new spectrum recorded. Line shapes (but not intensities) were indistinguishable before and after reduction. The relative signal intensities were approximated by comparing normalized amplitudes of the largest peak of the first derivative spectrum. Values were reproducible to ±20%.

Reaction of PE-CONHNHCSNH-TMPO with Aqueous 3 N HCl. The effect of 3 N HCl upon the ESR signal obtained from PE-CONHNHCSNH-TMPO was investigated in the same manner as experiments with the sodium ascorbate reduction except that aqueous 3 N HCl was employed instead of the ascorbate solution.

Fluorescence Measurements. Fluorescence spectra are uncorrected and were recorded with a Perkin-Elmer MPF-4 fluorescence spectrometer. The films were positioned in the sample compartment with a solid sample holder apparatus and front surface fluorescence measured. To obtain "solution" spectra, the films were wetted with the appropriate solvent, mounted between two microscope slide cover slips, and placed in the solid sample holder. An excitation wavelength of 340 nm was employed for the dansyl samples, and both the emission and excitation slit openings were 4 nm. The fluorescence of FITC films was measured by exciting at λ_{ex} 450 nm. The fluorescence maximum was 527 nm.

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The Question of Delocalization in "Anchored" Ions with Potential Trishomoaromatic Character. 1. Reduction of Tricyclo[5.4.1.$0^{4,12}$]dodeca-2,5,8,10-tetraene as a Route to the 10π11C Dianion

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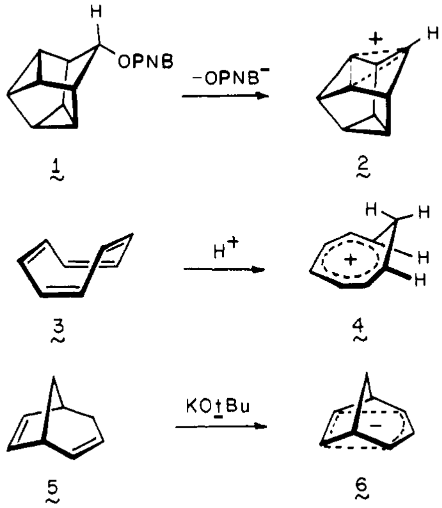
Abstract: The title compound (**13**), although not available from the pyrolysis of **11** (Scheme I), can be obtained in two steps from Schröder's hydrocarbon (**14**, Scheme II). The unprecedented $(CH)_{12}$ interconversions which result during these rearrangements show the richness of the interconnective energy surface. Dissolving metal reduction of **13** does not give rise to a spectroscopically characterizable dianion species, but methanol quenching provides two dihydro ($C_{12}H_{14}$) products and two isomeric $C_{12}H_{12}$ hydrocarbons. These transformations are discussed in terms of a highly basic dianion by virtue of its ensuing reactions. For comparison purposes, the reducibility of bicyclo[6.2.1]undeca-2,4,6,9-tetraene (**31**) has also been examined in the context of generating a bishomocyclooctatetraenyl dianion. The relationship of these observations to the general homoaromaticity phenomenon, particularly as regards the question of multiple interruption of the cyclic π-electron network, is discussed.

These exist two possible ways of attaining that level of electronic interaction which gives rise to homoaromatic delocalization.[2] In the first of these, a strained σ bond (preferably cyclopropyl) is positioned in the structural framework such that moderate rehybridization[3] can provide the necessary contiguous overlap (on one surface only!) of orbitals containing $(4n + 2)$ electrons. The solvolysis of **1** is exemplary. Its 10^{12}-fold solvolytic rate acceleration over 7-norbornyl,[5] which cannot be attributed to strain relief because the ensuing rearrangement is degenerate, is best understood in terms of charge development as in **2**. In fact, this trishomocyclopropenyl cation intermediate has been directly observed.[6] The other alternative is to make available an appropriate number of p-π orbitals such that electrophilic attack at one of these sites, ionization at an adjoining sp^3-hybridized center, or introduction of electrons by one of several reductive methods generates a similar type of cyclic conjugation. In larger molecules such as **3** which have adequate conformational flexibility, built-in structural constraints are unnecessary because those three-dimensional features necessary for overlap in the vicinity of the tetrahedral carbon (cf. **4**) can be realized without severe distortion.[7] In other cases typified by **5**, the absence of a rigid structural framework would be inimical to the operation of homoaromatic delocalization.[8]



Although the first of these phenomena has received considerable attention,[2,9] the second aspect has been less systematically investigated. This is perhaps because a series of polyunsaturated molecules having rigid geometry and properly canted π orbitals has not been generally available. In an attempt to develop our understanding of the homoaromaticity phenomenon, we have now conducted a detailed reactivity study of substrates which can serve as precursors to the "anchored" trishomoaromatic ions **7–9**.[10,11] Attention remains