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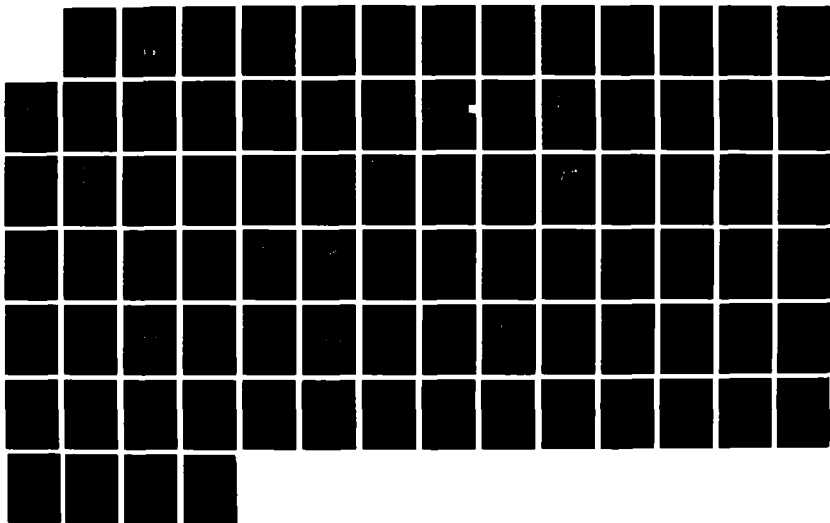
RECONSTRUCTION OF THE INTERFACE OF OXIDATIVELY
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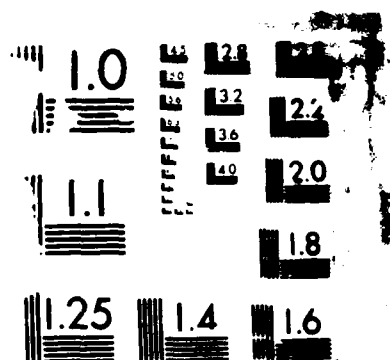
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Polyethylene (PE-CO₂H) and Derivatives on Heating"

by Stephen Randall Holmes-Farley, Robert H. Reamey,
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Reconstruction of the Interface of Oxidatively Functionalized
Polyethylene (PE-CO₂H) and Derivatives on Heating¹

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Abstract. Oxidation of low-density polyethylene film with aqueous chromic acid results in a material (PE-CO₂H) having hydrophilic carboxylic acid and ketone groups in a thin oxidatively-functionalized interface. This interface is indefinitely stable at room temperature. On heating in vacuum, it rapidly becomes hydrophobic and similar in its wettability to unfunctionalized polyethylene film. The progression of the contact angle with water from the initial value (55°) to the final value (103°) follows kinetics that suggest that the polar functional groups disappear from the interface by diffusion. The magnitude of the apparent diffusion constant derived from these

Cont'd

studies can be described approximately by an Arrhenius equation over a significant portion of the temperature range explored, with an Arrhenius activation energy of diffusion of ^{approx} 650 kcal/mol. Comparison of the properties of interfaces composed of carboxylic acid groups with those containing other species demonstrates that the structure of the interfacial groups also significantly influences the rate of reconstruction. In particular, reconstruction is slow when the interfacial functional groups are large and polar (e.g. esters of poly(ethylene glycol)) and when they have structures ^{that} result in low solid-air interfacial free energies (e.g. CF₃ moieties). Studies of reconstruction carried out with PE-CO₂H in contact with liquids such as water and perfluorodecalin suggest that reconstruction is driven initially by minimization of the interfacial free energy. A slower process--probably driven simply by the entropy of dilution of the concentrated interfacial functionality into the polymer interior--then results in further reconstruction. Contact angle is much more sensitive than XPS to the reconstruction process: reconstruction of that part of the interface influencing wetting is complete before a significant change in XPS signal intensities can be observed. This observation suggests limitations to the applicability of XPS to the study of phenomena such as adhesion. Experiments with a fluorescent reporter group (dansyl) support the conclusion that minimization of the interfacial free energy is important in determining the nature of the interface after reconstruction. ATR-IR spectroscopy indicates that even after migration into the film, all of the carboxylic acid groups of PE-CO₂H are accessible to aqueous base: that is, that the thermally reconstructed interface has the wetting properties of

unfunctionalized polyethylene but that the functional groups situated a short distance from the polymer-water interface can exchange ions with bulk water. Thermally reconstructed PE-CO₂H is thus a new type of thin-film ion-exchange resin. Samples that had previously been reconstructed by heating in vacuum could, to a limited extent, be made to become hydrophilic again by heating in water. As the length of the initial heating period increased, the ability to "recover" the polar groups was lost. Survey experiments on other interfacially modified polymers (for example, polypropylene treated with an oxygen plasma) indicate that the type of reconstruction examined in this paper is not confined to PE-CO₂H and its derivatives.

Introduction

Oxidation of low-density polyethylene film with aqueous chromic acid solution yields a material having carboxylic acid and ketone (aldenyl) groups in a thin interfacial layer.⁶⁻¹¹ We call this material polyethylene carboxylic acid (PE-CO₂H) to emphasize the dominant contribution of the carboxylic acid moieties to its interfacial properties, even though both carboxylic acid and ketone groups are present. The interface of unoxidized polyethylene (PE-H) is hydrophobic (the advancing contact angle of water on it is $\theta_a = 103^\circ$); the interface of PE-CO₂H is relatively hydrophilic ($\theta_a = 55^\circ$).⁶ Previous studies have examined in detail the ionization of the carboxylic acid groups of PE-CO₂H as a function of pH,⁶ and demonstrated the utility of contact angle measurements as a method for studying this ionization and other interfacial reactions.⁶⁻⁹

The hydrophilic character of the interface of PE-CO₂H is retained essentially indefinitely (months to years) at room temperature. On heating ($T = 35 - 110^\circ\text{C}$) the interface of PE-CO₂H becomes hydrophobic; its final state is indistinguishable from unfunctionalized polyethylene in its wettability and in certain other interfacial properties. The objective of this paper is to characterize this thermal reconstruction: What molecular-level processes are responsible for conversion of the hydrophilic interface of freshly prepared PE-CO₂H to a hydrophobic interface during heating, and what energetic factors drive these processes?

The only oxygen-containing functional groups present in PE-CO₂H are a 3:2 mixture of carboxylic acids and ketones.^{6,7} Only a fraction (perhaps 30%) of the functional groups present in PE-CO₂H are in that

part of the interface that determine wetting by short-range interactions.⁸ All of the functionality in the oxidized interface is, however, accessible to reagents in aqueous solution: in particular, all of the carboxylic acid groups of PE-CO₂H can be titrated with aqueous hydroxide ion.⁵⁻⁹ Our current model for the structure of the interface of PE-CO₂H is one in which the majority of the polyethylene chains reaching the interface terminate in carboxylic acid groups, and in which these functional groups are restricted to a thin (≤ 20 Å) layer. The underlying polymer is a mixture of crystalline and amorphous regions.¹² We see little evidence for different classes of interfacial groups reflecting these crystalline and noncrystalline regions. As a first approximation, we consider the functionalized interface of the polymer at room temperature to be a viscous glass. Even the small (~ 5 Å) motions that transfer groups from that part of the interphase that influences contact angle (the "contact angle interphase" or "a interphase") into the deeper part of the interphase that does not influence contact angle (the "sub-contact angle interphase" or "sub-a interphase") seem to be very slow at room temperature. At temperatures close to the melting point of the polymer, the rate of this transfer becomes rapid.

In studying the thermal reconstruction of the oxidatively functionalized interface of PE-CO₂H we wish to establish several points: First, how stable is this interface? How rapidly does the reconstruction occur, and what is the dependence of this rate on the characteristics of the functional groups present in the interface? This information is clearly critical to any uses of PE-CO₂H and its derivatives as substrates for interfacial chemistry. Second, what are

the mechanisms of the processes that result in changes in properties of PE-CO₂H on heating? Do these changes involve transformations or loss of interfacial functionality, or migration of this functionality into the interior of the polymer? What is (are) the driving force(s) for these processes? We envisage three limiting mechanistic alternatives: passive diffusion of the polar functionality away from the interface and toward the interior of the polymer, expulsion of the polar functionality from the interface to minimize interfacial free energy, and movement of polar functionality into the interior as a result of movement of polymer chains reflecting either relief of strain, crystallization, or random chain movement. Third, how sensitive are different analytical techniques to the movement of functional groups away from the interface of the polymer? We were most interested in comparisons of two surface-selective techniques--measurement of liquid-solid contact angles, and XPS (ESCA). Other analytical techniques used in this work--ATR-IR, fluorescence spectroscopy--are useful but not intrinsically sensitive to the position of the functional group with respect to the interface of the polymer. Wetting reflects primarily short-range forces, but there is no adequate molecular-level model of wetting for real or heterogeneous materials.^{5,8,13-29} XPS is a technique whose ability to discriminate surface from subsurface composition is determined by the finite escape depth (roughly 60 Å in polyethylene) of the ejected photoelectrons and the geometry of the detector relative to the sample.²² Fourth, what are the possible synthetic applications of thermal surface reconstruction? This type of process can, in principle, provide a method of preparing a new class of polymeric materials: that is, one

having a wide variety of organic functional groups close to but not exposed at its surface. How can thermal reconstruction be best used to prepare such materials? Fifth, what can be learned from thermal reconstruction concerning the composition and structure of the functionalized interfacial layer? Because PE-CO₂H is so convenient as a starting material to use in physical-organic studies in interfacial chemistry, we would like to try to define its functionalized interface--especially the three-dimensional distribution of functional groups in this interface--in as much detail as possible. Studies of interfacial reconstruction, and comparison of reconstructed and unreconstructed interfaces is relevant to this objective.

This paper concentrates on reconstruction resulting from heating PE-CO₂H and its derivatives to temperatures at which the underlying polymer softens. Evidence presented in the following sections indicates that reconstruction proceeds in two stages: First, a rapid rearrangement of the oxidized interface has the effect of moving most of the functional groups away from the contact angle interphase: we believe this small-scale rearrangement is governed by minimization of the solid-vapor interfacial free energy. Second, a slower process results in large-scale movement ($>10^3$ Å) of the functional groups into the interior of the polymer.

Synthetic Techniques

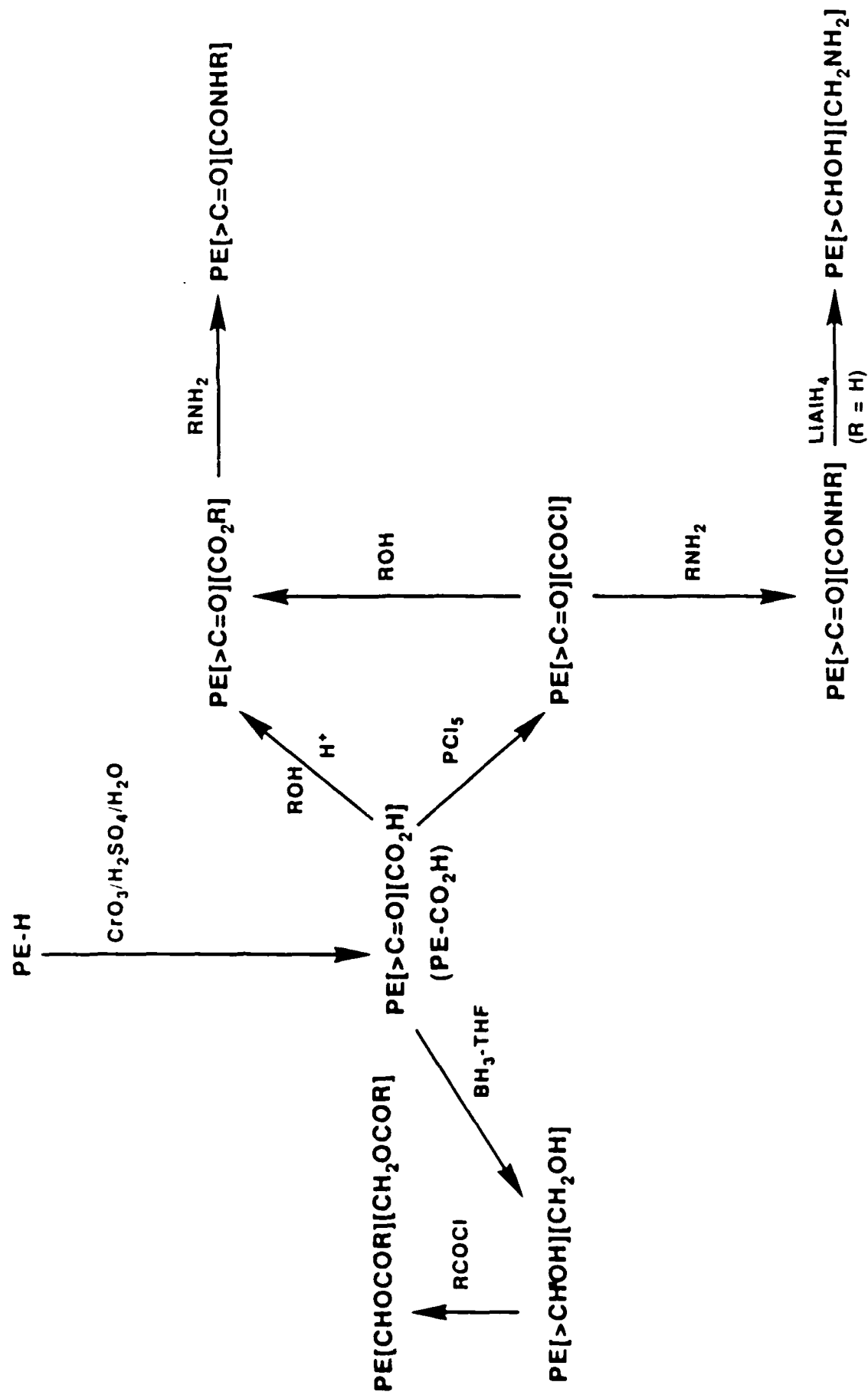
Polyethylene. Most of our work used commercial low density ($\rho = 0.92$ g/mL) biaxially oriented polyethylene film. This material (PE-H) was prepared for reaction by removing antioxidants and other additives by extraction with methylene chloride.⁶ For experiments

which we wished to explore the effect of residual strain in the polymer on the rate of interfacial reconstruction, we used film in which the residual strains remaining from the manufacturing process were eliminated or reduced by annealing, either before or after extraction, by heating under argon at 100 °C for 5 days.

We also conducted a limited number of experiments using ultra-high molecular weight polyethylene (UHMW, $\rho = 0.93$ g/mL), obtained as a rigid sheet.

Oxidation. All oxidations were conducted using the aqueous chromic acid solution of the composition used previously ($\text{CrO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O} = 29/29/42$; w/w/w).⁵ Oxidations were conducted for 60 s at 72 °C to produce PE-CO₂H, or for 10 min to produce a more heavily etched material. Previous studies of oxidation of polyethylene film have shown that these two treatments lead to materials with the same wetting characteristics.⁶ The interfacial morphology of the sample oxidized for 60 sec is similar to that of unoxidized polyethylene; the sample oxidized for a longer interval is rougher (as suggested by SEM photomicrographs having resolution limited to ~ 1000 Å).⁶

Chemical Derivatization and Sample Manipulation. We have worked with a number of derivatives of PE-CO₂H. Some of the synthetic methods used in this work are summarized in Scheme 1. Most of these synthetic methods have been detailed previously.⁵⁻⁹ The interface of oxidized polyethylene is resistant to contamination by impurities in the laboratory atmosphere. Samples were handled in the open laboratory, but were not exposed to the laboratory atmosphere longer than was necessary. They were stored under dry inert gas in a desiccator. These samples have also proved resistant to damage by



Scheme 1. Reactions used to modify the interface of polyethylene film (PE-H).

mechanical stress. They were handled carefully using needle-point tweezers, and measurements of interfacial properties were carried out on regions that had not been touched by the manipulating instruments.

Nomenclature. In this paper, as previously,⁵⁻⁹ defining the functionality present in the interface of polyethylene is a cumbersome task. We will, in general, ignore the ketone/aldehyde functionality present on PE-CO₂H. We note only that PE[CH₂OH], and derivatives of it, contain both primary and secondary hydroxyl species, resulting from the reduction of carboxylic acid and ketone groups respectively. We will designate the functionality present in the interface using a simple nomenclature: PE[R] designates a material in which the carboxylic acid groups introduced during the initial oxidation have been converted into the group R.

Reconstruction of the Interface of PE-CO₂H on Heating: Contact Angle and XPS

We have discussed the techniques used to measure contact angles of water on the functionalized interfaces of PE-CO₂H and its derivatives, and especially contact angle titration--that is, the measurement of contact angle as a function of pH.⁶ Detailed interpretation of contact angles in these systems in terms of interfacial free energies is complicated by the fact that the contact angles show very large hysteresis: the advancing angles, θ_a , that form the basis for most of this paper are stable and reproducible, provided that the relative humidity over the sample is controlled at 100%. Retreating contact angles, θ_r , are usually zero for polar derivatives of PE-CO₂H, and the drop edge seems to be effectively

pinned.⁹ The advancing contact angle shows only minor sensitivity to sample vibration, or drop size.⁹ Further, in instances in which it is possible to compare results inferred from measurement of contact angle with those from IR or fluorescence spectroscopy, the agreement is good.^{5,7} Nonetheless, the large hysteresis indicates that the contact angle is not measuring a system at thermodynamic equilibrium. We have not yet established whether the origin of the hysteresis lies in interfacial heterogeneity, in interfacial roughness, or in some other phenomenon such as swelling of the interphase in contact with liquid water.

In initial studies of the thermal reconstruction of the interface of PE-CO₂H and its derivatives, we subjected samples to controlled temperatures under vacuum or an inert gas for intervals of time, and then measured the contact angle of water on these samples; the content of oxygen in the interface was also measured using XPS.

Figure 1 shows the change in the contact angle of water on PE-CO₂H as a function of the time the polymer had been heated at 100 °C under vacuum (0.01-1 torr) and dry argon (inside an Abderhalden drying pistol jacketed with refluxing water) prior to examination; values of θ_a are given both for water at pH 1 and at pH 13. The contact angle at pH 13 is lower than the contact angle at pH 1 due to the conversion of the interfacial carboxylic acid groups to more hydrophilic carboxylate anions.⁶ We have previously demonstrated that conversion of interfacial carboxylic acid groups to carboxylate ions not only lowers the contact angle, but may also be accompanied by reconstruction of the θ interphase.⁸ We presume that this reconstruction is driven by solvation of the carboxylate ions. The

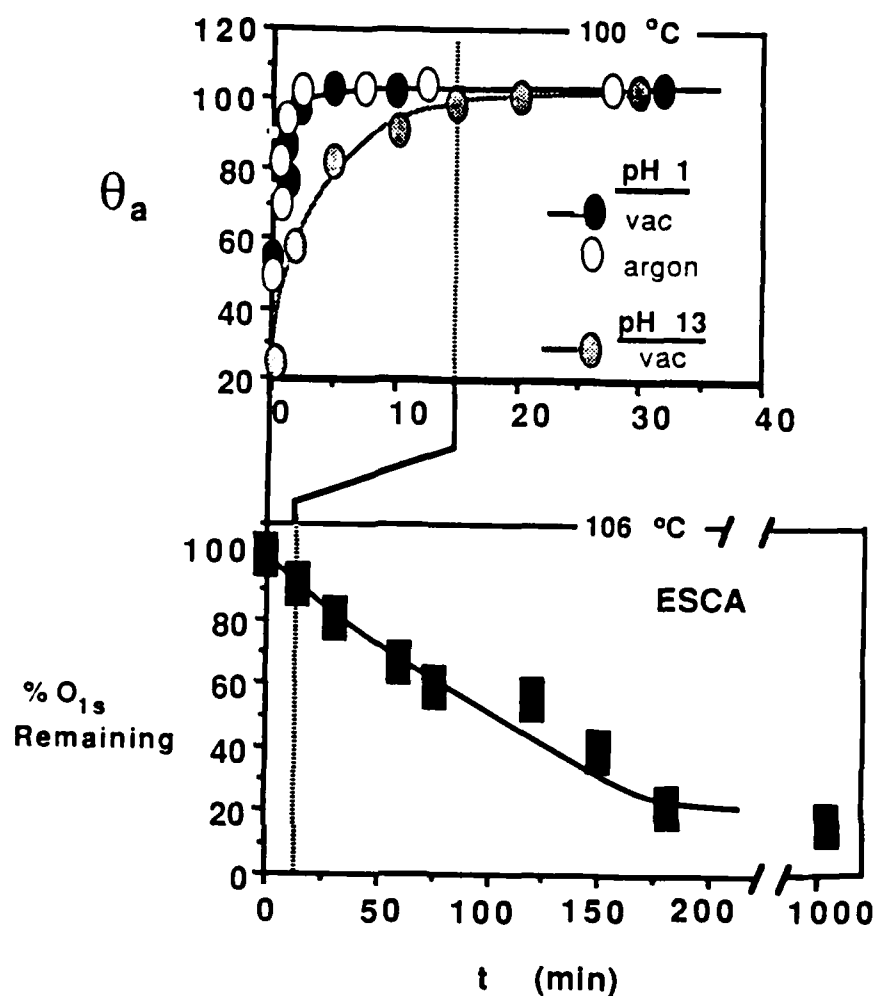


Figure 1. Top: The advancing contact angle (θ_a) of water on PE-CO₂H as a function of the time the polymer had been heated at 100 °C. Samples were heated in vacuum or under argon prior to determination of θ_a using water at either pH 1 or pH 13. The value of θ_a on PE-H does not change under these conditions. Bottom: The normalized XPS (ESCA) O_{1s} signal intensity obtained from PE-CO₂H as a function of time at 106 °C. Samples were heated under argon prior to examination by XPS.

contact angle of water at pH 1 on polymer samples heated for 5 min is the same as that observed on unoxidized polyethylene (103°); the contact angle of water at pH 13 has only reached 32° after the polymer has been heated for 5 min. We suggest, and will demonstrate in later sections, that after the polymer has been heated at 100°C for 5 min, the interfacial functional groups are a few angstroms under the surface. The drop of water at pH 1 is unable to sense these buried CO_2H groups, but the drop of water at pH 13 is apparently influenced by the CO_2^- groups, either through long-range interactions involving the electrostatic charges or through reconstruction of the interfacial layer, exposing some of the charged groups in the θ interphase.

Figure 1 also follows the disappearance of the functional groups from the interfacial region by monitoring the XPS oxygen signal intensity after heating at 106°C : although the temperatures used with the two sets of experiments displayed in this Figure are slightly different, the two are comparable. As the duration of heating increases, the O_{1s} signal decreases in intensity. The rate of disappearance of the oxygen signal is, however, much slower than the change in the contact angle at approximately the same temperature (Figure 1). We attribute this difference in the apparent rates of reconstruction to the different depth sensitivities of XPS and wetting. XPS samples functional groups within approximately the top $50\text{ \AA}$ of the polymer, although most of the signal probably originates in the top $25\text{ \AA}$ or less. Wetting samples a much thinner section of the interface (less than $10\text{ \AA}$, and probably $\leq 5\text{ \AA}$). Thus, as functional groups move away from the thin θ interphase into the deeper

regions of the polymer, they pass out of that region sensed by wetting well before they pass out of the thicker region sensed by XPS.

We believe that the residual O_{1s} signal remaining after 1000 min can be attributed to film contaminants (such as antioxidants) blooming to the surface. These contaminants can be seen in ATR-IR spectra of heated PE-H and PE-CO₂H (see below). In later sections we follow the reconstruction of samples containing other atomic labels using XPS at various take-off angles.

Thermal Reconstruction: ATR-IR

We assumed in the above analysis that the functional groups disappear from the θ interphase by migrating into the polymer, rather than by reacting or volatilizing. We tested this assumption using Attenuated Total Reflectance IR spectroscopy (ATR-IR). Although ATR-IR is a surface selective form of IR spectroscopy, it penetrates a much thicker region of the interface than either XPS or wetting (10,000 Å or more) and thus is expected to sense all but the deepest groups in the functionalized interface.³⁰ Figure 2 shows the carbonyl region of ATR-IR spectra of several polyethylene samples. The virgin film, before extraction with methylene chloride, contains several peaks in the region between 2000 and 1500 cm⁻¹. We attribute these peaks to additives (antioxidants, slip agents, antistatic agents) that are added to the film during manufacture. After extraction of the film with refluxing methylene chloride, these peaks disappear. Annealing a sample of extracted film for 1000 min at 100 °C causes them to reappear. Reextraction largely removes them. Oxidation of the polymer with chromic acid results in a large absorption at 1710

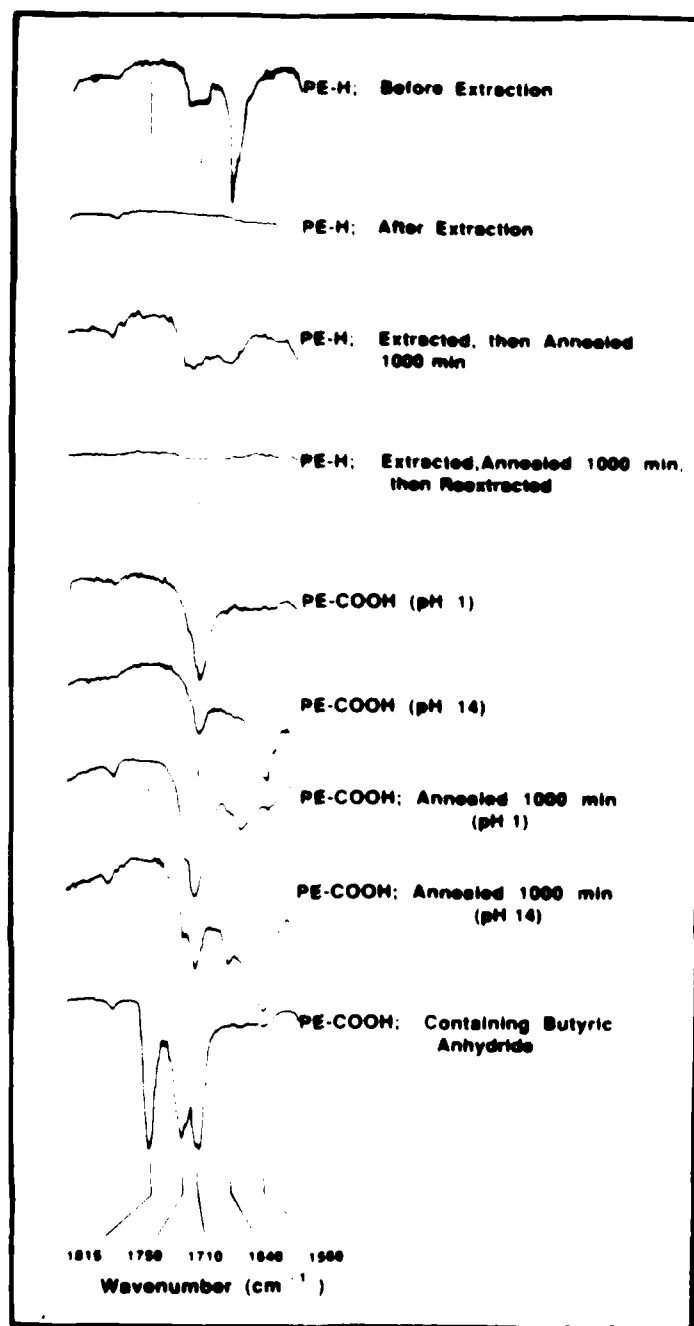


Figure 2. ATR-IR spectra of the carbonyl region of derivatives of PE-H. Since absolute absorbances are influenced by many experimental parameters (e.g. the degree of contact between the film and the KRS-5 crystal), only relative peak intensities within a single spectrum can be quantitatively compared.

cm^{-1} , which we have previously attributed to the interfacial carboxylic acid and ketone/aldehyde groups.⁶ Treatment of this interface with aqueous base results in a shift of the carboxylic acid peak to 1560 cm^{-1} , but leaves the ketone/aldehyde peak unchanged.

When a sample of $\text{PE-CO}_2\text{H}$ is heated in vacuum at 100°C for 1000 min--a time sufficient for the change in contact angle to be completed (1-2 min) and for the XPS (O_{1s}) signal intensity to decrease by approximately 80%--the intensity of the ketone and carboxylic acid peaks in the ATR-IR spectrum do not change appreciably. This observation establishes that the change in the wettability of the interface and in the O_{1s} XPS signal intensity is not due to reaction or to evaporation of a volatile component: the functional groups remain in the interfacial region sensed by ATR-IR. Examination of the peaks present after heating $\text{PE-CO}_2\text{H}$, and comparison of this spectrum with that obtained on heated PE-H (heated after extraction; Figure 2) suggest that some of the film additives have bloomed to the interface and contribute to the IR intensity (the shoulder on the peak at 1710 cm^{-1} and the peak just below 1640 cm^{-1}). Despite the quantitative uncertainty caused by this observation, the important conclusion--that the disappearance of polar, oxygen-containing functionalities from the interface on heating is due to diffusion of these functionalities deeper into the polymer--is certainly valid.

Figure 2 also shows the ATR-IR spectrum of a sample of $\text{PE-CO}_2\text{H}$ after thermal reconstruction, followed by treatment with aqueous base (pH 14). The intensity of the peak at 1560 cm^{-1} in this sample relative to that at 1710 cm^{-1} indicates that the majority of the carboxylic acid groups can still be deprotonated, even though they are

now below the θ interphase and the region sensed by XPS. Quantitation of the fraction of carboxylic acid groups that deprotonate on treatment with base is difficult because the absorbances due to contaminants in the film partially obscure peaks of interest, but we note that the ratio of the integrated absorbance at 1560 cm^{-1} (CO_2^- groups) to that at 1710 cm^{-1} (ketone and CO_2H groups) is the same in heated and unheated samples (approximately 0.75). The ability to deprotonate these functional groups without influencing the contact angle interphase, which we believe to be only a few angstroms away, is an important clue to the nature of the reconstructed interphase: the functional groups in it are accessible to aqueous base, but are not in sufficiently direct contact with the liquid to influence the contact angle.

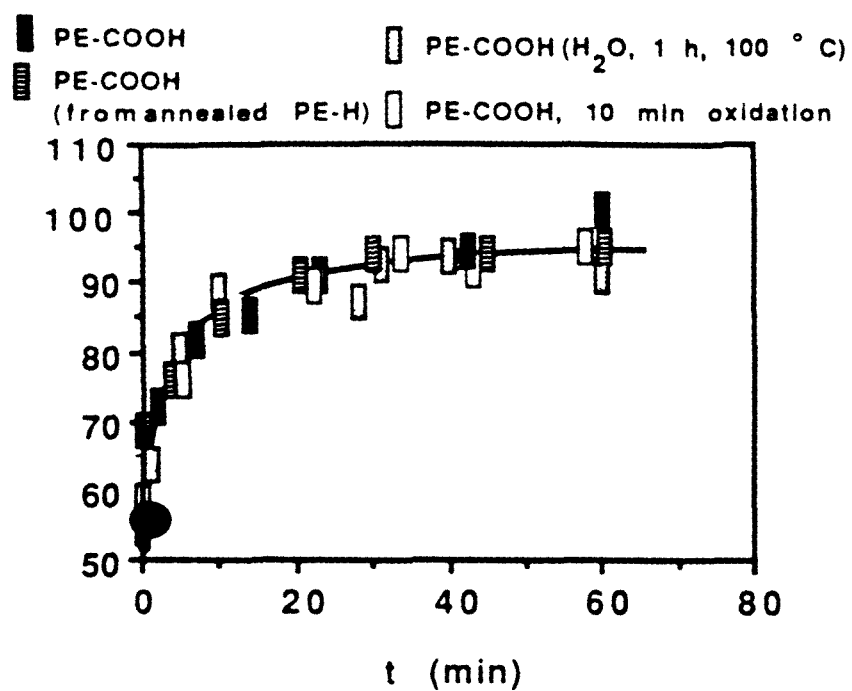
As a control, Figure 2 shows the ATR-IR spectrum of unheated $\text{PE-CO}_2\text{H}$ that had been soaked in neat butyric anhydride for 4 hours. The new peaks present at 1815 and 1750 cm^{-1} are indicative of an anhydride group, and are, we believe, due to butyric anhydride dissolved in the film. The absence of peaks characteristic of the anhydride moiety from the spectrum of $\text{PE-CO}_2\text{H}$ after heating demonstrates that the formation of anhydrides by elimination of water into the vacuum is not a significant process under these conditions.

~~~~~ ~~~~~Annealing PE-H Before Oxidation Does Not Change The Rate of Thermal ~~~~~Reconstruction of the θ Interphase of $\text{PE-CO}_2\text{H}$.~~~~~

To establish whether release of strain remaining from the manufacturing process contributed to the reconstruction of the functionalized interface of $\text{PE-CO}_2\text{H}$, we examined samples in which

these strains were eliminated or reduced by prior annealing. Before oxidation, but after extraction in refluxing CH_2Cl_2 , we heated samples of PE-H for 5 days at 100 °C. It is not clear that all manufacturing strain would be eliminated by this treatment.¹² This treatment is, however, enough to allow the types of movements involved in reconstruction of PE-CO₂H to take place many thousands of times (reconstruction of the contact angle interphase takes only a minute or two at this temperature). Figure 3 compares changes in the contact angle with time for samples of PE-CO₂H prepared from annealed and unannealed film, and establishes that there is no significant difference between these samples. Film samples (PE-H) that had been annealed for 5 days at 100 °C (vacuum) prior to extraction and oxidation also exhibited reconstruction at a rate similar to unannealed PE-CO₂H. We conclude that residual strain from manufacturing is not important in reconstruction of the interface of PE-CO₂H.

This figure also gives data for reconstruction of the θ interphases of two other samples. One was obtained by first heating PE-CO₂H in distilled water (pH 6-7) at 100 °C for 1 h (a process that does not result in reconstruction of PE-CO₂H: see below), followed by drying and thermal reconstruction at 65 °C in vacuum. The second was a sample of PE-CO₂H in which the chromic acid oxidation was allowed to proceed for 10 min, rather than the usual 1 min. This treatment produces a heavily etched, rough interface, and exposes deeper regions of the polymer film. The change in contact angle with time for both samples was indistinguishable from that of PE-CO₂H prepared by our standard procedure. We conclude from these experiments that the



Effects of pretreatments of PE-CO₂H on the change in the contact angle of water (pH 1) after heating in vacuum at 65 °C. Pretreatments: ■, no pretreatment; □, heated 1 h at 100 °C in distilled water (pH 6-7) prior to heating under vacuum; ▨, PE-CO₂H made from PE-H that had been preannealed at 100 °C in vacuum for 5 days prior to oxidation; □, PE-CO₂H that had been oxidized for 10 min instead of the usual 1 min. The filled circle at t = 0 indicates that all of the samples had $\theta_a = 54-57^\circ$ before heating in vacuum.

oxidation itself does not introduce (or reveal) strain in the sample whose release drives the reconstruction of the β interphase.

Temperature Dependence of the Rate of Reconstruction of the β Interphase

We have followed the reconstruction of the β interphase of PE-CO₂H by following the variation in contact angle with time for samples held at the chosen temperature in vacuum (Figure 4). All measurements were conducted using water at pH 1 to avoid the complications from interfacial reconstruction that seem to accompany ionization of the carboxylic acid groups at pH 13.⁸ As the temperature is reduced the time required to reconstruct the interface increases. The general shape of these curves and the limiting contact angle attained ($\theta_a = 103^\circ$) after complete reconstruction of the interface is the same for all temperatures examined. This similarity suggests that similar molecular-level processes cause reconstruction at high and low temperatures.

We have analyzed data of the type in Figure 4 semiquantitatively using a highly idealized model of the interface. In this model, we assume that the polar functional groups are initially localized in a very thin, uniform layer (Figure 5), and that these functional groups do not interact with one another.⁶⁻⁹ Reconstruction of the interface is treated as thermally activated diffusion of the polar functional groups along the concentration gradient and into the deeper regions of the polymer. Since the polymer is very thick compared with the original interfacial layer, the density of polar groups remaining in the β interphase drops to zero at long times. The polymer is

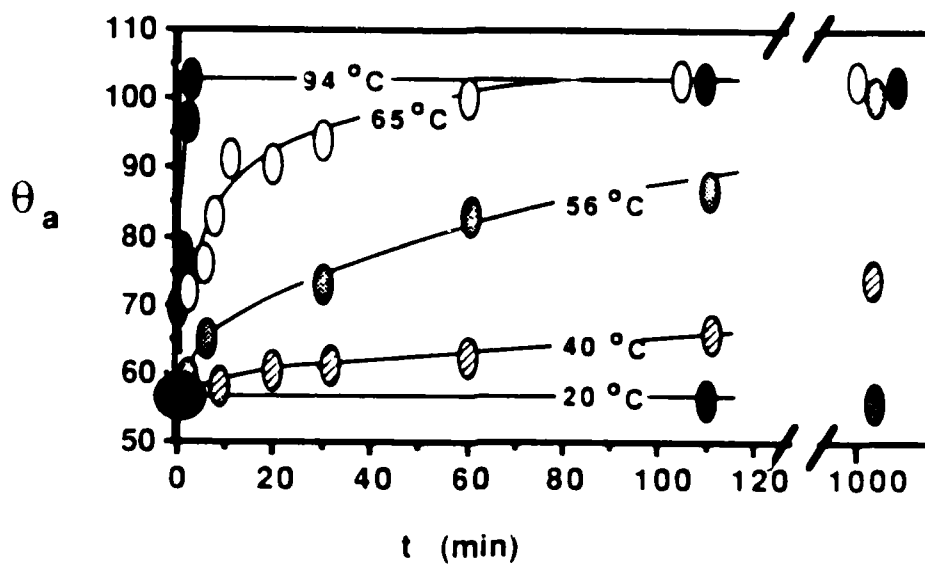


Figure 4. The contact angle of water (pH 1) on PE-CO₂H as a function of time of heating in vacuum at various temperatures (°C). The filled circle at $t = 0$ indicates that all samples had $\theta_a = 55-57^\circ$ prior to heating.

considered as a homogeneous isotropic medium. This model is not without overship in fact in many respects. For instance, the rigidity of the polymer functionalities, the behaviour of the phase at the interface, the fact that it is not a perfect string, etc. with one another. The effect of the polymer observed in the experiments with hydrogen-bonded polymers, such as the polymer functional groups in the interphase interface with water, is the influence with hydrogen bonding, the polymer is solid, etc. The model is homogeneous non-isotropic. Nonetheless, the experimental results previously to suggest that whether the set of strands in the polymer, the extent of oxidation, influence the rate of reconstruction, and the type of oxide based on randomly activated diffusion on the surface is straightforward one to examine.

The oxidation process diffusion away from a surface, which is the concentration of functional groups at a distance x from the surface, initially, and the polymer at the end, N , is the total number of functional groups in the interphase, and the initial amount at the surface, N_0 , at the beginning of the reconstruction process, D is the diffusion constant describing movement of functional groups into the polymer, and t is time, i.e.,

$$\frac{N - N_0}{N} = \frac{4Dt}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \sin^2 \frac{n\pi x}{2L} \quad (1)$$

$$N_0 = N \left(1 - \frac{4}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \right) \quad (2)$$

Integrating this concentration between $x=0$ and $x=L$, L is defined as the limit of the depth from which a functional group is able to influence with hydrogen bonding, a value that is smaller than

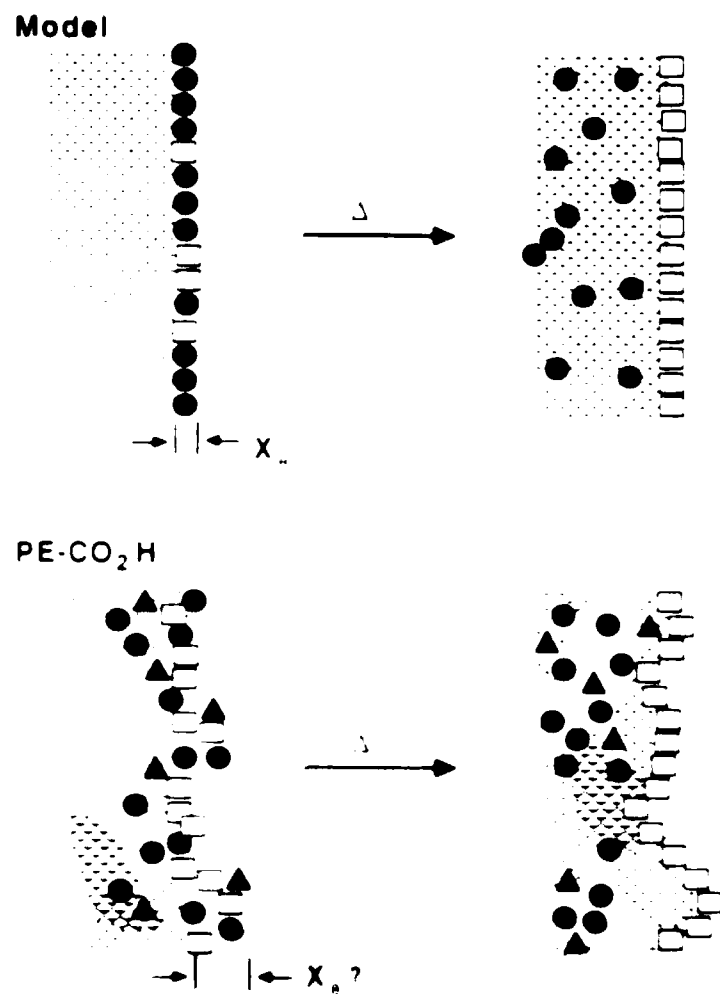


Figure 1. **Top**—An idealized model surface in which groups influence the contact angle are indicated by filled symbols for polar groups (high, etc.) and open symbols for nonpolar groups (low, etc.). During heating the polar groups diffuse away from the water/interphase (indicated by x_w) and into the bulk material, and are replaced by nonpolar groups (bottom). **Bottom**—A schematic illustration of the interface of a polymer with a rough surface. Roughness of the real interface, the distribution of functional groups, and the water density in the interphase are shown.

but that we do not know precisely, at an arbitrary time t yields the total number of functional groups that are in the δ -interphase and influence wetting (eq 2). We assume that all of the functional groups within the distance δ of the surface (i.e., those in the δ -interphase) influence wetting properties equally and that those beyond δ do not have no influence.^{32,33} This assumption is certainly not the only one that leads to a usefully simple model. We further assume, as stated above, that the interfacial free energies required to evaluate eq. 1 using Young's equation (eq. 3) can be expressed as a sum of contributions from the different types of functional groups making up the interface (eq. 4).

$$\gamma_{\text{int}} = \sum_{i=1}^n \gamma_i$$

where γ_i is the interfacial free energy contribution of the i th functional group.

$$\gamma_i = \gamma_i^d + \gamma_i^p + \gamma_i^h$$

$$\gamma_i^d = \gamma_i^d \left(\frac{A_i}{A} \right)$$

$$\gamma_i^p = \gamma_i^p \left(\frac{A_i}{A} \right)$$

$$\gamma_i^h = \gamma_i^h \left(\frac{A_i}{A} \right)$$

where γ_i^d , γ_i^p , and γ_i^h are the dispersive, polar, and hydrogen bonding components of the interfacial free energy of the i th functional group, respectively.

$$\gamma_i^d = \gamma_i^d \left(\frac{A_i}{A} \right)$$

$$\gamma_i^p = \gamma_i^p \left(\frac{A_i}{A} \right)$$

$$\gamma_i^h = \gamma_i^h \left(\frac{A_i}{A} \right)$$

In eq 4, the terms $\underline{A}_i$ are normalized "area fractions" of the interface occupied by the functional group i (equivalent to volume fractions in solution), and the term $\gamma_{i,1}$ is the interfacial free energy of an interface containing only the functional group i . If all of the functional groups comprising the interface (here, methylene, carboxylic acid, and ketone aldehyde) have approximately the same $\gamma_{i,1}$, $\underline{A}_i$ will be equal to $\underline{a}_i$ (the normalized fraction of the functional group i in the α -interphase). With these assumptions, the contact angle θ is given by eq 5. To reduce the problem further, we assume that the interface is composed only of polar (P, e.g. CO_2H) and non-polar (NP, e.g. CH_2) groups. With this assumption (eq 6), we can rewrite expression $f_{\cos \theta}$ in terms of the observable values of $\cos \theta_a$ at $t = 0$, $\cos \theta_t$, the value at time t , and $\cos \theta_\infty$, the value of the fully reconstructed system. The parameter $f_{\cos \theta}$ is a normalized value of $\cos \theta$: it goes from $f_{\cos \theta} = 1$ at $t = 0$, $f_{\cos \theta} = 0$ at $t = \infty$. Since essentially no polar groups will be left in the α -interface in the fully reconstructed system, $N_p^\infty = 0$. Substitution of the resulting eq 3 into eq 2 yields an expression relating $f_{\cos \theta}$ and D (eq 9). Carrying out the integration indicated in eq 9 yields eq 10 and 11. Evaluation of eq 11 at the time $t_{1/2}$ required for $f_{\cos \theta}$ to reach 0.5 gives eq 12 and 13: these equations provide a useful approximate method for estimating D . Equation 10 relates the change in $\cos \theta_a$ to the error function (erf) of the ratio of a constant³¹. Equation 11 indicates that a plot of the inverse error function of the change in $\cos \theta_a$ vs $1/(t)^{1/2}$ should be a straight line with slope equal to $x_a/(4D)^{1/2}$. Further simplification

yields eq 12, which relates D to the time, $t_{1/2}$, required to reach $f_{\cos \theta} = 0.5$. Numerical evaluation of eq 12 yields eq 13.

$$f_{\cos \theta} = \int_0^x \frac{1}{\sqrt{\pi Dt}} \exp(-x^2/4Dt) dx \quad (9)$$

$$f_{\cos \theta} = \text{erf}[x_0/(4Dt)^{1/2}] \quad (10)$$

$$\text{erf}^{-1}[f_{\cos \theta}] = [x_0/(4D)^{1/2}][1/t]^{1/2} \quad (11)$$

$$D = x_0^2 / [2 \text{erf}^{-1}(1/2)]^2 t_{1/2} \quad (12)$$

$$D = 1.09 (x_0^2) / t_{1/2} \quad (13)$$

$$D = A_0 \exp(-E_{a,D}/RT) \quad (14)$$

$$\frac{E_{a,D}}{R} + \ln \left(\frac{A_0}{1.09 x_0^2} \right) = \ln t_{1/2} \quad (15)$$

If D is assumed to be a thermally activated process following the Arrhenius equation and having activation energy $E_{a,D}$ (kcal/mol) and preexponential factor A_0 (having units cm^2/sec) (eq 14), combination of eq 13 and 14 yields eq 15.

Figure 6 shows a plot of $\text{erf}^{-1}[f_{\cos \theta}]$ vs $1/(t)^{1/2}$ for three representative temperatures. These curves deviate from straight line behavior primarily at small values of t (that is, for large values of $1/t^{1/2}$; these deviations occur over approximately the first 10-20% of the change in $\cos \theta_a$ (that is, the first 10-20% of changes in θ_a). At these small values of t the extent of reconstruction is

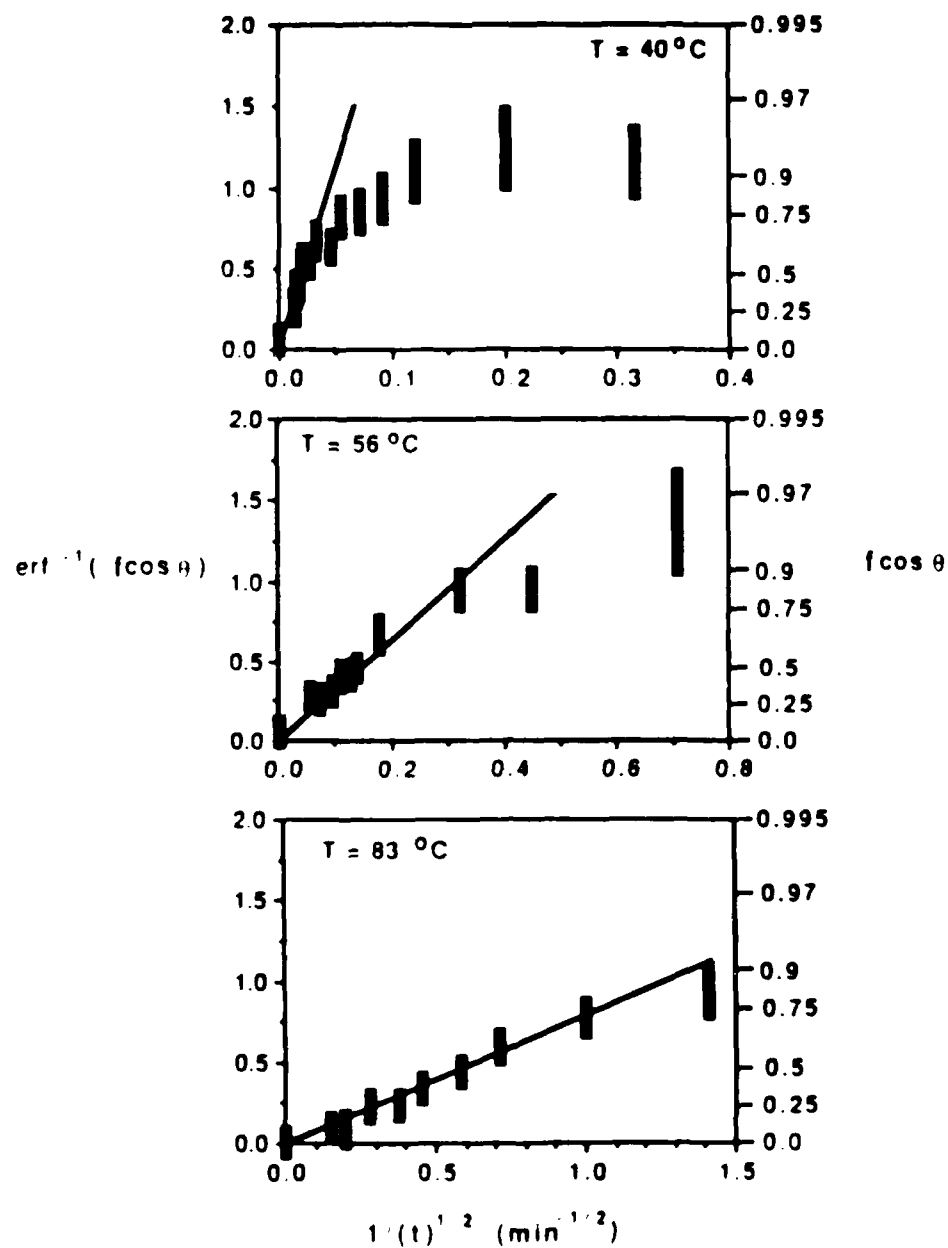


Figure 6. Plots of the change in the contact angle of water (pH 1) on PE-CO₂H as a function of time in vacuum at 40 °C (top), 56 °C (middle) and 83 °C (bottom) using data of the type displayed in Figure 4.

larger than would have been predicted based on the remainder of the reconstruction process. We emphasize that the deviations are relatively slight when expressed in units of $f_{\cos \theta}$. The maximum deviation between the predicted straight line and the data points is less than $f_{\cos \theta} = 0.1$, or <10% of the total change in $\cos \theta_a$.

The origin of this deviation (if real) might plausibly lie in the inadequacy of the assumption that all functional groups in the θ interphase influence wetting equally^{32,33} or in the existence of a low energy process (perhaps small reorientations of the functional groups) that influences the contact angle but occurs more rapidly than diffusion of the functional group into the polymer. In any event, the experimental data can be fitted to eq 11 approximately at the interval $0 < \text{erf}^{-1}(f_{\cos \theta}) < 0.75$ (that is, $0 < f_{\cos \theta} < 0.8$), and the observed deviations are not unexpected.

Figure 7 shows the time required to reach the half-point in the reconstruction process as a function of the temperature at which the reconstruction was carried out. In practice, the half-time was defined as the time required to reach $\theta_a = 80^\circ$, 80° being the half point in the change in $\cos \theta_a$ ($30^\circ = \cos^{-1} [(\cos 55^\circ + \cos 103^\circ)/2]$). The error bars were estimated by determining the time required for the contact angle to reach 77° and 83° (these numbers being at the limit of our experimental precision ($\pm 3^\circ$) from the mid-point of 80°). For the type of qualitative analysis in which we are interested, it is not essential that $\theta_a = 80^\circ$ correspond to the precise half-point in the reconstruction: it provides a reference value with which the rates of reconstruction can be compared.

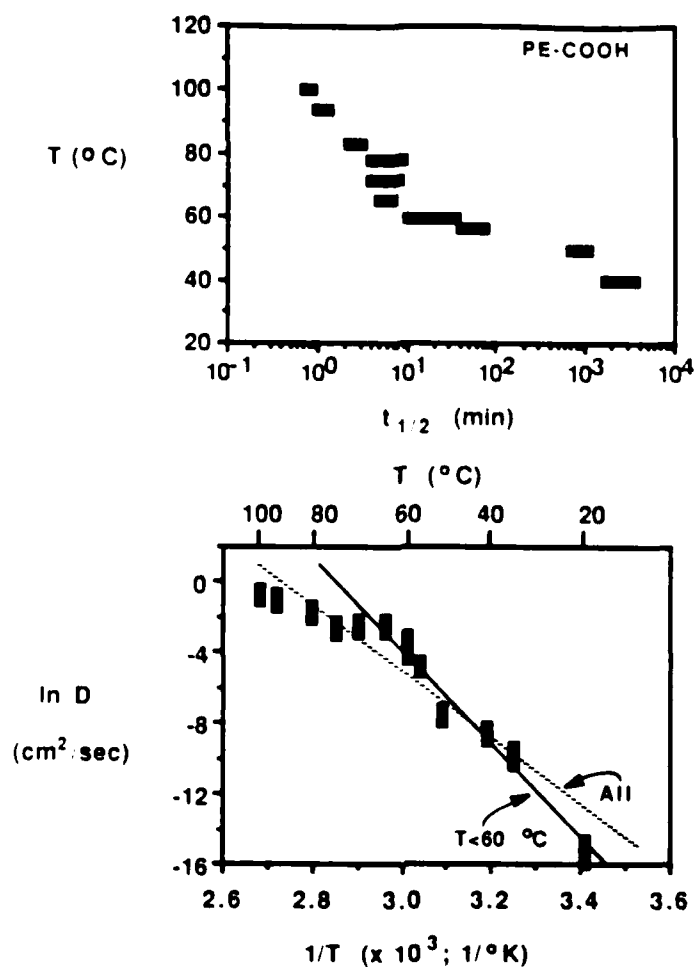


Figure 7. Top: Dependence of the half-time of reconstruction ($t_{1/2}$) of PE-CO₂H on temperature. The half-time is defined as the time required to reach θ_a , pH 1 = 80°. Bottom: Dependence of the calculated diffusion coefficient D on $1/T$ (derived from data in the upper portion of the figure using eq 13 and the assumption that $x_\theta = 5 \text{ \AA}$). The solid line is the least squares fit to the data determined at $T < 60^\circ\text{C}$. The dashed line is the least squares fit to all of the data. The slopes of these lines indicate activation energies of 50 and 37 kcal/mol, respectively.

The lower plot in Figure 7 shows the temperature dependence of D (estimated from eq 13). This equation gives D in terms of the parameter x_0 . We do not have an independent measure of this parameter, but we use a value of $x_0 = 5 \text{ \AA} = 5 \times 10^{-8} \text{ cm}$ in order to obtain a numerical estimate for D for comparison with other diffusion constants. It is unlikely that x_0 is greater than $10 \text{ \AA}$ (see below) and physically unreasonable that it be less than $1 \text{ \AA}$.³⁴ With this estimate, $D \approx 4 \times 10^{-23} \text{ cm}^2/\text{sec}$ at room temperature, and $D = 5 \times 10^{-17} \text{ cm}^2/\text{sec}$ at 100°C .³⁴

The value of $E_{a,D}$ is independent of the choice of x_0 (eq 15). The data in Figure 7 do not fit a single straight line over the entire range of temperatures. We suspect that the estimates of D are too low at temperatures above 60°C because the time required to equilibrate the sample at these temperatures is comparable to $t_{1/2}$ (5 min). The activation energy indicated by a least squares fit to the data at $T \leq 60^\circ \text{C}$ is $E_{a,D} \approx 50 \text{ kcal/mol}$; a least square fit to all the points yields $E_{a,D} \approx 37 \text{ kcal/mol}$.

These activation energies are large compared with activation energies for diffusion of small molecules. For examples, the activation energies for the diffusion of methyl bromide and isobutylene in low-density polyethylene film are 14 and 18 kcal/mol respectively at $20\text{--}60^\circ \text{C}$;³⁵ those for behenyl behenate ($\text{CH}_3(\text{CH}_2)_{20}\text{CO}_2(\text{CH}_2)_{21}\text{CH}_3$) are 23 and 7.5 kcal/mole in semicrystalline ($40\text{--}110^\circ \text{C}$) and molten ($110\text{--}160^\circ \text{C}$) polyethylene respectively.³⁶

Derivatives of PE-CO₂H: Dependence of the Rate of Reconstruction on
the Nature of the Interfacial Groups

Figure 3 shows the contact angle of water (pH 1) on a number of derivatives of PE-CO₂H, PE[R], as a function of the interval of time the polymer had previously been heated at 100 °C in vacuum. Reconstruction is slower for interfaces having lower interfacial free energies (higher values of θ_a) than PE-H than for those having higher interfacial free energies than PE-H. We have not followed the reconstruction of each of these interfaces in the detail with which we have followed the reconstruction of PE-CO₂H. We note, however, that a brief examination of several of them indicates that although the form of the reconstruction is similar to that observed for PE-CO₂H, the rates of reconstruction can be significantly different. For example, we compared (Figure 9) the ESCA F_{1s} signal intensity for PE[CH₂OCOCF₂CF₂CF₃] over a time period comparable to that described above for the reconstruction of PE-CO₂H (1000 min, 100 °C). This intensity decreases only slightly over an interval of time in which nearly all functional group contributions are lost from the XPS sample depth for PE-CO₂H. The retention of significant quantities of the fluorinated esters in the near surface region of the film is also consistent with the contact angle data described above (Figure 3); note that the contact angle with water is significantly larger than that of PE-H even after annealing PE-O₂C(CF₂)₂CF₃ at 100 °C for 1000 min. Qualitatively, these interfaces also show a high temperature dependence of the rate of reconstruction. For example, at 72 °C PE[CH₂OCOCF₂CF₂CF₃] shows no significant change in contact angle after 300 minutes of heating (for comparison, the rate of reconstruction of

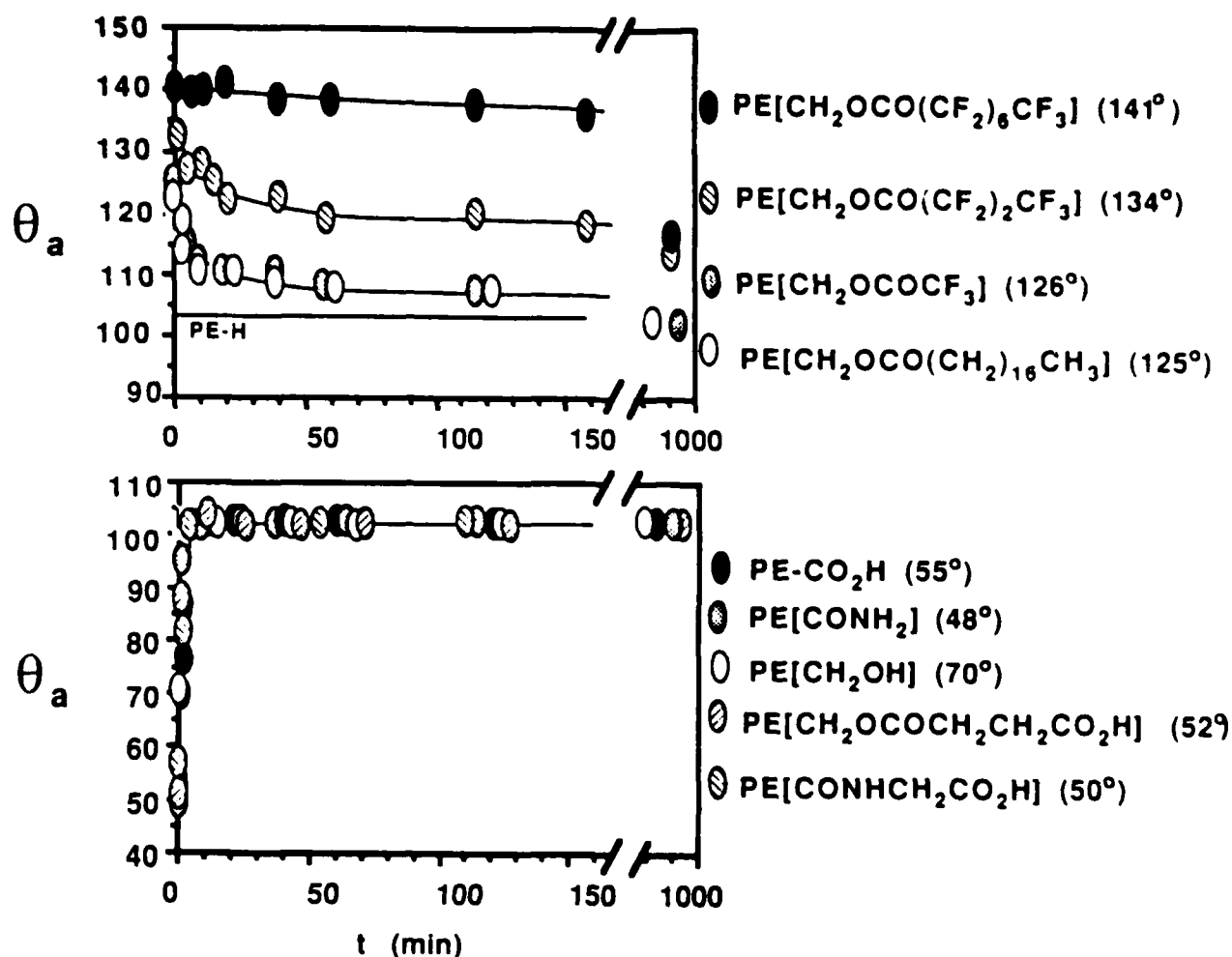


Figure 8. Dependence of the advancing contact angle of water (pH 1) on the time of heating (100 °C, vacuum) for various derivatives of PE- CO_2H . The upper figure contains data for samples with a lower interfacial free energy (higher θ_a) than PE-H. The lower figure contains data for samples with a higher interfacial free energy (lower θ_a) than PE-H. In both cases the data for PE-H are depicted by a continuous line (θ_a on PE-H remains unchanged at 103° during heating). For each sample, the contact angle at $t = 0$ is indicated in parentheses.

the θ interphase of PE-CO₂H is approximately ten times faster at 100 °C than at 72 °C). Another interesting example of the functional group dependence of the rate of these reconstructions is shown in Figure 9 for a strongly acidic interfacial carboxylic acid, PE-O₂C(CF₂)₃CO₂H. After 1000 min at 100 °C, a nearly 70% reduction in the fluorine content of this surface has been effected. The rate profile of this process also appears to be complex; its rate is intermediate between the rates of reconstruction determined by XPS for PE-CO₂H and PE-O₂C(CF₂)₂CF₃. It is intriguing to speculate that the trifluoropropyl spacer in PE-O₂C(CF₂)₃CO₂H may somehow contribute to the observed intermediate stability of this derivative, but no evidence presently supports this speculation. We have also examined whether preannealing the precursor PE-H film influences the rate of the reconstruction of PE-CO₂H derivatives. As shown in Figure 9 for PE-O₂C(CF₂)₃CO₂H, the effect of such preannealing on the rate of reconstruction is negligible.

Figure 10 plots the apparent diffusion constant characterizing diffusion (eq 13, $x_0 = 5 \text{ \AA}$) as a function of the initial value of $\cos \theta_a$ (pH 1), $(\cos \theta_a)_i$, before thermal reconstruction. The relative values of $(\cos \theta_a)_i$ are determined by $\gamma_{SV} - \gamma_{SL}$ (eq 3). Although the two are not separable, high positive values of $(\cos \theta_a)_i$ (i.e. low values of $(\theta_a)_i$) indicate a polar interface with a high value of γ_{SV} . Figure 10 indicates that there is a correlation between D and the interfacial free energy (especially γ_{SV}). All interfaces having free energies greater than PE-H (that is, all interfaces more polar than PE-H) reconstruct and form PE-H-like interfaces at approximately the same, relatively rapid, rate, while interfaces with free energies

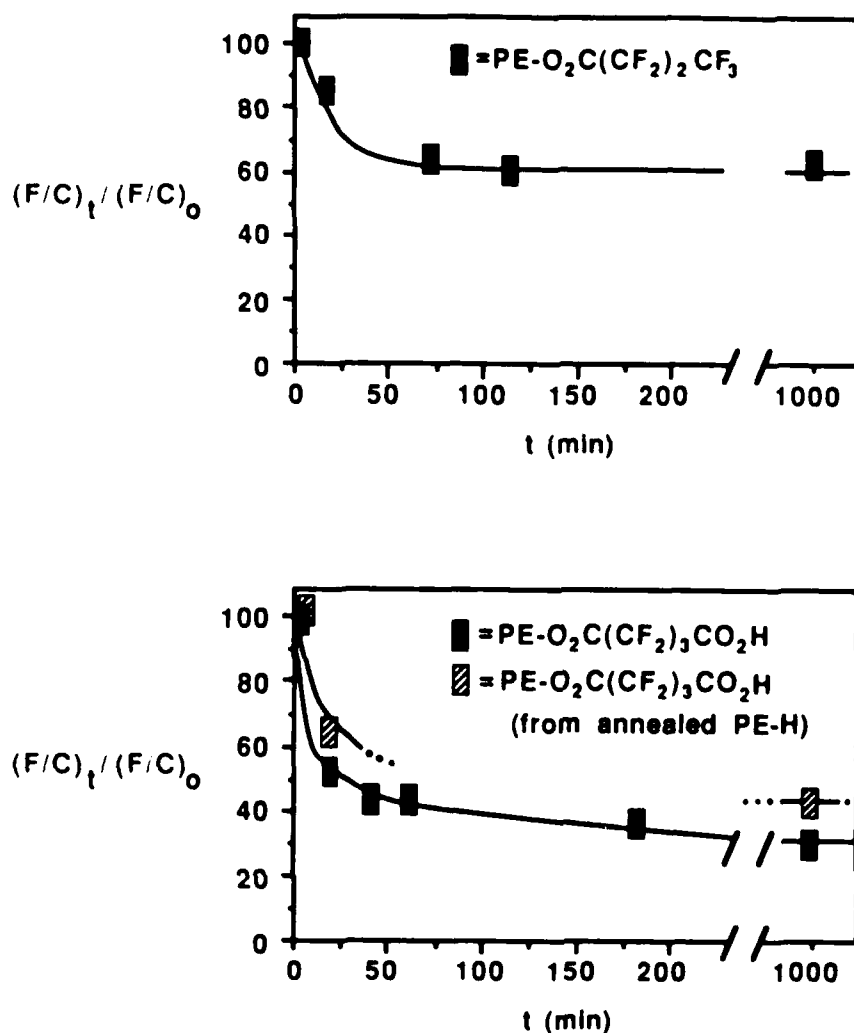


Figure 9. Top: XPS data showing the relative surface concentration of fluorine in PE-O₂C(CF₂)₂CF₃ as a function of the duration of heating at 100 °C in vacuum. Bottom: XPS data showing the relative surface concentration of fluorine in PE-O₂C(CF₂)₃CO₂H as a function of the duration of heating at 100 °C in vacuum. The PE-H used in preparing the annealed sample was obtained by heating at 100 °C for 24 h in vacuum.

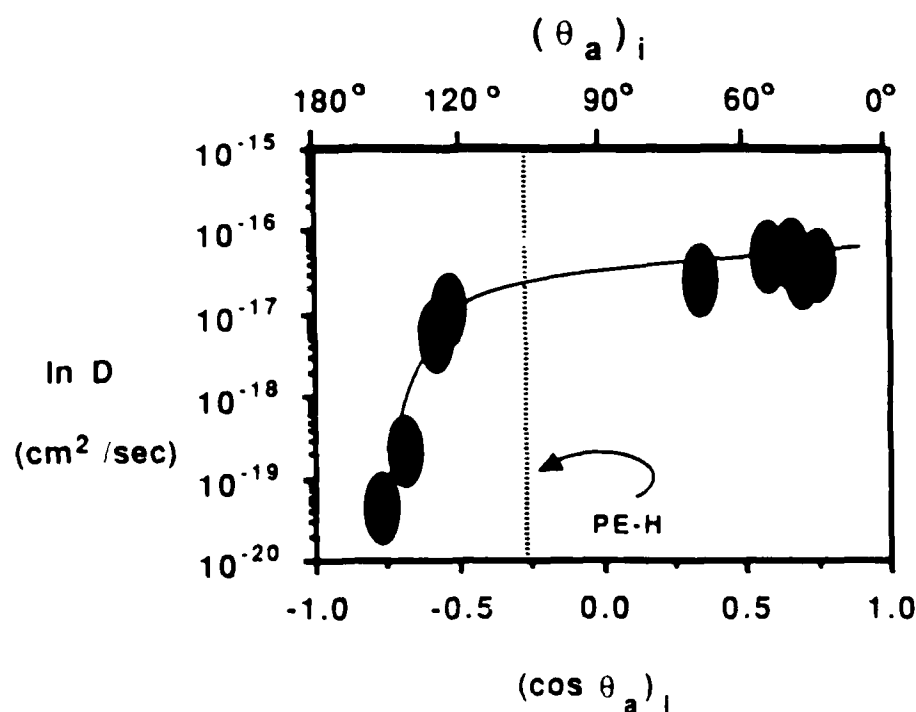


Figure 10. Dependence of the apparent diffusion coefficient (D , eq 13, assuming $x_\theta = 5 \text{ \AA}$) on the cosine of the initial contact angle $(\cos \theta_a)_i$ for the interfaces shown in Figure 3. The dotted line shows the value of $\cos \theta_a$ for unfunctionalized polyethylene (PE-H).

lower than PE-H reconstruct and form PE-H-like interfaces more slowly. This conclusion is in the expected direction, since it is energetically unfavorable to reconstruct the interface of, for example, $\text{PE}(\text{CH}_2\text{OC}(\text{CH}_3)_2)_n$ ($\cos \theta_1 = 0.47$) but energetically favorable to reconstruct $\text{PE}(\text{CH}_2\text{OC}(\text{CH}_3)_2)_n$ ($\cos \theta_2 = 0.67$) to form PE-H ($\cos \theta_3 = -0.22$).

In order to determine if the origin of the slow rate of reconstruction of interfaces such as that of $\text{PE}(\text{CH}_2\text{OC}(\text{CH}_3)_2)_n$ lies in the large size of the functional group, we examined the rate of reconstruction of a series of materials having high free energies (poly(ethylene glycol) esters, $\text{PE}(\text{CH}_2\text{OCH}_2\text{CH}_2)_n\text{H}$ of various lengths). Figure 11 shows curves of the time $t_{1/2}$ required for $f_{\cos \theta}$ to reach 0.5 and for the contact angle to reach $103^\circ \pm 3^\circ$. This latter value was chosen because it is within our experimental error ($\pm 3^\circ$) of an unmodified polyethylene surface (103°). It is clear from these figures that interfaces containing the longer esters ($n = 7, 10, \text{ and } 14$) reconstruct more slowly than interfaces containing the shorter esters ($n = 1, 2, \text{ and } 3$). The detailed thermodynamic origin of this difference is not clear, but it is important that the interfaces containing the short esters ($n = 1, 2, \text{ and } 3$) reconstruct relatively rapidly. We conclude that differences in the steric bulk of the fluorinated esters $\text{PE}(\text{CH}_2\text{OC}(\text{CF}_2)_n\text{CF}_3)$ ($n = 1-6$ --functional groups having lengths similar to the short poly(ethylene glycol)-derived esters--is not sufficient to account for the slow rates of reconstruction of the fluorinated esters. This conclusion supports the contention that the low interfacial free energies of the

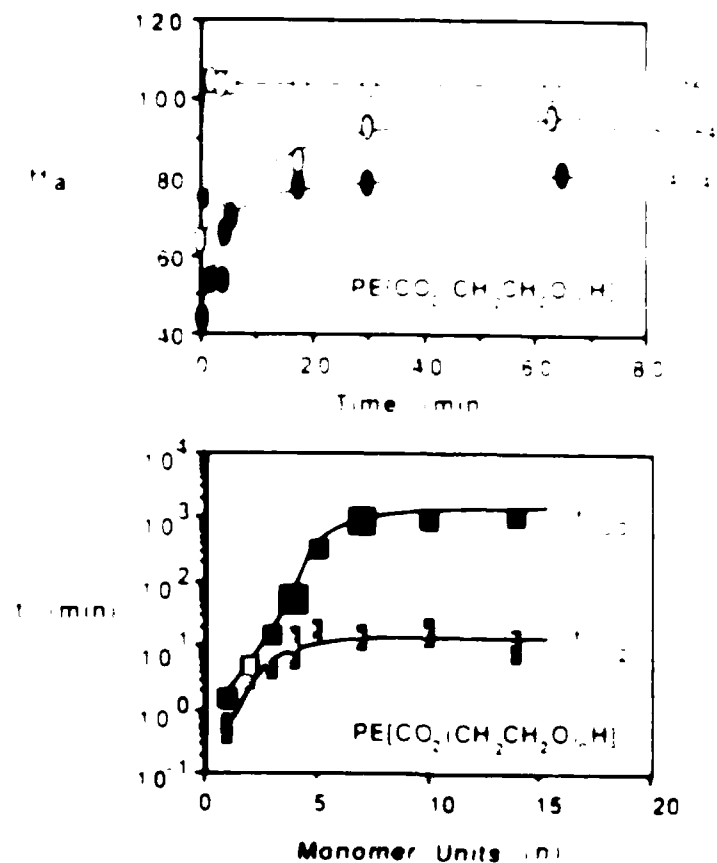


Figure 1. (Top) Representative data for the contact angle of water (θ_a) on $PE[CO_2(CH_2CH_2O)_4H]$ as a function of the time the polymer has been heated in air at 130°C. The contact angle in each interface prior to heating is indicated in parentheses. (Bottom) The dependence of t_{a1} and t_{a2} on the applied surface area (in square inches) for $PE[CO_2(CH_2CH_2O)_4H]$. The time required to reach θ_{a1} and θ_{a2} in the region of monomer units x is $t_{a1}(x)$ and $t_{a2}(x)$, respectively. Values of t_{a1} and t_{a2} were determined from graphs of the type in the upper portion of the figure.

[illegible]

the 1990s, the number of people in the world who are under 15 years of age is expected to increase from 1.1 billion to 1.5 billion. The number of people aged 65 and over is expected to increase from 200 million to 400 million. The number of people aged 15 and over is expected to increase from 3.5 billion to 4.5 billion. The number of people aged 15 and over is expected to increase from 3.5 billion to 4.5 billion. The number of people aged 15 and over is expected to increase from 3.5 billion to 4.5 billion.

[illegible]

• *How can we make the most of the time we have?*

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polymer: water (highly polar) and perfluorodecalin (nonpolar).

Figure 12 shows the contact angle of water on PE-CO₂H, PE-H (oxidized polyethylene), and PE[CO₂C₈H₁₇] as a function of time in distilled water at 100 °C. The films were immersed in boiling water for the time indicated, removed, and immediately dried under a stream of nitrogen. The changes in contact angle with the time of heating are significantly different from that observed after heating under argon or vacuum. The contact angle remains essentially unchanged on PE-CO₂H and PE-H, but on PE[CO₂C₈H₁₇] the contact angle reaches the same value as on PE-H in a few seconds, and after 30 seconds it has become more hydrophilic than PE-H.

These results again indicate that the interfacial free energy is important in determining the course of reconstruction. The polar carboxylic acid groups of PE-CO₂H are stable at the interface between polymer and water and do not disappear on heating. The unchanged contact angle on PE-H serves as a control, and indicates that migration of additives into the polymer interface is not important in these experiments. We attribute the decrease in contact angle on PE[CO₂C₈H₁₇] to reconstruction of the interface that maximizes the contact between the polar ester and ketone groups and the water. An alternative explanation is that some of the interfacial esters experience hydrolysis, leaving polar hydroxy groups on the surface. Previous work, however, suggests that hydrolysis of PE[CO₂C₈H₁₇] is slow (months) even in 1 N NaOH at room temperature.⁸

Figure 13 shows the course of reconstruction of these same interfaces in perfluorodecalin at 100 °C. The results obtained in these experiments are qualitatively similar to those observed for

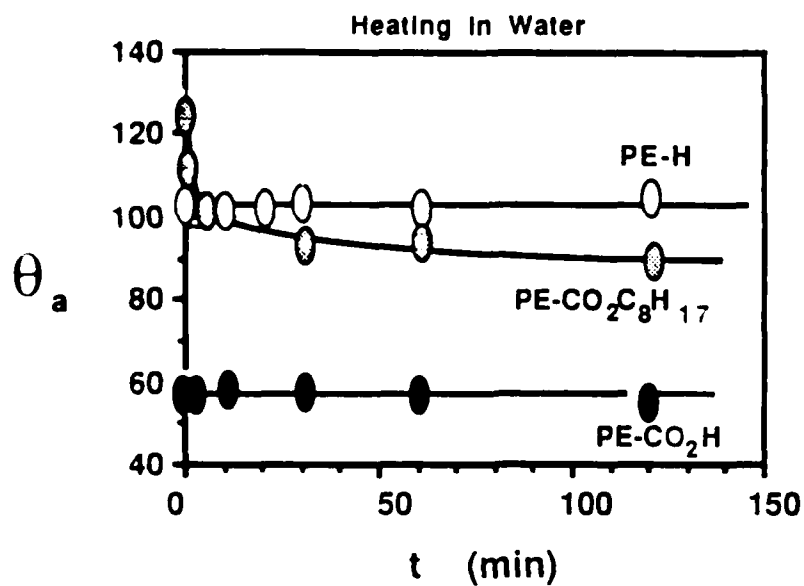


Figure 12. Dependence of the contact angle of water (pH 1) on time of heating in distilled water (pH 6-7, 100 °C) for PE-H (extracted), PE-CO₂H, and PE[CO₂C₈H₁₇].

heating in vacuum or under argon: the contact angle of water rises on PE-CO₂H, falls on PE[CO₂C₉H₁₇], and remains the same on PE-H. While it is possible that the perfluorodecalin is swelling the interfacial region of the film to some extent (cyclonhexane and perfluorodecalin are miscible when heated, but are not miscible at room temperature), it is clear that heating PE[R] in contact with a nonpolar liquid is qualitatively similar to heating with no contacting liquid phase.

Figure 13 also shows that first heating PE-CO₂H in water for 5 min does not significantly influence the rate of reconstruction observed while subsequently heating in perfluorodecalin. Thus, the factor that leads to the stability of the hydrophilic interface of PE-CO₂H while heating in water does not prevent this interface from reconstructing if later heated in contact with a nonpolar liquid.

~~~~~ Recovery of Interfacial Functional Groups That Have Migrated into the Polymer by Trapping at the Interface between Polymer and Water ~~~~~

Polar groups appear to be stable at the interface between PE-CO₂H and water at 100 °C: We observe no migration into the polymer interior. We hypothesized that it might be possible to "recover" polar groups that had migrated into the sub- θ interphase by heating the functionalized polymer in contact with a polar liquid. To test this hypothesis, we first prepared a series of samples of PE-CO₂H whose functionalized interfaces were partially reconstructed by heating at 78 °C in vacuum (this temperature was chosen for the reconstruction rather than 100 °C to give us better control over the extent of reconstruction). The contact angle of water (pH 1) was measured on these materials. They were then immersed in distilled

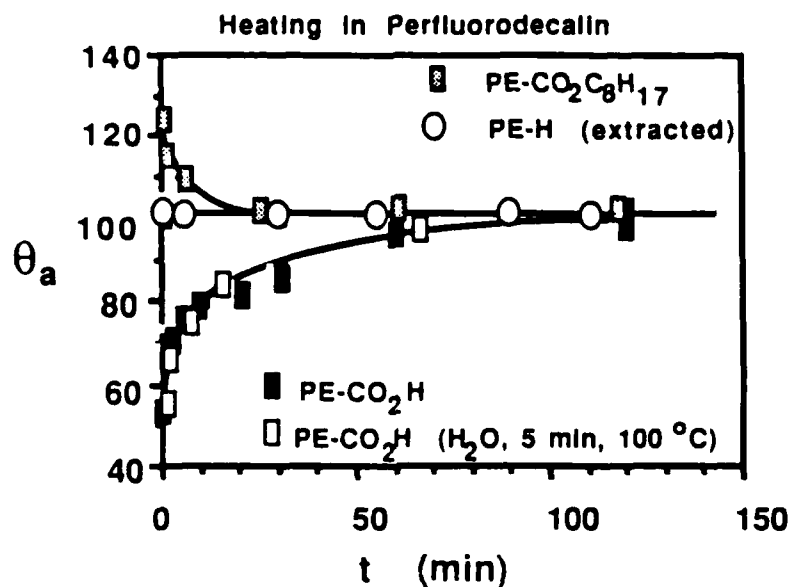


Figure 13. Dependence of the contact angle of water (pH 1) on time of heating in perfluorodecalin (100 °C) for PE-H, PE-CO₂H, and PE[CO₂C₈H₁₇]. The figure also shows the data for PE-CO₂H that had been treated in water (pH 6-7, 100 °C, 5 min, then dried) prior to heating in perfluorodecalin.

water (pH 6-7) at 100 °C for some interval, removed, dried, and the contact angle of water remeasured. Figure 14 (top) summarizes results. In each case, a part of the polar character of the interface lost by heating in vacuum is recovered during heating in water. If the period of heating in water was extended to 30 min, no further decreases in θ_a were observed.

Similar results were obtained if the initial heating was carried out at 100 °C (Figure 14, bottom), or in contact with perfluorodecalin (at 100 °C). In all experiments, the more extensive is the initial reconstruction of the interface by heating in vacuum or in perfluorodecalin, the smaller the ability to recover the CO₂H groups that migrated from the θ interphase into the sub- θ interphase (Figure 15).

These experiments establish that the thermal interfacial reconstruction is partially reversible. The similarity in the results obtained for interfaces reconstructed in vacuum at 100 °C and 73 °C and in perfluorodecalin suggests that the interfaces obtained by reconstruction in these processes are all very similar.

Depth Profiling during Reconstruction: XPS Does Not Give Interpretable Information

To locate the functional groups during reconstruction, we desired a technique that would indicate the depth of the functional groups in the interface to within a few Å. XPS is potentially applicable at this resolution. For an ideal, flat solid sample, the angle between the plane of the sample surface and the detector influences the depth sensitivity by determining the path length of the ejected electrons

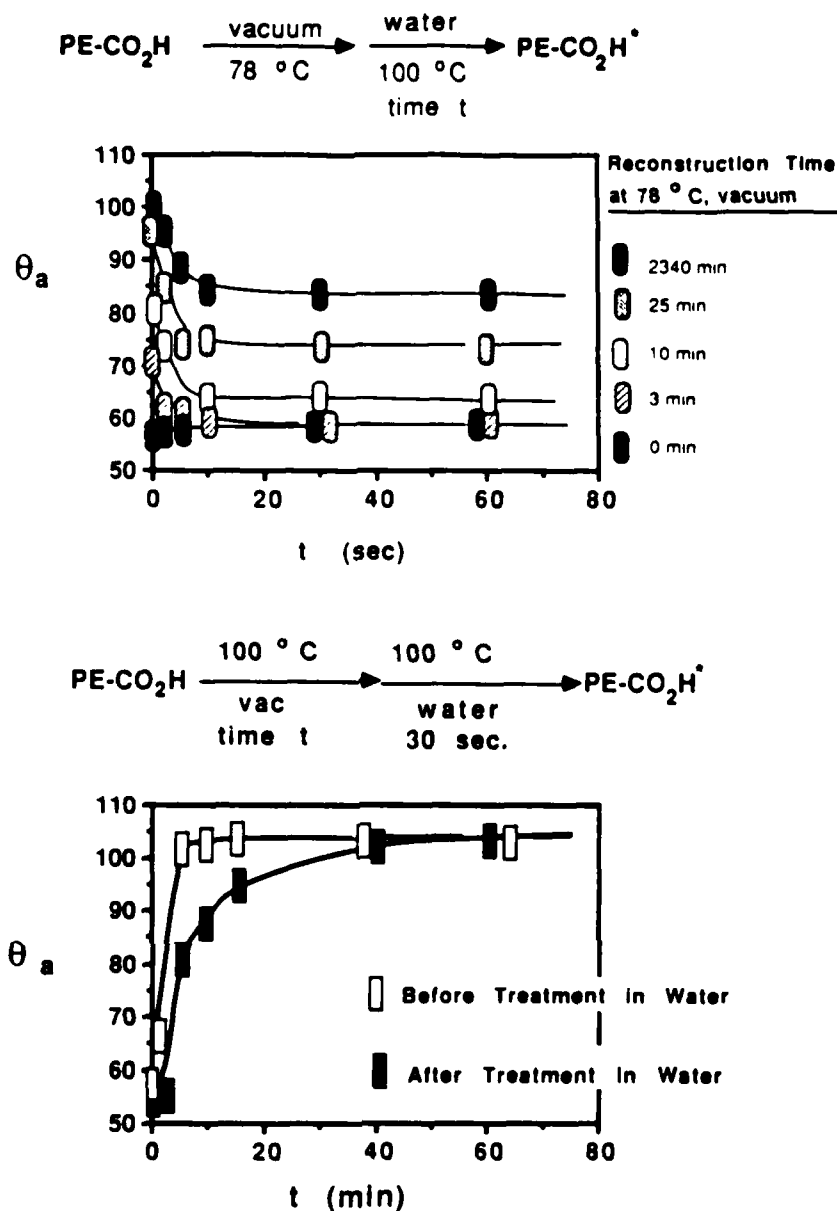


Figure 14. Top: Dependence of the contact angle of water (pH 1) on the time of heating in distilled water (100 °C, pH 6-7) for PE-CO₂H samples that had previously been heated in vacuum (78 °C) for various lengths of time. Bottom: The contact angle of water (pH 1) as a function of the time of heating of PE-CO₂H in vacuum (100 °C) prior to being heated in distilled water (100 °C, pH 6-7, 30 sec).

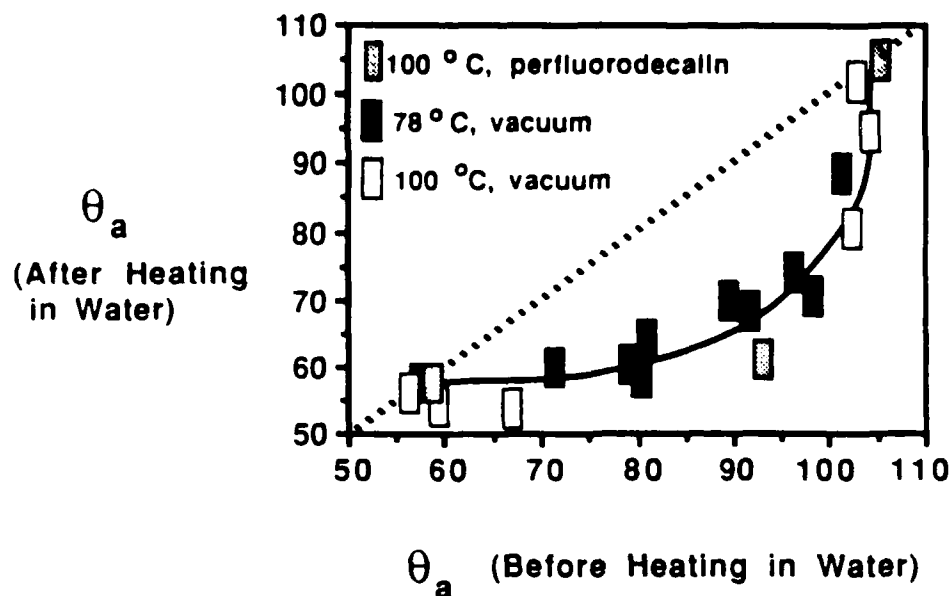


Figure 15. The contact angle of water (pH 1) on samples of PE-CO₂H after treatment in hot distilled water (pH 6-7, 100 °C, 30 sec) as a function of the contact angle prior to heating in water. Prior to the treatment in water, samples were partially reconstructed by heating in vacuum at 78 or 100 °C or by heating in perfluorodecalin (100 °C), to attain the various values of θ_a .

through the overlying material.³⁰ By varying this angle it is sometimes possible to determine a depth profile of functional groups in the interfacial region.

The sensitivity of XPS is usually assumed to drop off exponentially with depth into the sample (eq 16, where $I(x)$ is the intensity detected from groups at depth x into the sample and λ is the electron mean free path in the material of interest.³⁰

$$I(x) = I_0 \exp(-x/\lambda) \quad (16)$$

Multiplying the number of functional groups of a particular type at depth x and time t by the intensity expected from groups at that depth gives the signal intensity as a function of x and t (eq 17). Integrating this intensity over all depths gives the total intensity as a function of time (eqs 18-20). Substitution of eq 1 into eq 20 gives eq 21, which can be simplified to eq 22 where erf is the error function and $\text{erfc}(x) = 1 - \text{erf}(x)$.³¹

$$I(x,t) = I(x)N(x,t) \quad (17)$$

$$I(t) = \int_0^{\infty} I(x,t) dx \quad (18)$$

$$I(t) = \int_0^{\infty} I(x)N(x,t) dx \quad (19)$$

$$I(t)/I_0 = \int_0^{\infty} \exp(-x/\lambda) N(x,t) dx \quad (20)$$

$$I(t)/I_0 = 1/(\pi Dt)^{1/2} \int_0^{\infty} \exp(-x/\lambda) \exp(-x^2/4Dt) dx \quad (21)$$

$$\begin{aligned} I(t)/I_0 &= \exp(Dt/\lambda^2) [1 - \operatorname{erf}((Dt)^{1/2}/\lambda)] \\ &= \exp(Dt/\lambda^2) [\operatorname{erfc}((Dt)^{1/2}/\lambda)] \end{aligned} \quad (22)$$

Equation 22 indicates that as λ decreases (by using low-angle take-off, for example) the decrease in $I(t)/I_0$ with time for a particular reconstruction process becomes more rapid. In particular, when $I(t)/I_0 = 0.5$ (half of the signal has disappeared), eq 22 is satisfied when $Dt/\lambda^2 = 0.58$ (eq 23).

$$Dt_{1/2}/\lambda^2 = 0.58 \quad (23)$$

Equation 24 relates the apparent mean free path (λ') of the electrons ejected from a planar surface to the actual mean free path λ and the take-off angle θ_T .³⁰

$$\lambda' = \lambda \sin \theta_T \quad (24)$$

$$Dt_{1/2}/(\lambda \sin \theta_T)^2 = 0.58 \quad (25)$$

If, for example $\lambda = 35 \text{ \AA}$, then the apparent mean free path λ' would be $34 \text{ \AA}$ at a 75° take-off and only $12 \text{ \AA}$ at a 20° take-off. As a consequence, the half time ($t_{1/2}$, eq 25) of the change in signal intensity should be approximately 8 times longer at a take-off angle of 75° than at 20° .

Figure 16 shows the relative intensity of the XPS N_{1s} signal intensity $[I(t)/I_0]$ for PE[CONHCH₂CO₂H] samples after heating at 100°C in vacuum. Spectra were obtained at 75° and 20° take-off

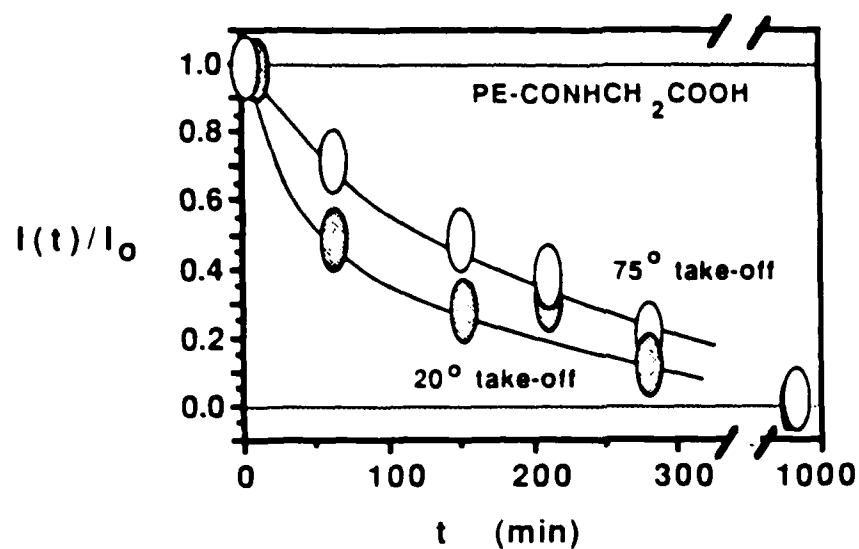


Figure 16. The XPS N_{1s} signal intensity remaining ($I(t)/I_0$) for PE[CONHCH₂CO₂H] as a function of the time of heating in vacuum (100 °C). Samples were analyzed at take-off angles of $\theta_T = 20^\circ$ ($\odot$) and $\theta_T = 75^\circ$ ($\circ$).

angles. The data in this figure show only a small difference between the rates of decrease of the signal intensity at the two take-off angles. We attribute this discrepancy between experiment and the prediction of eq 25 to the roughness of the polymer-vacuum interface. We believe that our samples are quite rough⁵ and that the increase in λ' is not as great as predicted due to this roughness.

We conclude that while low-angle XPS is more surface selective than normal spectroscopy conducted at high take-off angles, detailed interpretation of the increased selectivity is impractical due to our limited knowledge of the polymer interfacial morphology.³⁷

Equation 23 can be used to estimate the diffusion constant D , if a value is assumed for λ . If we assume $\lambda = 35 \text{ \AA}$,³⁰ then $D = 0.9 \times 10^{-17} \text{ cm}^2/\text{sec}$. This value is similar to that estimated by contact angle on this same material ($D = 5 \times 10^{-17} \text{ cm}^2/\text{sec}$; Figures 3 and 9, assuming $x_g = 5 \text{ \AA}$).

Depth Profiling during Reconstruction: Wetting

In the absence of a direct analytical tool capable of following the migration of functional groups out of the θ interphase during reconstruction, we have obtained information using an indirect technique based on measurement of contact angle following chemical modification of functionality in the sub- θ interphase. We first allow the interface of PE[CH₂OH] to reconstruct thermally in vacuum for various lengths of time. This reconstruction is carried on past the point at which the interface has become indistinguishable by contact angle from that of PE-H; that is, all the hydroxyl groups have migrated out of the θ interphase. The buried hydroxyl groups, which

do not themselves influence the contact angle properties ($\theta_a = 103^\circ$), are then allowed to react with perfluorinated anhydrides having different (fluoroalkyl) chain lengths. If the anhydrides are sufficiently long, the fluorinated tail will extend into the interphase and influence the contact angle (Figure 12). If the anhydrides are too short or if the OH groups are too far from the interface, the fluorinated tails will not influence the contact angle.

Figure 13 shows the contact angle observed for water (θ_a) on samples obtained by heating PE-[CH₂OH] for various lengths of time and then acylating the buried hydroxyl groups with either trifluoroacetate, hexafluorobutyrate, or perfluorooctanoate anhydride. Figure 14 also shows the contact angle on these reconstructed interfaces of PE-[CH₂OH] before reaction with the anhydrides ($\theta_a = 103^\circ$ for all except that at $t = 0$ unreconstructed; $\theta_a = 79^\circ$). After 5-20 min of heating, the hydroxyl groups have migrated out of the α interphase, since the contact angle on these samples is indistinguishable from that of unoxidized polyethylene. After these hydroxyl groups have been acylated, the wetting properties of the samples change markedly. Even for the shortest anhydride the contact angle is nearly as high as for the unreconstructed interface after reaction with the same anhydride. This similarity in wetting properties suggests that a significant proportion of the hydroxyl groups are very close to the interface (2-5 Å) and that even the short tail of the trifluoroacetate ester is able to reach up into this interphase and influence wetting.

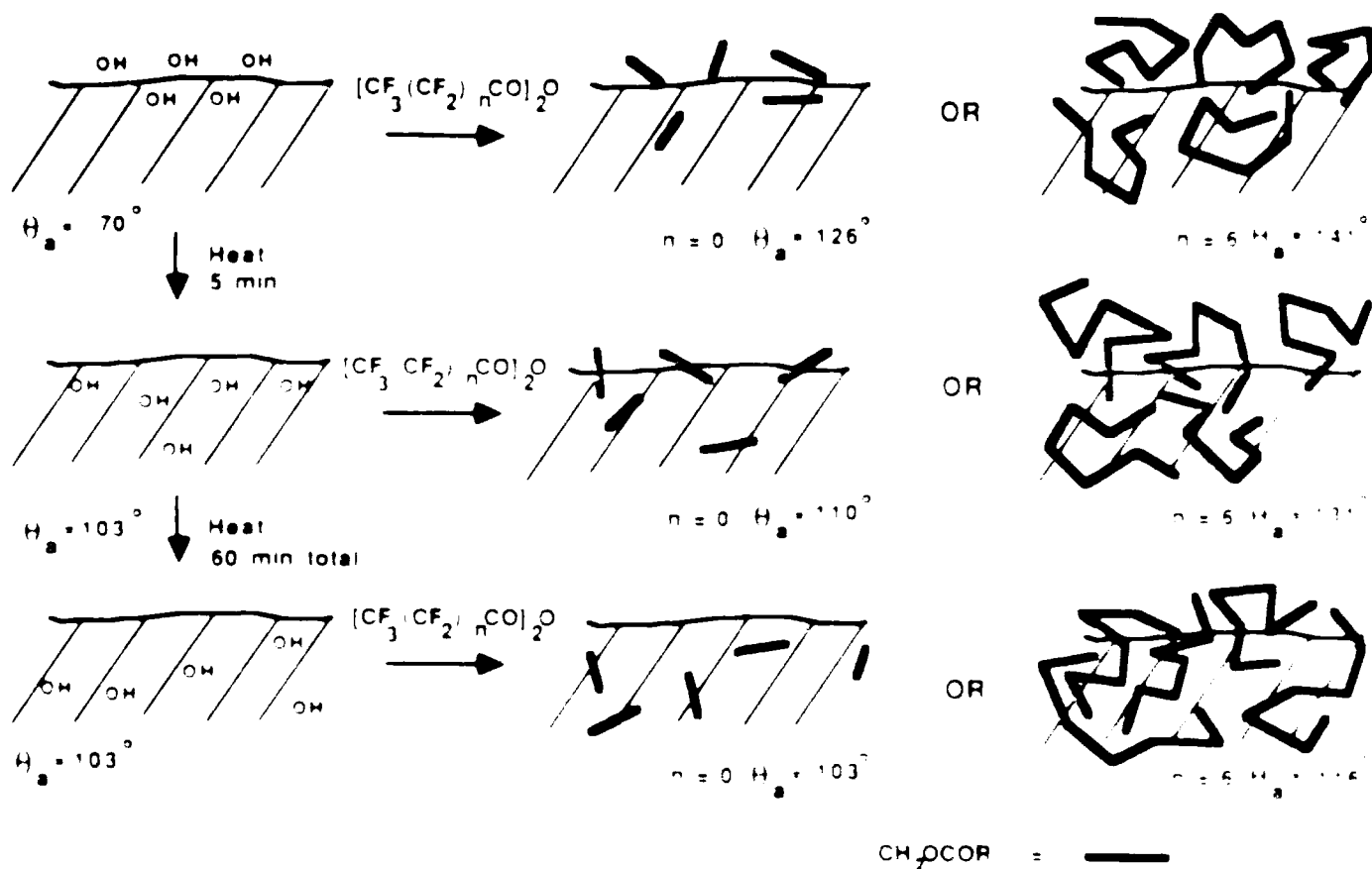


Figure 17. Schematic illustration of depth profiling of polyethylene surfaces. PE(CH_2OH) is first allowed to reconstitute at 100°C, vacuum, for various lengths of time, after which the bound $-OH$ groups are allowed to react with perfluorinated anhydrides of various sizes (center column). The contact angles H_c are then determined on these interfaces to test the character of the new interphase. The contact angle of water on a virgin polyethylene is 103°.

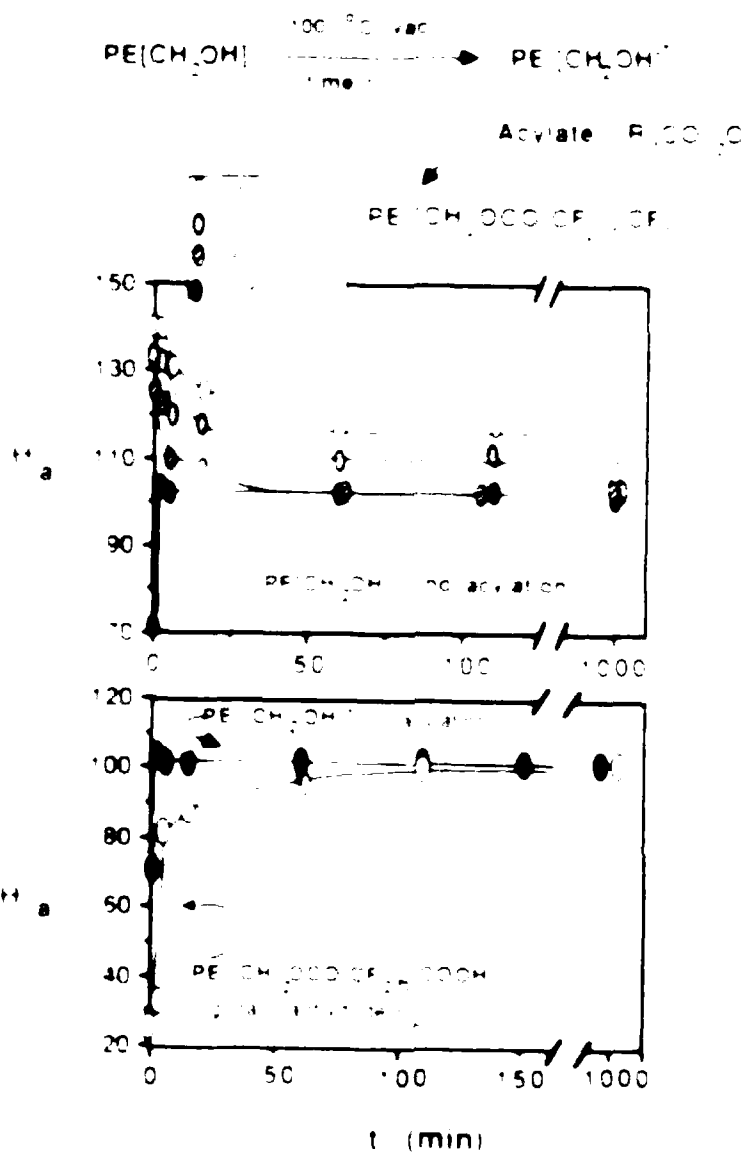


Figure 1. Apparent activation energy changes as a function of time for the thermal degradation of poly(ethylene glycol) (PE) and poly(ethylene glycol) (PE) after activation with $\text{R}_2\text{CO}_2\text{C}$ at 100°C under vacuum. The apparent activation energy changes as a function of time for the thermal degradation of poly(ethylene glycol) (PE) and poly(ethylene glycol) (PE) after activation with $\text{R}_2\text{CO}_2\text{C}$ at 100°C under vacuum. The apparent activation energy changes as a function of time for the thermal degradation of poly(ethylene glycol) (PE) and poly(ethylene glycol) (PE) after activation with $\text{R}_2\text{CO}_2\text{C}$ at 100°C under vacuum.

After longer periods of heating (60 min) the shorter esters cannot reach the θ interphase (although an ATR-IR peak at 1790 cm^{-1} establishes that fluorinated esters are present). The longer esters can, however, still reach the θ interphase and influence wetting. We believe that in these samples many of the hydroxyl groups are located more than $5\text{ \AA}$ but less than $10\text{ \AA}$ deep (Figure 17). After very long heating times (1000 min) even the longest perfluorinated esters influence the wetting properties only slightly, and the shorter ones have no influence at all. This result is consistent with the observation that after these long heating periods polar groups have largely disappeared from the region of the interface examined by xPS. In this latter case the majority of the hydroxyl groups are probably more than $10\text{ \AA}$ deep.

These acylation reactions are fully reversible by treating the samples with 1 N NaOH . In all cases, this treatment results in an interface with wetting properties indistinguishable from that before acylation ($\theta_a = 103^\circ$). The anhydride can then be used to reacylate the still buried hydroxyl groups: the resulting materials have the same contact angles as the initially formed, esterified interface. The reversibility established by this experiment is important in demonstrating that the reaction between the hydroxyl groups and the anhydrides does not itself reconstruct the interface: If reaction with the anhydride had brought the hydroxyl moiety up into the θ interphase, then upon hydrolysis the interface should have had a contact angle significantly lower than the observed 103° . Since the contact angle observed after hydrolysis of the ester moieties was indistinguishable from that obtained before acylation of the buried

hydroxyl groups, we infer that no reconstruction has taken place during either acylation or hydrolysis.

A related type of experiment can be carried out using an anhydride that reacts with the buried hydroxyl groups and generates a hydrophilic interphase (e.g. perfluoroglutaric anhydride). Acylation of unreconstructed $\text{PE}[\text{CH}_2\text{OH}]$ with this anhydride produces $\text{PE}[\text{CH}_2\text{OCO}(\text{CF}_2)_3\text{CO}_2\text{H}]$, a material that is similar in its hydrophilicity to $\text{PE}-\text{CO}_2\text{H}$ at pH 0 but that exists at pH 5 as the more hydrophilic carboxylate anion.⁹ Figure 13 shows the contact angle (pH 6) on these materials as a function of the time of heating the $\text{PE}[\text{CH}_2\text{OH}]$ at 100 °C in vacuum before treating it with the anhydride. Again it is clear that the CO_2H groups introduced into the interphase by this acylation extend into the θ interphase and influence the contact angle, even when the hydroxyl groups of $\text{PE}[\text{CH}_2\text{OH}]$ are themselves unable to do so. The change in the contact angle as a function of the time used in the thermal reconstruction is qualitatively similar to that observed for the hydrophobic ester in experiments involving acylation with perfluorobutyric anhydride. The ability of both hydrophilic ($-\text{CF}_2\text{CF}_2\text{CO}_2\text{H}$) and hydrophobic ($-\text{CF}_2\text{CF}_2\text{CF}_3$) esters to influence wetting, suggests that extreme hydrophobicity is not responsible for their ability to influence wetting when the hydroxyl groups, to which they become attached, do not. We note, however, that the acid-containing interface generated by acylation with perfluoroglutaric anhydride may itself reconstruct on exposure to water, in a process driven by solvation of the carboxylate anion (see Figure 1): this reconstruction may result in CO_2H groups "blooming" into the θ interphase. The interpretation of experiments involving

perfluoroglutaric anhydride is thus less clear than those involving acylation with the hydrophobic anhydrides.

Reconstruction Followed Using a Fluorescent Dansyl Group

In a previous paper, we described synthetic methods that attach the dansyl [5-(dimethylamino)naphthalene-1-sulfonyl] group to the functionalized interface of PE-CO₂H and its derivatives (Scheme I).⁷ The dansyl probe has two useful properties that can be used to study the reconstruction of PE[dansyl] during heating: the fluorescence emission maximum and the quenching of fluorescence upon protonation of its dimethylamino moiety.

The emission maximum of dansyl is a function of the dielectric constant of the surrounding medium (or more generally, of some function of the local polarity). In water, for example, the dansyl group has $\lambda_{\text{max}} = 560$ nm (yellow) and in hexane it has $\lambda_{\text{max}} = 460$ nm (blue).⁷ From the emission maximum exhibited by PE[dansyl] in contact with water we have concluded that the local dielectric constant in the functional interface of PE[dansyl] is low ($\epsilon \approx 6$ to 10).⁷ Reconstruction of PE[dansyl] should allow the dansyl groups to migrate into the polymer film. Examination of a sample of PE[dansyl] thermally reconstructed in vacuum or in contact with a liquid phase and then examined in contact with water should give an independent measure of the polarity of the water/polymer interface after reconstruction.

Figure 19 shows the emission maximum of PE[dansyl] in distilled water (pH 6-7) as a function of the time of heating at 100 °C under various conditions: in vacuum, in contact with distilled water (pH

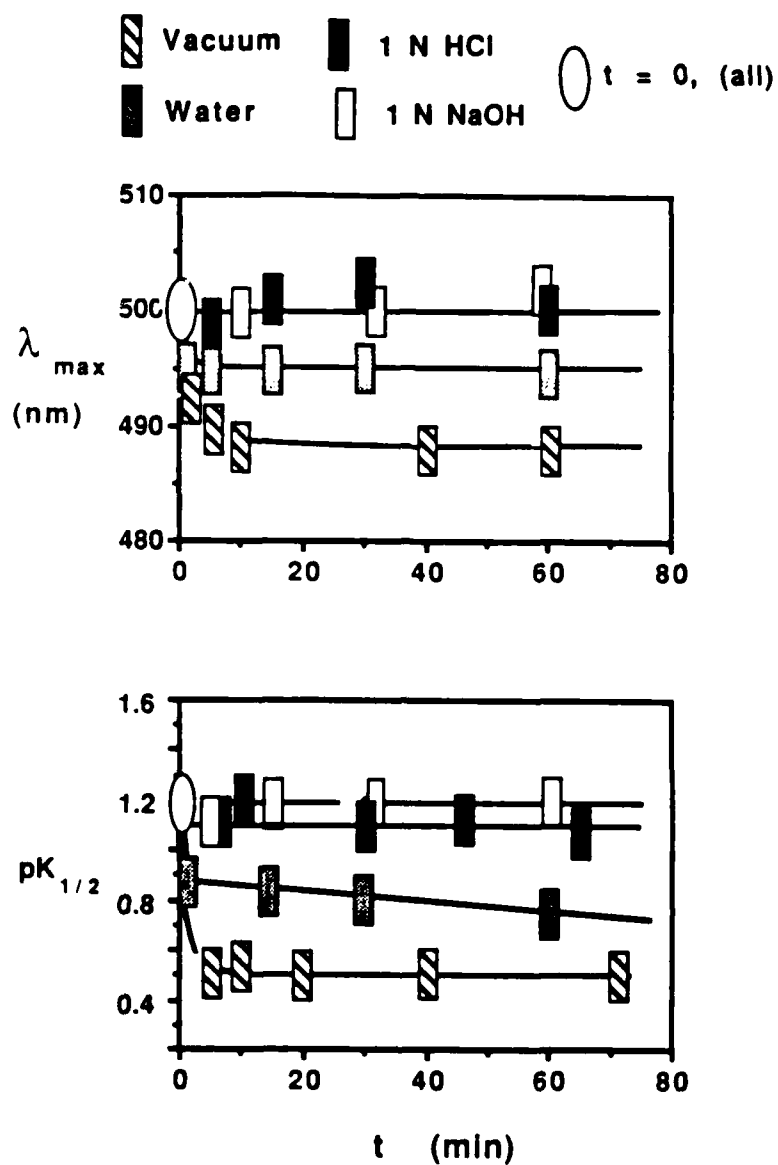


Figure 19. The emission maximum (λ_{max} , top) and $pK_{1/2}$ (bottom) of PE[dansyl] ($PE[CO_2H][CONH-dansyl]$)⁷ as a function of the time of heating (100 °C) in various solvents. Samples were removed from the solutions in which they were heated and were examined at room temperature in distilled water.

5.6), in 1 N HCl, and in 1 N NaOH. Heating in vacuum clearly results in a shift in the emission maximum to shorter wavelength, suggesting that the probe moves to a less polar environment, as expected. The smaller, but still significant, decrease in λ_{max} upon heating in distilled water is useful in understanding the molecular-scale phenomena governing the reconstruction process. The dansyl groups of PE[dansyl] are attached to only approximately 30% of the carboxylic acid moieties originally present in PE-CO₂H. A sample of PE[dansyl] being heated in water thus contains one dansyl group for every five other polar functionalities (carboxylic acids and ketones).⁷ The ketone and unreacted carboxylic acid groups are more polar than the dansyl group and thus the interfacial free energy between the film and the aqueous phase will be lowest when these polar groups are in the σ interphase, not when the less polar dansyl groups are present.

The dansyl group can be made to be more polar, however, by reconstructing the functionalized interface of PE[dansyl] under conditions where the dansyl group is either protonated at the dimethylamino moiety (1 N HCl) or is deprotonated at the sulfonamide moiety (1 N NaOH). Under these conditions the dansyl groups should be more hydrophilic than unionized dansyl groups and perhaps more hydrophilic than carboxylic acid or ketone groups. The observation that reconstruction of PE[dansyl] under these conditions does not result in a decrease in λ_{max} (Figure 19) supports this hypothesis.

If the charge on the dansyl groups rather than ionic strength or some related factor is the cause of the difference between reconstruction of PE[dansyl] in water and in acid or base, the reconstruction should result in dansyl groups moving away from the σ

interphase at any pH at which the dansyl moieties are not charged. Figure 20 shows the emission maximum of the dansyl group of samples of PE[dansyl] (in distilled water) as a function of the pH of water in which the sample had been heated for 60 sec. This figure also shows the contact angle on a similar (untreated) surface, containing dansyl groups, as a function of pH. The drop in θ_a in the lower plot at values of pH above 9 and below 2 has been previously demonstrated to result respectively from the deprotonation of the ArSO_2NH group and the protonation of the $\text{ArN}(\text{CH}_3)_2$ group, respectively, of the dansyl moiety.⁷ The excellent correlation between the emission maximum after heating in water and the contact angle observed for interfaces containing dansyl groups supports the hypothesis that the migration of dansyl groups away from the θ interphase is prevented when the dansyl moiety is charged (and thus very hydrophilic) but is not prevented when the dansyl moiety is uncharged.

Another useful feature of the dansyl probe is the completeness with which its fluorescence can be quenched by protonation of the dimethylamino moiety.⁷ In aqueous solution, the pK_a of the dansyl group is 3.6, while attached to the interface the $\text{pK}_{1/2}$ is 1.2 (the $\text{pK}_{1/2}$ is defined as the value of solution pH at which the fluorescence is half quenched; it is equivalent to pK_a except that the protonation of interfacial groups does not always exhibit the simple relationship between pH, pK_a , and the degree of ionization exhibited by molecules in solution).⁷ We have attributed the decreased basicity of the interfacial dansyl groups of PE[dansyl] to the low dielectric constant in the interfacial region.⁷ Reconstruction of the interface of PE[dansyl] can thus be monitored in two additional ways: the $\text{pK}_{1/2}$ of

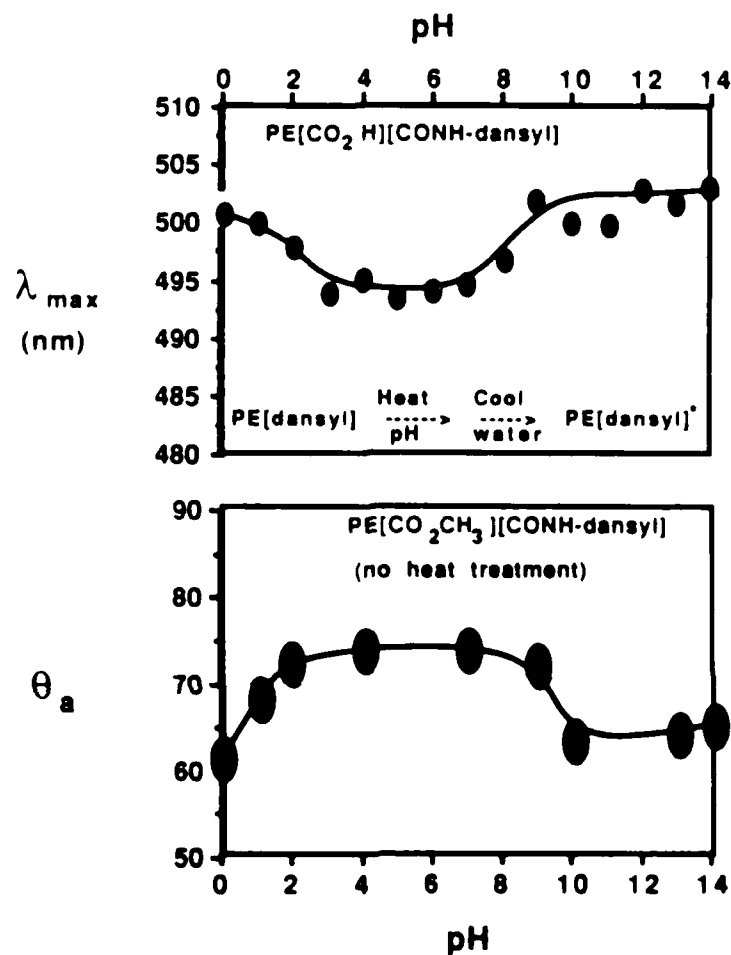


Figure 20. Top: Dependence of the emission maximum ($\lambda_{\max}$) on the pH of the solutions in which $\text{PE}[\text{dansyl}]$ ($\text{PE}[\text{CO}_2\text{H}][\text{CONH-dansyl}]$)⁷ was heated for 60 sec at 100 °C. Samples were rinsed and analyzed in distilled at room temperature. Bottom: Dependence of the water contact angle on the pH of the aqueous drop on untreated $\text{PE}[\text{dansyl}]$ ($\text{PE}[\text{CO}_2\text{CH}_3][\text{CONH-dansyl}]$).⁷

reconstructed PE[dansyl] in contact with water can be determined and might be expected to decrease as the dansyl groups migrate into the bulk; the ability to quench all (or only some) of the dansyl groups after reconstruction would yield information concerning the access of the migrated surface groups to aqueous protons.

Figure 19 shows the $pK_{1/2}$ of PE[dansyl] in contact with water as a function of the time of reconstruction under various conditions at 100 °C. The results parallel those obtained for the λ_{max} during heating: in vacuum the $pK_{1/2}$ shifts to lower values; in water the $pK_{1/2}$ also shifts slightly, but not as much as those heated in vacuum; samples heated in 1 N NaOH or 1 N HCl do not exhibit a shift in the $pK_{1/2}$ when later examined in water. This, the hypotheses that the dansyl groups migrate into the polymer during heating in vacuum or water, but not when heated in water under conditions where the dansyl groups are charged and thus very hydrophilic, is supported by this experiment.

The fluorescence emitted from dansyl moieties in all samples can be completely quenched in 50% (w/w) H_2SO_4 . The fluorescence emitted from dansyl cadaverine nonselectively adsorbed deep into the film from toluene solution⁷ is not quenched by this or any strength of sulfuric acid up to 98%. Thus, all of the dansyl groups, even after reconstruction, are accessible to aqueous protons. This latter result is consistent with the observation that CO_2H groups that had been allowed to migrate into the polymer were still accessible to aqueous hydroxide ion (Figure 3).

Reconstruction of Other Types of Interfaces

In order to determine if the types of reconstruction observed for PE-CO₂H are relevant to other types of functionalized polymers, we have examined the wetting properties of several related systems. Figure 21 shows the change in the contact angle of water on ultrahigh molecular weight polyethylene that had been oxidized in a manner similar to that used for PE-H. The resulting material, UHMW-CO₂H⁶ appears to reconstruct in a manner similar to that observed on the low-density film PE-CO₂H, though the rate of reconstruction is significantly lower. A brief survey also suggests that the interfaces of materials made by chromic acid oxidation of nylon and polyester also become hydrophobic on heating. Figure 21 also shows similar data for the reconstruction of polypropylene and polyethylene that had been treated with an oxygen plasma (forming PPP and PPE, respectively). These interfaces, too, appear to reconstruct in a manner analogous to that observed for PE-CO₂H.

Summary and Conclusions

The functionalized interfaces of PE-CO₂H and derivatives reconstruct when heated sufficiently to cause mobility of the polymer chains. This section summarizes a number of conclusions concerning the mechanism of thermal reconstruction.

- 1) The wetting properties of the interface of PE-CO₂H and derivatives change during thermal reconstruction. The rate and direction of the change depends on the nature of the contacting phase (vapor or liquid) and the type of functional groups present in the interface. The change in wettability of the polymer reflects

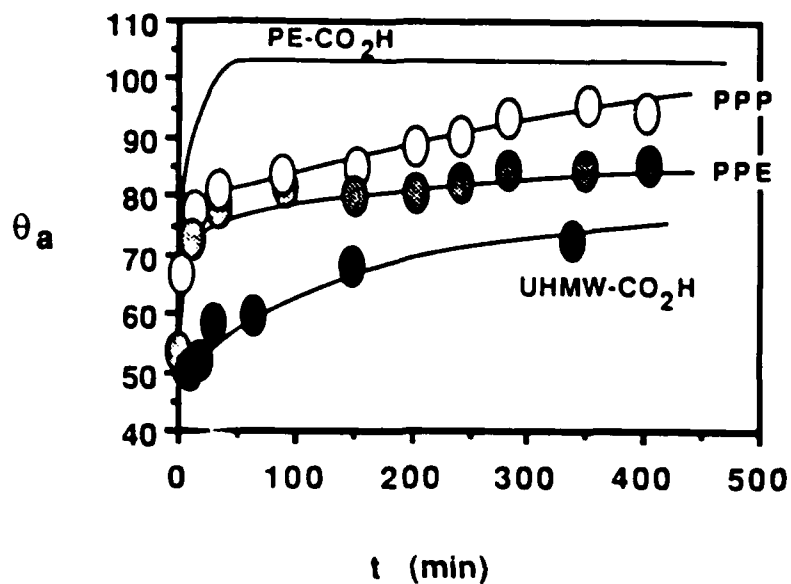


Figure 21. Dependence of the contact angle of water (pH 1) on the time of heating for PE-CO₂H and O₂ plasma-treated polypropylene (PPP) and polyethylene (PPE) (reconstructed at 78 °C in vacuum), and for UHMW-CO₂H (ultra-high molecular weight polyethylene oxidized with chromic acid; reconstructed at 72 °C in vacuum).

replacement of some or all of the functional groups in the α interphase with methylene groups from the bulk polymer. The change in wetting characteristics takes place orders of magnitude faster than changes detected by XPS (at either normal or low angle take-off). We attribute this difference to the extreme surface selectivity of wetting (see below).

2) The rate of reconstruction increases with temperature in a manner approximately described by the Arrhenius equation. The activation energy is approximately 50 kcal/mol. At room temperature, the functionalized interface is stable for months or years; at 100 °C it is stable only for minutes. The rate of reconstruction of the α interphase changes by more than six orders of magnitude over this range in temperature. The rate roughly follows Arrhenius behavior over the range $T = 20-60$ °C. When $T > 60$ °C, the rate of reconstruction is slower than expected, perhaps because the rate of reconstruction is comparable to, or faster than, the rate of heating of the sample. The observed value of E_a is not unreasonable: the diffusion of small molecules through polyethylene has activation energies of 10-20 kcal/mol. Over the limited range of temperatures fitted by the Arrhenius equation, the apparent diffusion constant for the polar functionality is $D \approx 2 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ (at 60 °C), assuming $x_d = 5 \text{ \AA}$.

3) The migration of functional groups away from the interface appears to be dominated by minimization of the interfacial free energy and by dilution of the interfacial functional groups in the polymer interior. Release of residual strain in the film does not seem to be important. When an interface with a high interfacial energy, such as

PE-CO₂H/vacuum or PE(CO₂CH₃)₂/water, is heated the system reconstructs and minimizes the interfacial free energy. This initialization is accomplished by replacing the interfacial groups with methylene groups from the bulk.

Reduction of the interfacial free energy also permits groups that have been allowed to diffuse into the bulk to be recovered. For example, polar groups disappear from the θ interphase during heating in vacuum, but can be recaptured (in part) by heating in water.

4) The functional groups do not migrate far during reconstruction before they no longer influence wetting: wetting is sensitive to only the top ~ 10 Å of the functionalized interface in these systems. Wetting is appreciably more surface sensitive than XPS. Experiments comparing changes in the contact angle with water and the XPS signal intensity during reconstruction of PE-CO₂H indicate that contact angle is sensitive to a much thinner region of the interface than is XPS, even with a 20° take-off angle. In addition, changes in the wettability of partially reconstructed interfaces on derivatization of functional groups in the sub- θ interphase suggest that groups need only migrate a few Å to leave the θ interphase. Thus, wetting senses only a few Å into the polymer and is, at this time, the most surface selective technique that can be routinely applied to these types of materials. One implication of this work is that the use of XPS to study phenomena such as wetting and adhesion will almost necessarily lead to ambiguous results: for other than very smooth samples, XPS does not have the surface sensitivity required to distinguish the θ interphase from the sub- θ interphase. We note that the θ interphase of reconstructed PE[R] consists of

methylene groups and is probably not swollen by the contact with water. It is possible that in systems in which the polymer is in a wetting contact with water, the polymer, the water, and the reagents are in contact and the contact angle may increase.

5. As the size of the functional groups in the α interphase increases, the rate of reconstruction decreases. The observation that materials having the composition $\text{PE}_{1-x}\text{G}_x$ (eq. 1) where $x = 0.14$, demonstrates that as the polar functional groups increase, the rate at which they migrate into the polymer is greatly retarded. The time required to eliminate polar moieties from the α interphase by thermal reconstruction is nearly 100 times longer for $x = 0.14$ than for $x = 0$. This observation suggests that if it is desirable to keep polar functional groups in the α interphase of a polymer at high temperature, then these groups should have high molecular weight.

6. Functional groups that have migrated into the polymer are still accessible to reagents in aqueous solution in contact with the film even when the wetting properties have become similar to unmodified polyethylene film. Carboxylic acid groups that have migrated more than $10 \text{ \AA}$ into the polymer (based on the decrease in the intensity of the XPS signal) can still be deprotonated when the film is put into contact with aqueous hydroxide ion, a reagent that has very low solubility in polyethylene. Similarly, daisy groups that have migrated into the film can still be protonated by aqueous acid. In both of these systems, the wettability of the reconstructed interface is indistinguishable from that of unmodified polyethylene film.

The importance of this work is that it provides a systematic and comprehensive review of the literature on the topic of the role of the family in the development of the child. The author discusses the various factors that influence the child's development, including the family environment, the child's temperament, and the child's social interactions. The author also discusses the various methods used to study the role of the family in the development of the child, including experimental methods, correlational methods, and qualitative methods. The author concludes that the family plays a crucial role in the development of the child, and that the quality of the family environment is a key factor in determining the child's outcome.

The type of family environment that a child grows up in can have a significant impact on the child's development. For example, children who grow up in a family with high levels of warmth and support tend to have better outcomes than children who grow up in a family with low levels of warmth and support. The author discusses the various factors that influence the family environment, including the parents' characteristics, the child's characteristics, and the social context. The author also discusses the various methods used to study the family environment, including observational methods, self-report methods, and experimental methods. The author concludes that the family environment is a key factor in determining the child's outcome, and that the quality of the family environment is a key factor in determining the child's outcome.

Experimental Section

General. All solvents were reagent grade and were used as received. Water was distilled in a Corning Model AG-1b glass distillation apparatus. XPS spectra were determined either on a Physical Electronics Model 543 spectrometer (Mg K_{α} X-ray source, 100-eV pass energy, 10^{-3} to 10^{-9} torr, machine calibrated according to ASTM STP 699) or a Kratos XSAM-800 spectrometer (Mg K_{α} X-ray source, hemispherical analyzer) operated in a fixed analyzer transmission mode with an instrumental resolution of 1.1 eV. Angular dependent XPS spectra (75° and 20°) were obtained on this latter instrument.

Sample Heating. Samples were heated in vacuum ($0.1 - 1$ torr) or argon in a drying tube jacketed with the refluxing vapor of a chosen solvent (e.g., water for 100°C , methylene chloride for 40°C). Samples heated at 106°C were heated under argon in an oven. The samples were laid face-up on a cardboard holder and left in the chamber for the desired period of time. These samples were not further treated before contact angle measurement. Samples heated in water were simply immersed in boiling water for the desired period of time. These samples were removed and immediately dried under a stream of nitrogen to prevent spotting of the surface by contaminants in the water. Samples heated in 1 N NaOH , 1 N HCl , or perfluorodecalin were immersed in a tube of the solvent, which was surrounded by refluxing water vapor. Samples heated in perfluorodecalin were removed and dried in a stream of nitrogen; samples heated in 1 N HCl or 1 N NaOH were rinsed several times in distilled water and dried similarly.

ATR-IR Measurements. Film pieces were cut to the size of the KRS-5 (thallium bromide/iodide, 45°) crystal faces and pressed

against the faces with an MIR (Perkin-Elmer) sample holder. Films treated with 1 N NaOH (pH 14) were blotted dry with filter paper and were dried in the air for 30 min prior to determination of spectra.

Rectangular pieces of thin cardboard the same size as the film pieces were inserted between the films and the steel sample holder to distribute the pressure on the film evenly. Transmission spectra were obtained on a Perkin-Elmer Model 598 spectrometer.

Contact Angle Measurements. Contact angles were determined on a Kline-Hart Model 100 contact angle goniometer equipped with an environmental chamber by estimating the tangent normal to the radius of the drop at the intersection between the sessile drop and the surface. These measurements were determined 5-20 sec after application of the drop. The humidity in the chamber was maintained at 100% by filling the wells in the sample chamber with distilled water. The temperature was not controlled and varied between 20 and 30 °C. The volume of the drop used was always 1 μ L. The samples were cut to a size of 0.5 x 2 cm and attached by the back of the sample to a glass slide using two-sided Scotch tape to keep the sample flat. The reported values are the average of at least eight measurements taken at different locations on the film surface and have a maximum error of $\pm 3^\circ$.

Polyethylene (PE-H). Low-density biaxially blown polyethylene (thickness 0.005 cm thick; $\rho = 0.92$) was gift from Flex-O-Glas Inc (Houston, TX, Model DRT-600B). The film was cut into 10 x 10-cm squares. These samples were extracted by suspending the film in refluxing toluene for 24 h to remove antioxidants and other film additives. The samples were dried under vacuum (20 °C, 0.01 torr, 4 h) or in air

(20 °C, 4 h) prior to oxidation to remove any residual solvent. Those samples not to be oxidized were stored under dry argon. In all cases, experiments were performed on the side of the film facing the inside of the stock roll. Some samples were heated for 5 days at 100 °C in vacuum (0.01 torr), either before or after extraction, to relieve some of the strain introduced into the film during manufacture.

PE-CO₂H. PE-H was oxidized by floating on H₂SO₄/H₂O/CrO₃ (29/42/29; w/w/w) at 72 °C for 60 s. The samples were rinsed 4 times in distilled water and once in acetone, dried in air for 1 h, and stored under dry argon. The samples are indistinguishable from PE-H to the unaided eye. The samples had a peak in the ATR-IR spectrum at 1710 cm⁻¹.

UHMW-CO₂H. Ultrahigh molecular weight polyethylene sheet (1/3" thick, ρ = 0.93 g/mL; AIN Plastics Inc, Mount Vernon, NY) was cut into 2 x 2 cm slabs. These slabs were oxidized by floating them on the chromic acid solution used to oxidize PE-H for 2 min at 72 °C. The slabs were removed, rinsed several times in water, once in acetone, and dried in air. These samples were not extracted prior to oxidation.

PE[CH₂OH] and Derivatives. PE-CO₂H was treated with excess 1 M BH₃-THF (Aldrich) at 50 °C for 20 h under argon. The films were rinsed twice in water, soaked in 1 N HCl for 5 min and rinsed 3 times in water. The carbonyl ATR-IR peaks were absent and a new peak appeared at 3350 cm⁻¹. This material also contains secondary hydroxyl groups resulting from the reduction of ketone groups: PE[CH₂OR] = PE[>CHOR][CH₂OR]. In order to generate PE[CH₂OCO(CF₂)_nCF₃], PE[CH₂OH] was allowed to react with neat [CF₃(CF₂)_nCO]₂O (Lancaster Synthesis,

just enough to cover the film surface) for 13 h at room temp. The films were rinsed 5 times in methanol, 2 times in acetone, and twice in water. The ATR-IR spectrum (of $n = 0$) showed new peaks at 1790 ($\text{CF}_3\text{CO}_2\text{R}$), 1165, and 1225 cm^{-1} (C-F). $\text{PE}[\text{CH}_2\text{OH}]$ was reacted with stearic acid chloride (Fluka, 5 g) in acetone (50 mL) containing 5 mL of triethylamine for 13 h. The film was removed, rinsed in methanol, water, acetone, and hexane, and dried in air to form $\text{PE}[\text{CH}_2\text{OCO}(\text{CH}_2)_{16}\text{CH}_3]$. Alternatively, to form $\text{PE}[\text{CH}_2\text{OCOCH}_2\text{CH}_2\text{CO}_2\text{H}]$, $\text{PE}[\text{CH}_2\text{OH}]$ was treated with 30 mL of acetone containing 10 g of succinic anhydride and 1 mL of triethylamine for 1 h. The film was rinsed in acetone, water, and then methanol before being dried in air.

"Buried" $\text{PE}[\text{CH}_2\text{OCOR}]$. $\text{PE}[\text{CH}_2\text{OH}]$ was heated for the desired period of time at 100 °C in vacuum. These samples were then immersed in neat perfluorinated anhydride (acetic, butyric, octanoic, or glutaric) for 18 h at room temperature. These samples were removed, dried in air, and rinsed in water several times followed by acetone once to remove any residual anhydride or acid. The samples were again dried and the contact angle was determined.

$\text{PE}[\text{COCl}]$. $\text{PE}-\text{CO}_2\text{H}$ was soaked in 30 mL of dry diethyl ether containing 3 g of PCl_5 for 1 h at room temperature. The film was quickly removed and used immediately without workup to minimize hydrolysis of the acid chloride groups by ambient water vapor.

$\text{PE}[\text{CONH}_2]$. $\text{PE}[\text{COCl}]$ was put directly into concentrated NH_4OH for 20 min, rinsed in water (5 times) and methanol (twice), and then dried in the air. ATR-IR showed new peaks at 1400 cm^{-1} (C-N), 3150 cm^{-1} (NH), 1560 cm^{-1} (NH), and 1660 cm^{-1} (C=ONH); ESCA N/O ratio = 0.58 (0.60 expected for full reaction).

$\text{PE}[\text{CONHCH}_2\text{CO}_2\text{H}]$. $\text{PE}[\text{COCl}]$ was immersed in a 2 M aqueous solution of glycine (adjusted to pH 10 with NaOH). After 10 min the film was removed, rinsed in water (5 times) and methanol (once) and dried in the air. ESCA N/O ratio = 0.29 (0.27 expected for full reaction).

$\text{PE}[\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]$. $\text{PE}[\text{COCl}]$ was immersed in the appropriate neat liquid poly(ethylene glycol). Lower n values were the pure compounds (n = 1 and 2 were obtained from Fisher; n = 3 and 4 were obtained from Aldrich). The higher n values were molecular weight mixtures and the reported n values are indicative of the average molecular weights (n = 5, 7, 10, and 14 were all obtained from Aldrich). After 1 h the films were removed, rinsed 7 times in water and once in acetone, and allowed to dry in air.

$\text{PE}[\text{dansyl}]$. $\text{PE}[\text{COCl}]$ was immersed in an acetone solution of dansyl cadaverine (Sigma, 100 mg/5 mL acetone) for 5 sec. The film was removed, rinsed twice in acetone, twice in water, soaked in NH_4OH (sat.) for 10 min, rinsed twice in water, twice in methanol, and allowed to dry in the air. This surface was characterized in detail previously.⁷ It ($\text{PE}[\text{CO}_2\text{H}][\text{CONH-dansyl}]$) contains ketones, unreacted carboxylic acids, and dansyl amides. This material is, however, not useful for determining the ionization of the dansyl group (by changes in the water contact angle as a function of pH) due to the ionizable carboxylic acids present. The surface used to determine the contact angle changes with pH on a dansyl-containing surface ($\text{PE}[\text{CO}_2\text{CH}_3][\text{CONH-dansyl}]$) was made similarly, except that methanol was substituted for the acetone. This synthetic procedure results in an interface containing ketones, methyl esters, and dansyl amides.⁷ Materials made in this manner were not used in the reconstruction experiments because

of the likelihood of hydrolysis of the methyl esters percent under some of the conditions employed.

$\text{PE}[\text{CO}_2\text{C}_8\text{H}_{17}]$. PE-CO₂H was soaked in anhydrous octyl alcohol (50 mL) containing sulfuric acid (10 mL) at 40 °C for 72 h. The films were rinsed in octyl alcohol, water several times, and methanol once, followed by drying in air.

Plasma-Treated Polypropylene (PPP) and Polyethylene (PPE). Polypropylene (1/16-in sheet, AIN Plastics Inc, Mount Vernon, NY) and unextracted PE-H were treated with an oxygen plasma in a Harrick Plasma Cleaner model PDC-23G. The samples were treated for 10 and 90 min for PPE and PPP, respectively, at the medium setting, at an oxygen pressure of 200 torr. The samples were rinsed in ethanol twice and allowed to dry in air. Untreated PP had $\theta_a = 116^\circ$ (pH 1); this value was reduced to 67° after plasma treatment. PE-H had a contact angle of 103° , which was reduced to 53° .

Notes and References

- 1) This work was supported in part by the Office of Naval Research. The Materials Research Laboratories at Harvard and M.I.T. made available indispensable spectroscopic facilities.
- 2) IBM Predoctoral Fellow in Polymer Chemistry, 1984-86.
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- 31) Crank, J. The Mathematics of Diffusion; Oxford University Press: London, 1956; p 11. The error function is defined as
$$\text{erf}(x) = [2/(\pi)^{1/2}] \int_0^x e^{-z^2} dz .$$
- 32) For information on short range (1-10 Å solid-liquid interactions see: Israelachvili, J. Intermolecular and Surface Forces: With Application to Colloidal and Biological Systems; Academic Press, London, 1985.
- 33) The dependence on distance from the surface of the interactions that influence wetting depends on the nature of the groups involved and on the liquid. For pure van der Waals forces, these interactions fall off as r^{-6} ; electrostatic interactions involving permanent dipoles fall off as r^{-3} . The real system may be further complicated by swelling of the interface by liquid and the influences of surface microtopology. The model used here is a step function: interaction between a functional group in the polymer and a wetting liquid is constant between $x = 0$ and $x = x_\theta$, and zero for $x > x_\theta$. This model is a sufficient departure from physical reality, that results from it should be considered very approximate. Further, the size ("diameter") of a single functional group is comparable to x_θ , and the use of any diffusional treatment is problematic in this circumstance. Despite these deficiencies, the model is tractable and useful in providing a semi-quantitative appreciation of the factors influencing diffusion out of the θ interface.
- 34) We set the lower limit for x_θ (1 Å) using the argument that in order for a functional group to be shielded from the contacting aqueous phase, the minimum overlayer possible would be a small

atom: thus, $x_0 \geq 1 \text{ \AA}$. For information on short range (1-10 $\text{\AA}$) interactions see: Israelachvili, J. Intermolecular and Surface Forces: With Application to Colloidal and Biological systems; Academic Press, London, 1985.

- 35) Analysis of the diffusion constants themselves are less useful because a value for x_0 (the maximum depth from which wetting can sense buried functional groups: that is, the thickness of the σ interphase) must be assumed. We note, however, that the diffusion coefficients estimated from eq 13 are very low. At 60 $^{\circ}\text{C}$, for example, $D = 9 \times 10^{-4}$ in units of x_0^2/sec . If we assume that wetting senses groups 5 $\text{\AA}$ deep in the polymer ($x_0 = 5 \text{ \AA}$), then the diffusion constant is approximately $2 \times 10^{-18} \text{ cm}^2/\text{sec}$, a value nearly 11 orders of magnitude lower than that of small organic molecules in polyethylene (e.g., $D = 5 \times 10^{-7} \text{ cm}^2/\text{sec}$ for methyl bromide at 60 $^{\circ}\text{C}$): Rogers, C. E. In Physics and Chemistry of the Organic Solid State; Fox, D.; Labes, M. M.; Weissberger, A., Eds.; Interscience Publishers: New York, 1965; Vol. 2, p 540.
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- 37) In our experiments the samples may even experience a change in roughness during heating. Thus, variable take-off angle XPS could not be used to determine depth profiles in an unambiguous manner on our samples, even if λ were known precisely. We note also that after 1000 min the N_{1s} signal disappears entirely, while the oxygen signal on this sample ($\text{PE}[\text{CONHCH}_2\text{CO}_2\text{H}]$) and on $\text{PE-CO}_2\text{H}$ (Figure 1) does not. We attribute this residual N_{1s} signal to film contaminants.

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Captions

Scheme 1. Reactions used to modify the interface of polyethylene film (PE-H).

Figure 1. Top: The advancing contact angle (θ_a) of water on PE-CO₂H as a function of the time the polymer had been heated at 100 °C. Samples were heated in vacuum or under argon prior to determination of θ_a using water at either pH 1 or pH 13. The value of θ_a on PE-H does not change under these conditions. Bottom: The normalized XPS (ESCA) O_{1s} signal intensity obtained from PE-CO₂H as a function of time at 106 °C. Samples were heated under argon prior to examination by XPS.

Figure 2. ATR-IR spectra of the carbonyl region of derivatives of PE-H. Since absolute absorbances are influenced by many experimental parameters (e.g. the degree of contact between the film and the KRS-5 crystal), only relative peak intensities within a single spectrum can be quantitatively compared.

Figure 3. Effects of pretreatments of PE- CO_2H on the change in the contact angle of water (pH 1) after heating in vacuum at 65 °C. Pretreatments: $\blacksquare$, no pretreatment; $\square$, heated in air at 100 °C in distilled water (pH = 1) prior to heating under vacuum; $\blacksquare$, PE- CO_2H made from PE-H that had been preannealed at 100 °C in vacuum for 3 days prior to oxidation; $\square$, PE- CO_2H that had been oxidized for 10 min instead of the usual 1 min. The filled circle at $t = 0$ indicates that all of the samples had $\theta_3 = 54\text{--}57^\circ$ before heating in vacuum.

Figure 4. The contact angle of water (pH 1) on PE- CO_2H as a function of time of heating in vacuum at various temperatures (°C). The filled circle at $t = 0$ indicates that all samples had $\theta_3 = 55\text{--}57^\circ$ prior to heating.

Figure 5. Top: An idealized model surface in which groups influence the contact angle are indicated by filled symbols for polar groups (CO_2H , etc.) and open symbols for nonpolar groups (CH_2 , etc.). During heating the polar groups diffuse away from the γ interphase (indicated by x_3) and into the bulk material and are replaced by non-polar groups. Bottom: A schematic illustration of the interface of PE- CO_2H indicating the roughness of the real interface, the multiplicity of functional groups, and the heterogeneity of the underlying material.

Figure 10. Dependence of the advancing contact angle of water upon the surface free energy of the solid. The solid line is the least squares fit to the data for the γ_{solid} values determined by the method of Figure 10. The dashed line is the least squares fit to the data for the γ_{solid} values determined by the method of Figure 11.

Figure 11. Dependence of the advancing contact angle of water upon the surface free energy of the solid. The solid line is the least squares fit to the data for the γ_{solid} values determined by the method of Figure 10. The dashed line is the least squares fit to the data for the γ_{solid} values determined by the method of Figure 11. The slopes of these lines indicate activation energies of $\sigma_{\text{H}_2\text{O}}$ and $\sigma_{\text{H}_2\text{O}}$, respectively, derived from data in the upper portion of the figure using eq. (4), and the assumption that $\sigma_{\text{H}_2\text{O}} = 0$. The solid line is the least squares fit to the data determined at $P_{\text{H}_2\text{O}} = 0$. The dashed line is the least squares fit to all of the data. The slopes of these lines indicate activation energies of $\sigma_{\text{H}_2\text{O}}$ and $\sigma_{\text{H}_2\text{O}}$, respectively.

Figure 12. Dependence of the advancing contact angle of water upon the time of heating at 10^{-4} torr vacuum for various derivatives of Pc-10 . The upper figure contains data for samples with a lower interfacial free energy (higher $\gamma_{\text{H}_2\text{O}}$ than Pc-10). The lower figure contains data for samples with a higher interfacial free energy (lower $\gamma_{\text{H}_2\text{O}}$ than Pc-10). In both cases the data for Pc-10 are depicted by a continuous line. $\gamma_{\text{H}_2\text{O}}$ for Pc-10 remains unchanged at 1.37×10^{-2} J/m² during heating. For each sample, the contact angle at $t = 0$ is indicated after the parentheses.

Figure 9. Top: XPS data showing the relative surface concentration of fluorine in $\text{PE-O}_2\text{C}(\text{CF}_2)_2\text{CF}_3$ as a function of the duration of heating at 100°C in vacuum. Bottom: XPS data showing the relative surface concentration of fluorine in $\text{PE-O}_2\text{C}(\text{CF}_2)_3\text{CO}_2\text{H}$ as a function of the duration of heating at 100°C in vacuum. The PE-H used in preparing the annealed samples was obtained by heating at 100°C for 24 h in vacuum.

Figure 10. Dependence of the apparent diffusion coefficient (D_a , eq. 13, assuming $x_0 = 5 \text{ \AA}$) on the cosine of the initial contact angle $(\cos \theta_a)_i$ for the interfaces shown in Figure 3. The dotted line shows the value of D_a for unfunctionalized polyethylene (PE-H).

Figure 11. Top: Representative data for the contact angle of water (pH 1) on $\text{PE}[\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]$ as a function of the time the polymer had been heated (100°C , vacuum). The contact angle on each interface prior to heating is indicated in parentheses. Bottom: The dependence of $t_{1/2}$ (the time required for half-reconstruction, $\alpha = 0.5$, eq 5) and t_{100} (the time required to reach 100°) on the number of monomer units n in $\text{PE}[\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]$. Values of $t_{1/2}$ and t_{100} were determined from curves of the type in the upper part of the figure.

Figure 12. Dependence of the contact angle of water on the duration of heating in distilled water (pH 5-7) for the polymers PE-H (extracted), $\text{PE-CO}_2\text{H}$, and $\text{PE}[\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{H}]$.

dependence of the contact angle of water (pH 1) on time of heating in perfluorodecalin (100 °C) for PE-H, PE-CO₂H, and PE[CO₂C₈H₁₇]. The figure also shows the data for PE-CO₂H that had been treated in water (pH 6-7, 100 °C, 5 min, then dried) prior to heating in perfluorodecalin.

Top: Dependence of the contact angle of water (pH 1) on time of heating in distilled water (100 °C, pH 6-7) for PE-CO₂H samples that had previously been heated in perfluorodecalin for various lengths of time. Bottom: Dependence of the contact angle of water (pH 1) as a function of the time of heating of PE-CO₂H in vacuum (100 °C) prior to treatment in distilled water (100 °C, pH 6-7, 30 min).

Dependence of the contact angle of water (pH 1) on samples of PE-CO₂H that had been treated in distilled water (pH 6-7, 100 °C, 30 min) and then heated in perfluorodecalin (100 °C) for various lengths of time. The contact angle prior to treatment in perfluorodecalin is indicated by the treatment in water.

Dependence of the contact angle of water (pH 1) on samples of PE-CO₂H that had been treated in distilled water (pH 6-7, 100 °C, 30 min) and then heated in perfluorodecalin (100 °C) for various lengths of time. The contact angle prior to treatment in perfluorodecalin is indicated by the treatment in water.

Figure 17. Schematic illustration of depth profiling using contact angles. PE[CH₂OH] is first allowed to reconstruct (100 °C, vacuum) for various lengths of time (left). The "buried" -OH groups are allowed to react with perfluorinated anhydrides of various sizes (center and right). The contact angle (H₂O, pH 1) is determined on these interfaces to test the character of the θ interphase. The contact angle of water on unoxidized polyethylene is 103°.

Figure 18. Depth profiling using contact angles as described schematically in Figure 17. The contact angle (after reaction) is monitored as a function of the time of heating of PE[CH₂OH] (100 °C, vacuum) prior to reaction with perfluorinated anhydrides.

Figure 19. The emission maximum ($\lambda_{\max}$, top) and $pK_{1/2}$ (bottom) of PE[dansyl] (PE[CO₂H][CONH-dansyl])⁷ as a function of the time of heating (100 °C) in various solvents. Samples were removed from the solutions in which they were heated and were examined at room temperature in distilled water.

Figure 20. Top: Dependence of the emission maximum ($\lambda_{\max}$) on the pH of the solutions in which PE[dansyl] (PE[CO₂H][CONH-dansyl])⁷ was heated for 60 min at 100 °C. Samples were removed and analyzed in distilled water at room temperature. Bottom: Dependence of the water solubility, $\log S$, of the polymer on the pH of the solutions in which it was heated for 60 min.

Figure 21. Dependence of the contact angle of water (pH 1) on the time of heating for PE-CO₂H and O₂ plasma-treated polypropylene (PPP) and polyethylene (PPE) (reconstructed at 78 °C in vacuum), and for UHMW-CO₂H (ultra-high molecular weight polyethylene oxidized with chromic acid; reconstructed at 72 °C in vacuum).

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