Thermal Reconstruction of the Functionalized Interface of Polyethylene Carboxylic Acid and Its Derivatives

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1. INTRODUCTION

Chemical modification of the surface of a polymer changes its free energy of inter-action with contacting solids or liquids while leaving its bulk physical properties largely unchanged. The ability to control interfacial interactions by chemical modification of a surface is important for applications involving properties, such as adhesion,[1,6]* biocompatability,[7,9] printability,[10] static discharge,[11] that depend on wetting or on hydrophilicity.[12,13] We[14,20] and others[21,29] have studied the relations between the structures of the surfaces of surface-modified polymers and their wettability. The meaning of the phrase *structure of the surface* in this context is not sharply defined, but includes those characteristics of the solid–liquid interface—functional group types, orientation, and distribution; surface topology; bulk polymer properties—that influence wetting. These studies have led to a useful understanding of the factors that control wetting, phrased in the qualitative terms of physical organic chemistry.

Our research has explored synthetic methods for introducing organic func-tional groups at the surface of polyethylene and has examined the thermal stability of the resulting functionalized interfaces in detail.[30] We chose polyethylene for a number of reasons: low dielectric constant, absence of functional groups, trans-

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* For an example of work with surface-modified, low-density polyethylene, see Ref. 4.

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parency in many regions of spectroscopic utility, ready availability. This review summarizes our work in this area and related work from other groups.[27,31-45]

1.1. Surfaces, Interfaces, and Interphases

The field of surface chemistry encompasses a wide range of disciplines having interfacial phenomena as a common interest. The terminology of the field must therefore accommodate a wide range of systems varying in their degree of ideality (e.g., in flatness or in uniformity).

In the context of this review, the term *surface* refers to the face of a solid (or of a liquid) directly exposed to the environment, without reference to any contacting phase. The term *interface* refers to the contact between a surface and a second phase (solid, liquid, or gas). The term *interphase* refers to a surface or interface and some portion of the underlying solid.

Organic surfaces, for example, of polymers or of thin films, present difficulties in nomenclature not often encountered in inorganic systems. Some liquids penetrate or "swell" organic surfaces, creating a state of matter intermediate between solid and liquid. Since this situation defies simple and precise description, we use general terms such as *interfacial region* to emphasize the complex, environmentally determined nature of the interface.

We have used a range of analytical techniques to characterize the interface of surface-modified polyethylene. Measurement of solid–liquid contact angles (θ),[15,20,46,50] X-ray photoelectron spectroscopy (XPS),[15,20,51] attenuated total reflectance infrared spectroscopy (ATR-IR),[20,30,52] and fluorescence spectroscopy[15,17] have been especially useful. Each of these techniques provides information about the constitution of a layer of different thickness at the polymer surface.

For clarity, it is convenient to define different "interphases" associated with the depth sensed by the various analytical tools available for probing the functionalized surfaces (Fig. 1). The "θ interphase" refers to the outer 5–10 Å of a solid — the portion relevant to wetting *(vide infra)*. Likewise, the "XPS interphase" refers to approximately the outer 50 Å — the portion sensed by X-ray photoelectron spectroscopy.[51]* The "ATR-IR interphase," the deepest interphase of interest, refers to the outer micron or more.[52] We were particularly interested in comparing the information provided by contact angles and XPS, since these techniques are the most sensitive to the composition of the *outermost* part of a surface.

In some cases, functional groups too deep to influence wetting — that is, outside the θ interphase — are nonetheless accessible to reagents in solution. We refer to the portion of the solid where this type of interaction is possible as the "sub-θ interphase." The depth of the sub-θ interphase is determined by permeability, pore structure, and liquid–solid interactions, and is generally less well defined than those associated with analytical techniques. The depth of the sub-θ interphase is intermediate between those of the XPS and ATR-IR interphases.[20]

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* *XPS interphase* is an approximate term; the intensity of the signal for a given atom type is usually assumed to drop off exponentially as a function of depth: $I_d = I_0 \exp(-d/\lambda)$, where d is the distance of the atom of interest from the surface, λ is the inelastic mean free path of the photoelectron in the medium of interest, and I_d and I_0 refer to the same experimental geometry.
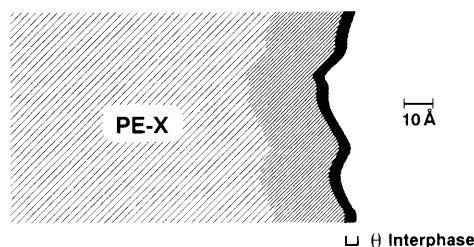
FIGURE 1. Schematic illustration of the various "interphases," labeled with the associated analytical techniques, making up the interfacial region of PE-CO$_2$H and its derivatives.

1.2. Synthesis of Surface-Modified Polyethylene and Nomenclature Used in Describing These Systems

Modification of the surface of polyethylene (PE-H) is straightforward, albeit not always easily controlled. Several reagents and methods have been reported for the oxidative derivatization of the surface of PE-H, including chromic acid, oxygen (or other gaseous) plasmas, flames, and graft polymerization.[53] Most of our work has focused on PE-H oxidized with aqueous chromic acid.

Treatment of low-density PE-H ($\rho = 0.919$ g/cm^3; melt index $= 2$) with aqueous chromic acid introduces a thin (10–20 Å) interfacial region composed of carboxylic acids (30%), ketones and aldehydes (20%), and unreacted methylene groups (50%).[15,17,18,20] The presence of oxidized functional groups, particularly the carboxylic acid moieties, greatly modify the interfacial properties of this material. The carboxylic acid groups are also useful as the starting point for further chemical elaboration (Scheme 1).
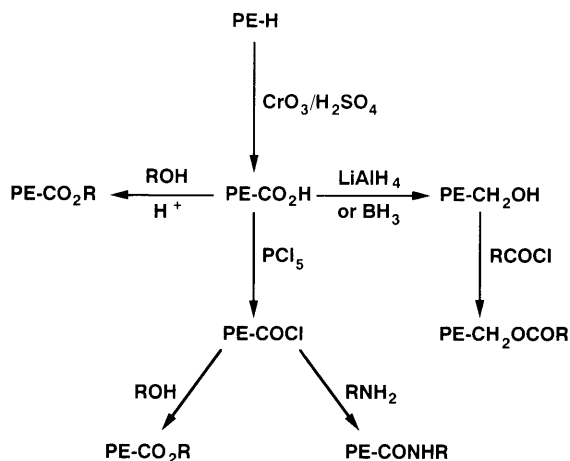
SCHEME 1. Representative reactions used to convert the surface of polyethylene (PE-H) to "polyethylene carboxylic acid" (PE-CO$_2$H) and derivatives. Reprinted with permission from reference 14. Copyright © 1988 Data Trace Chemistry Publishers.

FIGURE 2. Scanning electron micrographs of PE-H (a), and PE-CO$_2$H oxidized for 1 min (b) or for 6 min (c) with aqueous chromic acid at 72 C. Reprinted with permission from reference 18. Copyright © 1985 American Chemical Society.

To emphasize the central role of the carboxylic acid groups of polyethylene oxidized with chromic acid, we call the oxidized material *polyethylene carboxylic acid* (PE-CO$_2$H). By analogy, we designate *derivatives* of this material as PE-X, where X specifies the surface-bound functional groups. Oxidation with chromic acid etches the polymer, leaving the surfaces of PE-CO$_2$H and its derivatives rougher than that of PE-H. Figure 2 shows scanning electron micrographs of PE-H and of PE-CO$_2$H (oxidized with chromic acid at 72 C, for 1 min and for 6 min) for comparison.

1.3. The Role of Thermodynamics in Determining Interfacial Properties and the Kinetics of Their Approach to Equilibrium

In any application of a modified polymer surface, a critical concern is the stability of the surface. The phrase *modified polymer surface* implies the existence of two distinct, spatially separated regions of the polymeric solid: the bulk of the material and the interfacial region containing the functional groups introduced by the modification. Concentration of the functional groups at the solid vapor or solid–liquid interface may or may not be thermodynamically stable. Diffusion of these groups into the bulk will almost always be entropically favorable.* Enthalpically, they may be more stable at (or in) the solid–vapor or solid–liquid interface, depending on the details of the interactions of the groups comprising bulk, interface, and any contacting condensed phase.[54] The *apparent rate* at which a system not at equilibrium moves toward equilibrium depends on the probes being used to examine the system. In particular, the solid–liquid interface of a surface-modified polymer will reach what appears to be an equilibrium state more quickly when observed using wetting to probe the interface than when using ATR-IR. Only small motions (< 10 Å) of the functional groups are required to bring a solid–liquid interface to apparent equilibrium by wetting; much larger motions ($\approx 10^6$ Å) are

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* We note, however, that the combinatorial (ideal) entropy of mixing is usually very small for mixtures of polymers.

required to achieve a spatial distribution that appears to be close to equilibrium by ATR-IR.[52]

The thermal reconstruction of surface-modified polyethylene provides a convenient (although complex) system for kinetic investigation, since the rates at which the interfaces reconstruct are slow at room temperature but rapid at temperatures approaching 100 C (the melting point of polyethylene is about 115 C). Our studies of the kinetics and mechanism of reconstruction focused on several questions: Is the instability of the interfaces due to chemical reactions of the oxidized functionality, to loss of short chains bearing this functionality (by volatilization or solubilization), to diffusion of this functionality into the bulk of the polymer, or to small conformational changes of the functional groups at the interface? What are the driving forces that lead to thermal reconstruction in these systems?

At the outset of this work, we recognized three possible driving forces for diffusion of polar functionality into the bulk of the polymer: minimization of interfacial free energy, entropy of mixing (passive diffusion), and relaxation of mechanical stresses introduced during manufacture of the films.

The central conclusions from our work are that (1) reconstruction initially involves conformational changes of the polymer chains in the interfacial region, driven by the tendency to minimize interfacial free energy; and (2) in a slower process, interfacial functional groups passively diffuse into the bulk of the polymer. As expected, the initial composition of the interface (the surface of the polymer and any contacting phase) plays a critical role in determining the composition of the interface at equilibrium and the rate at which the system reaches equilibrium.

2. WETTABILITY AS A PROBE OF SURFACE STRUCTURE

The sensitivity of studies of wetting to the composition of the outermost part of a surface make it, in principle, a valuable method for monitoring reconstruction. In practice, however, detailed interpretation of contact angles, especially on polymer surfaces, is difficult because the factors that determine γ_{sl} and γ_{sv} [Eq. (1)] are only partially defined, since the surfaces are heterogeneous and rough. To aid in interpreting the relation between the structure of an interface and its wetting behavior, we have explored some structurally well-defined model systems, namely ordered monolayers of n-alkanethiols on gold.

2.1. Contact Angles: Definitions and Background

A solid–liquid contact angle is the angle formed at the three-phase contact of a drop of liquid with a surface.[46 50] An advancing contact angle (θ_a) is the static, kinetically stationary angle formed after a drop has advanced across a surface, for instance, after liquid has been added to the drop. A receding contact angle (θ_r) is the angle formed after a drop has receded across the surface, for instance, after liquid has been removed from the drop. The contact angles presented in this chapter are *advancing* contact angles. The contact angles on surface-modified polyethylene, presented in this chapter, were measured by the sessile drop technique.[47]

The contact angles on monolayers on gold were measured either by the sessile drop or a related technique.[55] Although the different experimental techniques used to measure θ_a give different values, the qualitative trends of most interest in our work are largely independent of the technique used.

Hystereses in the wetting experiments [$\theta_a - \theta_r$, or correspondingly, $\Delta(\cos \theta) = \cos \theta_a - \cos \theta_r$] on surface-modified polyethylene were high ($40-90°$)[56] in all cases, indicating that the systems were not at equilibrium. We have not, however, studied this aspect of the system in detail. According to most descriptions, both theoretical and empirical, the causes of hysteresis include heterogeneity and roughness of the surface,[48,57] and reorganization of functional groups in the interfacial region.[36,40,45,58,60]

Young's equation [Eq. (1)] relates $\cos \theta$ to the local balance of forces operating at the three phase line (Fig. 3):[61]

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \tag{1}$$

where

θ = contact angle

γ = interfacial free energy, where the interface is
     specified by subscripts: s = solid, l = liquid,
     v = vapor

The quantity $\cos \theta$ is proportional to the difference in interfacial free energies ($\gamma_{sv} - \gamma_{sl}$); we therefore report values of $\cos \theta$, rather than θ, in discussions of surface free energies. Since contact angles are related to interfacial free energies, measurements of the wettability of polymer surfaces can provide qualitative information about the identity, distribution, and orientation of interfacial functionality. The utility of these measurements as probes of functional group identity and position is limited, however, by the importance of additional factors that affect contact angles: roughness and morphology of the surface, swelling of the solid by the contacting liquid, and heterogeneity in the chemical environment of functional groups in the interfacial region. Inferences relating wetting to surface composition are most reliable when surfaces of comparable topology are compared.

The ways in which roughness can affect contact angles are many and complex: important parameters include the scale of length and the topological details of the roughness.[57,62-64] Approaches to describing the relation between roughness and contact angles have, to this point, been empirical and/or approximate. The most common approach to describing the effect of roughness is to treat the observed (i.e.,
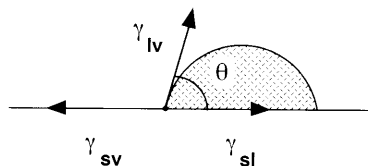

FIGURE 3. Schematic illustration of a sessile drop of liquid in contact with a solid surface, showing important parameters: the contact angle θ; the solid-liquid interfacial free energy γ_{sl}; the liquid-vapor interfacial free energy γ_{lv}; and the solid-vapor interfacial free energy γ_{sv}.

apparent) value of $\cos \theta_{obs}$ as the product of an *intrinsic* $\cos \theta_i$ and a "roughness factor" r [Eq. (2)]:[65 68]

$$\cos \theta_{obs} = r \cos \theta_i \tag{2}$$

The quantity r is defined as the ratio of the actual surface area to the area projected from the surface onto a flat, parallel surface. In addition to the effect of roughness described by Eq. (2), a drop of liquid in contact with a sufficiently rough surface can trap pockets of air to form a "composite" [(solid + air)–liquid] interface, thereby raising the observed contact angle.

For polymers, the morphology of a surface can play a significant role in determining its wetting behavior. Schonhorn and Ryan[27,69] showed that the critical surface tension of wetting (γ_c),* and hence θ_a, on polyethylene depends strongly on the degree of crystallinity in the interfacial region. Although we have not measured the rates of etching by chromic acid of amorphous and of crystalline PE-H, we expect that they are different. Preferential etching of one of these regions (presumably the amorphous) may therefore modify the interface — in its roughness and crystallinity— of the polymer in its wetting behavior.

Many hydrocarbon and halocarbon solvents penetrate or "swell" the interfacial region of PE-CO_2H and its derivatives. Swelling of the interfacial region of a solid by a contacting liquid necessarily changes the composition of the interface, and makes the interpretation of wetting data difficult. For this reason, we limited our studies of wetting on surface-derivatized polyethylene to wetting *by water*, since water does not swell polyethylene. Swelling of polyethylene by organic solvents also limits the solvents that can be used successfully in the preparation of these surfaces.

Chemical heterogeneity at a surface leads to contact angles *averaged* over the interfacial functionality.[66 68] Cassie's equation [Eq. (3)] describes this situation explicitly: $\cos \theta$ on a surface composed of regions of different composition, each having a normalized area fraction (A_i), is a weighted average of the values of $\cos \theta$ that would be observed on the pure surfaces ($\cos \theta_i$):

$$\cos \theta = \sum A_i \cos \theta_i \tag{3}$$

The lack of detailed knowledge about the spatial distribution of functional groups on the surfaces of PE-CO_2H and its derivatives complicates interpretations of wetting experiments.

2.2. Reconstruction of the Surface of PE-CO_2H: Initial Observations

The surface of unoxidized polyethylene (PE-H) is hydrophobic ($\theta_a = 103°$ for water); the surface of PE-CO_2H is relatively hydrophilic ($\theta_a = 55°$ for water at pH 1). At room temperature, the hydrophilicity of the surface of PE-CO_2H is retained almost indefinitely (months to years). At elevated temperatures ($T = 35–110°C$), however, the surface of PE-CO_2H becomes hydrophobic; its final

* The critical surface tension of wetting (γ_c) is an experimentally convenient, albeit *qualitative*, measure of γ_{sv}.[70]
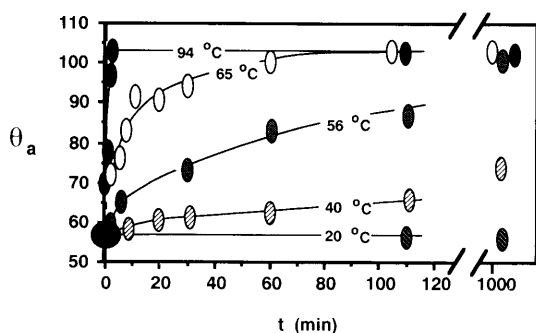
FIGURE 4. Advancing contact angles of water (pH 1) on PE-CO$_2$H as a function of the time the film had been heated at various temperatures under vacuum. Reprinted with permission from reference 30. Copyright C 1987 American Chemical Society.

state is indistinguishable from unoxidized polyethylene in its wettability by water (Fig. 4).* In earlier papers, Ter-Minassian-Saraga and co-workers had reported similar behavior for a related material, produced by oxidizing PE-H with a mixture of sulfuric acid and potassium chlorate.[28]

These observations led us to examine *how* the surface of PE-CO$_2$H (and its derivatives) reconstructs on heating. We use the term *reconstruct* broadly to include (1) "passive" diffusion of functional groups into the bulk of the polymer, and (2) conformational changes at the surface that affect its wettability.

2.3. Model Systems for Studies of Wetting: Self-Assembled Monolayers (SAMs) of Alkanethiols on Gold

The surface of PE-CO$_2$H is structurally complex, both in chemical composition and in morphological detail. The interactions between its surface and a contacting liquid phase are, consequently, also complex. For this reason, we have examined structurally well-defined—that is, chemically and morphologically homogeneous (compared to PE-CO$_2$H)—surfaces as models. These studies provided a basis for understanding the character, and the scales of length, of the interactions relevant to the study of reconstruction of polymer surfaces by measuring their wettability by water.

Long-chain alkanethiols adsorb from solution onto gold surfaces and form monolayers (called self-assembled monolayers, SAMs) in which the sulfur atoms are coordinated to gold and the hydrocarbon chains are densely packed, all-*trans*, and tilted about 30° from the normal to the surface (Fig. 5).[55,70,81]† As a result of this geometry, the organic–air interface is populated predominantly by the functional groups at the termini of the alkyl chains.

These SAMS are useful in studying the relations between microscopic structures (molecular identity and orientation) and macroscopic properties (wetting and adhesion). Synthetic organic chemistry provides techniques for systematically varying the physical properties of these SAMs by modifying the molecular precursors

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* For comparison, we treated ultrahigh molecular weight polyethylene with aqueous chromic acid and followed the reconstruction of the resulting surface by measuring contact angles of water. As expected, its surface reconstructed more slowly than did that of PE-CO$_2$H.[30]

† For adsorption of a sulfur-containing protein onto gold, see Ref. 75; for adsorption of sulfur-containing polystyrene onto gold, see Ref. 76.
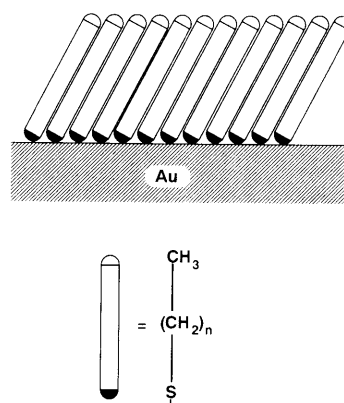
FIGURE 5. Schematic illustration of a self-assembled monolayer formed by adsorption of n-alkanethiols on gold.

from which they are assembled. This approach allows control over the identity and orientation of interfacial functional groups, along with their distance from the gold substrate and their depth from the organic–air interface.

2.3.1. Sensitivity of Wetting to the Depth of Interfacial Functional Groups

We believe that the measurement of contact angles constitutes the most surface-sensitive (if not the most easily interpretable) method now available for characterizing organic interfaces, especially solid–liquid interfaces. In order to probe the sensitivity of wetting experiments to the depth of interfacial functional groups, we have examined the variation in the contact angle of water (and other liquids) on SAMs formed by adsorption of mercaptoethers, $HS(CH_2)_{16}OC_nH_{2n+1}$, on gold, as a function of the length of the n-alkyl group C_nH_{2n+1}.[82] Figure 6 relates $\cos \theta_a$ of water to the length of the terminal alkyl chain. Contact angles on two additional surfaces are added for reference: (1) a SAM of an unsubstituted n-alkanethiol [$HS(CH_2)_{21}CH_3$] on gold, a model for an oriented hydrocarbon monolayer surface in which there are no ether functionalities, and (2) polyethylene glycol [$-(CH_2CH_2O)_n-$, PEG], a substance containing a high concentration of exposed ether groups.*

In the SAM obtained from $HS(CH_2)_{16}OCH_3$, the ethereal oxygen atom is close to the solid–liquid interface, and the surface is relatively hydrophilic ($\theta_a = 75°$). Contact angles of water on SAMs from $HS(CH_2)_{16}OR$, $R = n$-butyl or longer, in contrast, approach that on a SAM from $HS(CH_2)_{21}CH_3$ ($\theta_a = 116°$). Terminal n-alkyl groups having lengths of approximately 5 Å or more appear to shield the ethereal oxygen atom from contact with water. These results indicate that the θ interphase, for water, constitutes only approximately the outermost 5 Å of the surface.† This value (5 Å) probably reflects both through-space dipolar interactions and hydrogen bonding between the interfacial functional groups and water that has diffused into the topmost part of the monolayer.

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* Polyethylene glycol is soluble in water, so contact angles were measured immediately (~ 1 s) after application of the drops.

† The depth of the "θ interphase" depends on the choice of liquid used in the wetting studies. On SAMs with structure $Au/AuS(CH_2)_{16}OR$, hexadecane apparently senses only about the top 2 Å of the surface.
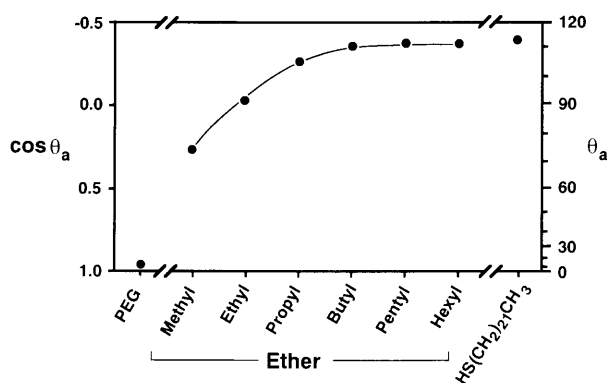
FIGURE 6. Advancing contact angles of water on SAMs of $AuS(CH_2)_{16}OR$ on gold, as a function of the length of the alkyl chain R. The contact of water on polyethylene glycol (a model for a surface in which ether groups are exposed) and on a SAM of docosanethiol on gold (a model for a surface in which ether groups are completely buried) are added for comparison. Reprinted with permission from reference 82. Copyright c 1988 American Chemical Society.

We have obtained similar results in other systems:

1. The wetting behavior of SAMs obtained from mercaptoamides $HS(CH_2)_{11}$ $CONHC_nH_{2n+1}$ varies with the length of the terminal n-alkyl chain. much as does that of the SAMs from mercaptoethers.[83]

2. The wetting behavior of SAMs obtained from simple n-alkanethiols $[HS(CH_2)_nCH_3]$ on gold also varies with the number of carbons in the alkane chain. The contact angle on these SAMs varies smoothly from about 77 for ethanethiol to about 110 for hexanethiol; the angles for longer chains are consistently between 110 and 114 . We infer that alkyl chains of approximately six carbons in length are sufficient to shield the contacting drop of water from interaction (whether van der Waals or dipole-induced dipole) with the underlying gold.* The value of six carbons is actually an upper limit, since SAMs from smaller thiols $(n < 5)$ may be more disordered (vide infra) than their longer homologues $(n > 5)$.[55,73]

3. The highly disordered surfaces of PE-CONHR and PE-CO$_2$R show variations in contact angle as a function of the length of the n-alkyl group (R) that are surprisingly similar to those observed for the ordered SAMs.[85] We infer that the size of the pendant alkyl group, and not the degree of order in the arrangement of these groups, is crucially important in masking the underlying polar functionality.[70]

2.3.2. Interfacial Order and Wetting

Since SAMs of organosulfur compounds on gold are structurally well defined. they provide useful model systems for probing the effect of interfacial structure in studies of wetting. SAMs on gold derived from mixtures of two ω-hydroxy-alkanethiols, $HS(CH_2)_{19}OH$ and $HS(CH_2)_{11}OH$, differing in the length of their polymethylene chains, show a variation in their contact angles with water as a function of the ratio of concentrations of the two components on the surface.[86] Figure 7 relates two interfacial properties ($\cos \theta_a$ and ellipsometric thickness of the adsorbed monolayer) to the ratio of concentrations of the two components in the

* Clean, bare gold is wet by water.[84]

FIGURE 7. Advancing contact angles of water on, and ellipsometric thicknesses of, SAMs derived from mixtures of $HS(CH_2)_{19}OH$ and $HS(CH_2)_{11}OH$ on gold, as a function of the ratio of concentrations of the two thiols in the solutions from which they were adsorbed. Adapted with permission from reference 86b. Copyright © 1989 American Chemical Society.
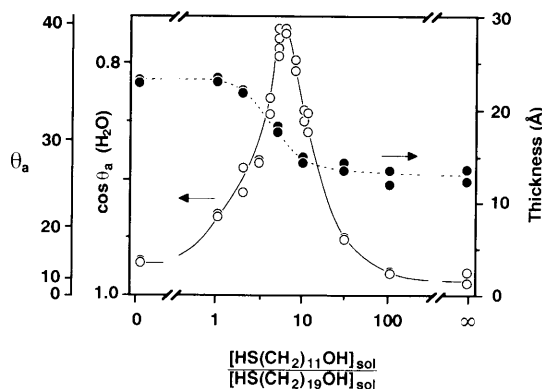
solutions from which the SAMs were formed. The ellipsometric data allow us to relate the ratio of concentrations of the two components in solution to the ratio of their concentrations on the surface. We infer from comparison of wetting, XPS, and ellipsometry that the midpoint in thickness corresponds to the SAM containing equal concentrations of the two components.* For the molecules used as components of these SAMs, ellipsometry is sensitive primarily to the average thickness of the organic film. This thickness is directly related to the average composition in monolayers composed of mixtures of molecules of different lengths (Fig. 8).

The contact angles of water on these surfaces show a marked dependence on the composition of the organic thin films. SAMs composed of the pure ω-hydroxythiols give very low contact angles (< 15), consistent with close-packed, crystalline-like arrays,† exposing hydrophilic hydroxyl groups at the surface. SAMs composed of mixtures of the thiols give contact angles (15°–40°) higher than those on the pure SAMs, and consistent with mixtures of hydroxyl and methylene groups in the θ interphase. We infer from the wetting behavior, and from infrared data,[87] that the outermost part of the mixed SAMs are disordered and liquidlike (Fig. 8). Polarized reflectance infrared spectroscopy provides a valuable method of determining the orientation of the CH_2 groups of the polymethylene chains with respect to the plane of the gold surface. We hypothesize that the disorder in the outer parts of the monolayers causes an increase in the contact angle of water, relative to that on the pure SAMs, by exposing hydrophobic methylene groups. The maximum contact angle for this system is observed on the surface nearing roughly equal concentrations of the two thiols. We infer that this composition also gives rise to the highest degree of disorder for this system at the interface. This system is important because it provides an example of the successful correlation of molecular-scale structure with a macroscopic physical property.

* Compositions of the SAMs are not the same as the compositions of the solutions from which they were formed. The preference for $HS(CH_2)_{19}OH$ at the surface is not surprising, since the longer alkyl chain provides a greater molecular surface to participate in energetically favorable van der Waals interactions with neighboring chains.

† Polarized external reflectance FTIR spectra of a SAM of $HS(CH_2)_{16}OH$ on gold showed CH_2 symmetric and asymmetric stretching vibrations at 2851 cm⁻¹ and 2919 cm⁻¹, frequencies that are indicative of crystalline packing of polymethylene chains.[73]

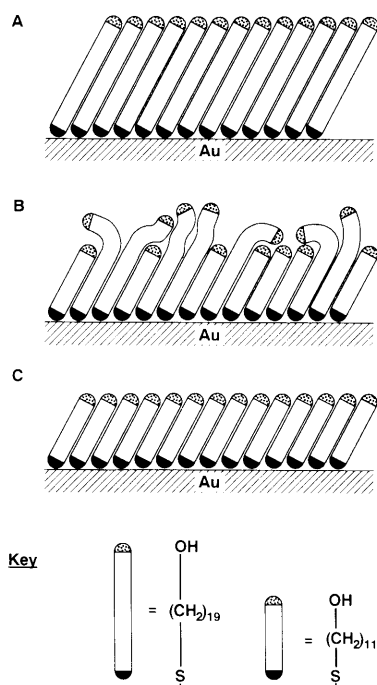FIGURE 8. Schematic illustration of SAMs of hydroxy-terminated thiols on gold: (A) SAM derived from pure $HS(CH_2)_{19}OH$; (B) SAM derived from equal amounts of $HS(CH_2)_{19}OH$ and $HS(CH_2)_{11}OH$; (C) SAM derived from pure $HS(CH_2)_{11}OH$.

2.4. Wetting Experiments on PE-X

Unlike SAMs of alkanethiols on gold, the surfaces of $PE-CO_2H$ and its derivatives are chemically and morphologically complex. Although interpreting studies of wetting at the surface of derivatized polyethylene is complicated, we have developed experiments that give qualitative (but useful) information about the θ interphase. An example is the variation of the contact angle of water on $PE-CO_2H$ with the pH of the contacting drop, an experiment we call *contact angle titration* (Fig. 9).[18,19] The surface of $PE-CO_2H$ is hydrophilic ($\theta_a = 55°$) relative to that of PE-H. Ionization of the acid groups leaves charged carboxylate ions that are more hydrophilic than neutral CO_2H groups; hence, the contact angle of a drop of water having a high pH ($\geqslant 11$) is low ($\theta \approx 20°$).

Given that SAMs formed by adsorption of ω-mercaptocarboxylic acids on gold are wet by water at all values of pH, it is curious that $PE-CO_2H$ reaches a limiting value of θ ($20°$) at low pH. In fact, we know of no derivative of $PE-CO_2H$ whose contact angle of water is less than $20°$. This fact may reflect the heterogeneity of these modified surfaces: methylene groups are probably always present in the θ interphase of these surface-modified polymers. Although the number of carboxylic acid groups per unit area in the interfacial region of the SAMs on gold are comparable to the same of $PE-CO_2H$,[17,80] the numbers and arrangements of these groups in the θ *interphases* are probably different.

At the surface of PE-X, sufficiently hydrophilic functional groups (for instance, COO^-) probably adsorb water of hydration at high values of relative humidity at which contact angles are measured. If the polar functional groups (or clusters

FIGURE 9. Variation in the advancing contact angle of water on PE-CO$_2$H as a function of pH. Data for PE-H and two nonionizable derivatives (PE-CO$_2$CH$_3$ and PE-CH$_2$OH) are included for reference. Reprinted with permission from reference 18. Copyright © 1985 American Chemical Society.
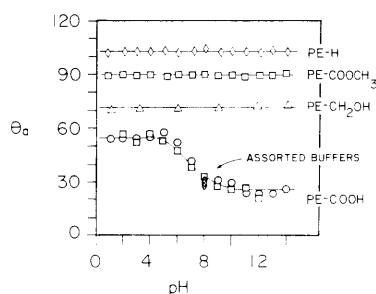
of them) are well enough separated by methylene groups, the water hydrating them may not condense; as a result, the hydrophilicity of the surface would reach a limiting value, characteristic of a mixture of "puddles" of water dispersed on a background of hydrophobic methylene groups (Fig. 10).

2.5. Sensitivity of Wetting to Small Conformational Changes Within the θ Interphase

It has long been recognized that the surfaces of polymers bearing polar functional groups can reorient, when in contact with polar condensed phases, to expose the polar functionality. This behavior has been reported for the surfaces of several polymers, including hydrogels,[40,41] oxidized polyethylene, other surface-modified polymers,[42-44] polyethylene grafted with acrylic acid[45] or other polar molecules,[60] and several unmodified polymers having polar substituents.[58] Most studies have focussed on the relation between the mobility of interfacial polar functional groups and the hysteresis in the contact angles of polar liquids.

The *ortho*-anthranilate amide (**1**) of PE-CO$_2$H provides a remarkable example of this type of behavior: it shows a surprisingly large change with pH in its wettability by water (Fig. 11).[88] At low pH ($\leqslant$4), the advancing contact angle of water is about 110 (i.e., the surface is more hydrophobic than unfunctionalized
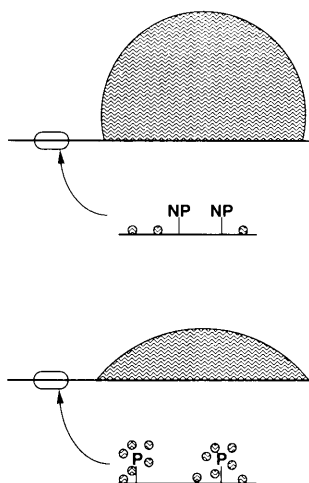
FIGURE 10. Stylized illustration of our model for the surface of PE-X near a contacting drop of water, where X is a polar functional group (P) and where it is a nonpolar functional group (NP). The small filled circles represent adsorbed water molecules. The polar groups are fully hydrated, but well enough separated so that the water of hydration does not condense.
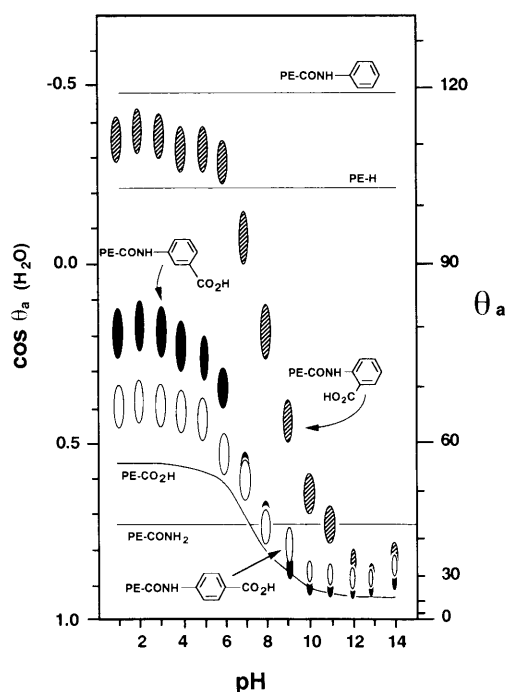
FIGURE 11. Variation in the advancing contact angle of water on PE-CO$_2$H and several of its anilide derivatives as a function of pH. Data for PE-H and PE-CONH$_2$ are included for reference. Reprinted with permission from reference 88. Copyright © 1988 American Chemical Society.

polyethylene); at high pH ($\geqslant 12$), it is ca. 33°. The *meta-* and *para-*isomers show less pronounced variations, though larger than that of PE-CO$_2$H.

The difference in the contact angles of water (low pH) between **1** and unfunctionalized polyethylene (PE-H) cannot be interpreted solely in terms of hydrophobicity, since the surface of **1** is rougher than that of PE-H (see Section 2.1). Figure 11 includes data for surfaces bearing the unsubstituted anilide amide (PE-CONHC$_6$H$_5$, **2**) and for the parent amide (PE-CONH$_2$) for comparison. The contact angle of water (pH $\leqslant 4$) on **2** is only 9° higher than that on **1**, suggesting that the phenyl ring efficiently shields *both* the amide and carboxylic acid groups of **1** from the contacting drop of water. The contact angle of water on PE-CONH$_2$ ($\theta_a = 43°$; invariant with pH) provides an indication of the degree to which the hydrophilic amide group is shielded by the phenyl ring in **1** and **2**. The high hydrophobicity of **1** and **2**, despite the presence of polar amide and acid groups, is in qualitative agreement with the data from SAMs on gold derived from HS(CH$_2$)$_{16}$OC$_n$H$_{2n+1}$: a nonpolar organic group having about six carbon atoms seems able largely to shield a polar group from a contacting drop of water.

We believe that the large decrease in the contact angle of water on **1** (as the pH of the contacting drop is varied from 1 to 14) is due to a conformational change of the amide groups concomitant with ionization of the carboxylic acid moieties at the solid–liquid interface (Scheme 2). We suggest that when in contact with acidic water, **1** adopts conformation **3**, burying the polar functionality; when in contact with basic water, **1** adopts conformation **4**, exposing the polar functionality and allowing solvation of the carboxylate ions. We attribute the preference for conformation **4** to the favorable heat of solvation of the carboxylate ion. Rationalizing

3   **4**
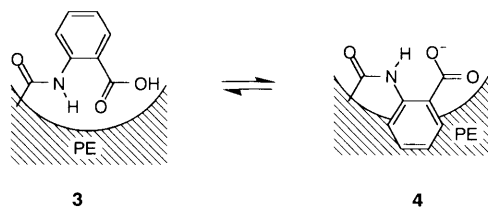
SCHEME 2. Proposed conformational changes by **1** when in contact with water at acidic or neutral (**3**) and at basic (**4**) pH's. Reprinted with permission from reference 88. Copyright ©️ 1988 American Chemical Society.

conformation **3** is more difficult: why should **1** adopt a conformation that minimizes energetically favorable polar interactions and hydrogen bonding between the amide–acid groups and the contacting water? One possibility is that strong hydrogen bonding (amide–amide, acid–amide, and acid–acid) between the functional groups present at the surface of **1** make it possible for this material to present a low-energy surface composed predominantly of aromatic $C-H$ bonds. The relatively low contact angle of water (pH 1, $\theta_a = 84°$) on the N-methyl derivative of **1**, which cannot take part in hydrogen bonding involving $N-H$ moieties, may reflect the importance of such interactions.

3. RECONSTRUCTION OF THE INTERFACE OF PE-CO₂H AND DERIVATIVES ON HEATING

With the background in Sections 1 and 2, the remainder of this chapter describes experiments with which we and others have examined the thermal mobility of functional groups in polyethylene, especially in the interfacial region. The reactions presented in Scheme 1 provided versatility in controlling some of the parameters in the experiments, particularly the polarity and size of the surface-bound functional groups. Several characteristics of the surfaces, however, could not be controlled: microscopic roughness, and chemical and morphological heterogeneity.

3.1. Comparison of Results from Wetting and XPS

Figure 12 shows the contact angles of water (measured at both pH 1 and 13) on PE-CO₂H as a function of the time of heating (at 100°C) under argon and in vacuum; XPS data for the oxygen 1s (O_{1s}) signal are included to provide complementary information about the evolution in composition of the interfacial region on heating at approximately the same temperature (106°C).

Several points deserve comment. Water at pH 1 ceases to sense the hydrophilic functionality of PE-CO₂H after it has been heated at 100°C for 5 min; samples heated under argon and in vacuum are indistinguishable in their wetting behavior. We attribute the change in wetting behavior on heating to diffusion of the polar functionality into the bulk of the polymer and out of the θ interphase. Water at pH 13 ceases to sense the polar functionality only after about 15 min on heating at 100°C. The greater apparent depth sensitivity of wetting by basic water (relative to that by acidic water) may reflect long-range electrostatic interactions between the
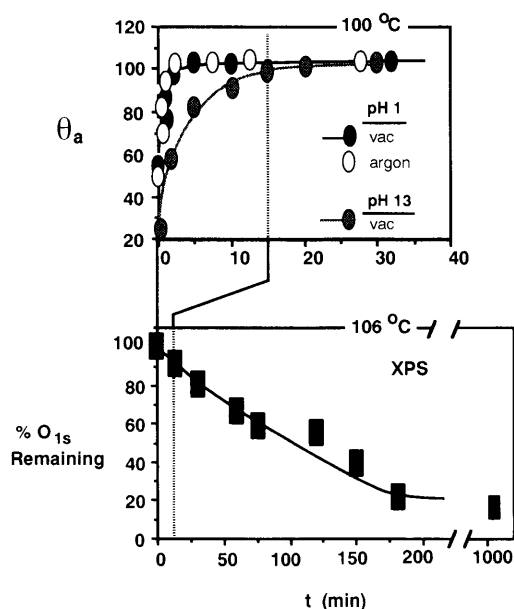
FIGURE 12. (Top) Advancing contact angles of water (pH 1 and 13) on PE-CO_2H as a function the time the film had been heated at 100 C. Data are included for samples heated in vacuum and heated under argon. (Bottom) The normalized intensity of the O_{1s} XPS signal from PE-CO_2H as a function of the time the film had been heated at 106 C. Reprinted with permission from reference 30. Copyright c 1987 American Chemical Society.

polar aqueous phase and the carboxylate ions, or reconstruction of the interface driven by solvation of the carboxylate ions.

The oxygen content of the interfacial region of PE-CO_2H. as measured by XPS, and in contrast to that inferred from wetting, diminishes only slightly (by about 5%) during the first 5 min of heating. We attribute this difference in the apparent rates of reconstruction measured by wetting and by XPS to the different depth sensitivities of these techniques. After 5 min of heating, the polar oxygen-containing groups have diffused out of the θ interphase but still remain (for the most part) within the XPS interphase. The decrease in intensity of the O_{1s} signal is due to attenuation of the signal (scattering of photoelectrons) by methylene groups between the oxygen atoms and the detector. We attribute the residual O_{1s} signal remaining after 1000 min of heating to contaminants in the film blooming to the surface.*

3.2. Results from ATR-IR

Attenuated total reflectance infrared spectroscopy samples a thick portion of the polymer interphase ($> 10,000$ Å), and allows quantitative analysis of functional groups within that region. Results from ATR-IR spectroscopy suggest that the mechanism of the disappearance of polar functionality is diffusion into the bulk of the polymer; we found no evidence for volatilization or for chemical reactions of the polar functionality. Figure 13 shows ATR-IR data for polyethylene films treated under a variety of conditions. Before extraction with methylene chloride, the film has several peaks between 2000 and 1500 cm^{-1}; we attribute these peaks to film

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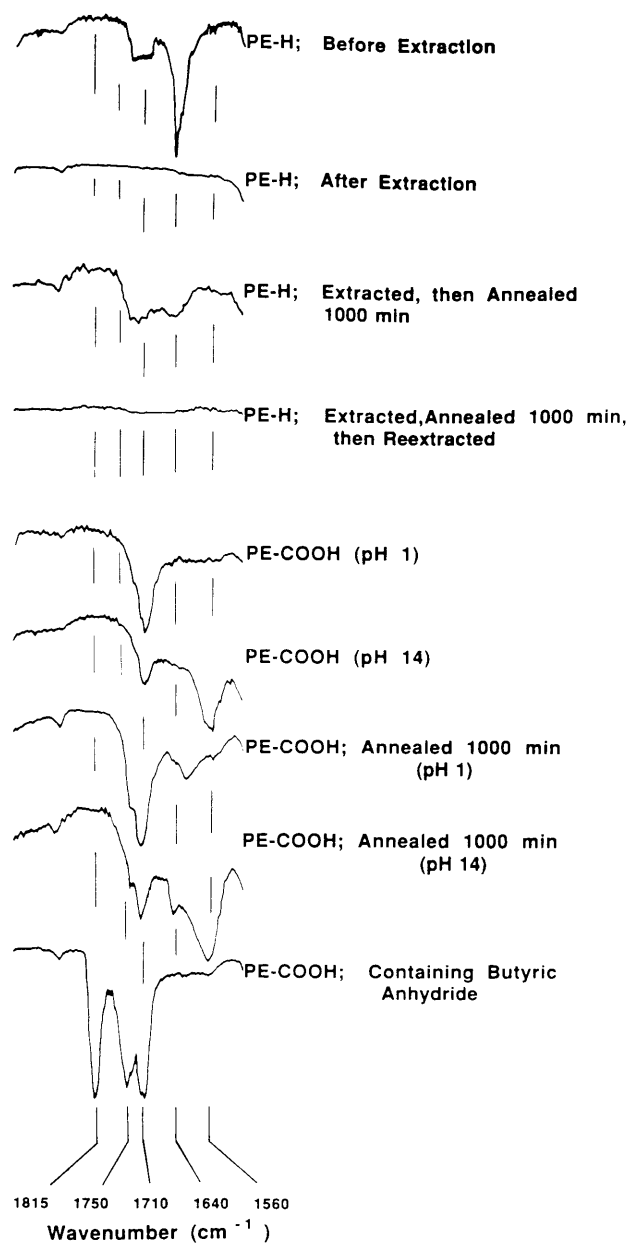* Additives introduced during manufacture of the film include antioxidants, slip agents, and antistatic agents.

FIGURE 13. The 2000–1500 cm⁻¹ regions of ATR-IR spectra of PE-H and PE-CO₂H, treated under a variety of conditions. Reprinted with permission from reference 30. Copyright © 1987 American Chemical Society.

additives. Extraction with methylene chloride removes the contaminants giving rise to these peaks. Heating the extracted film at 100°C for 1000 min causes the peaks to reappear; reextraction again causes them to disappear. These results are consistent with the idea that contaminants bloom to the surface of these films on heating. The ATR-IR spectrum of fully protonated PE-CO₂H shows a broad absorption centered at 1710 cm⁻¹ that we attribute to the C=O stretching modes of the carboxylic acids and ketones and aldehydes. Deprotonation of PE-CO₂H

with water at pH 14 shifts approximately 75% of the $C=O$ peak to lower energy, characteristic of carboxylate ions; the remainder, assigned to the ketone–aldehyde moieties, remains unchanged. After heating PE-CO_2H at 100°C for 1000 min, its ATR-IR spectra (protonated and deprotonated) are approximate superpositions of the spectra of PE-CO_2H and annealed PE-H (blooming film contaminants).

The blooming of film contaminants to the surface of PE-CO_2H on heating prevents straightforward quantitation of the amount of carboxylic acid before and after heating. We note, however, that the ratio of the integrated absorbance at 1560 cm^{-1} (CO_2^- groups) to that at 1710 cm^{-1} (ketone–aldehyde and CO_2H groups) is the same (~ 0.75) in heated and unheated samples. These results indicate that the CO_2H groups do not volatilize on heating to 100°C.

Another interesting aspect of the spectrum of the sample heated and then treated with base is that although the CO_2H groups are well outside of the θ and XPS interphases, these groups are still accessible to aqueous hydroxide ion. We have studied this phenomenon in detail, and we designate the portion of the film where it is relevant as the *sub–θ interphase* (Section 1.1).[20]

An alternative explanation for the changes in the wetting behavior of PE-CO_2H on heating is that the carboxylic acid moieties in the interfacial region can condense to form anhydrides. To test this hypothesis, we treated a sample of PE-CO_2H with butyric anhydride and compared its ATR-IR spectrum to that of reconstructed PE-CO_2H. The butyric anhydride diffused into the polymer, giving rise to well-separated peaks at 1815 and 1750 cm^{-1}. These peaks are absent in all of the other spectra, indicating that condensation of carboxylic acid groups to anhydrides does not occur to a significant extent under our experimental conditions.

3.3. Kinetic Model for Reconstruction of the Interface of PE-CO_2H

We have examined in detail the kinetics of reconstruction of the interface of PE-CO_2H. We treated the reconstruction as a thermally activated process, whose kinetics could be described by the Arrhenius equation

$$D = A_D \exp\left(\frac{-E_{a,D}}{RT}\right) \tag{4}$$

where

$D = $ rate of diffusion

$A_D = $ preexponential factor

$E_{a,D} = $ energy of activation for diffusion

This approach had important advantages. First, it was the simplest and most straightforward approach available; the reconstruction of the interfacial region of PE-CO_2H is complex, and describing its kinetics by even this simple model required several approximations. Our limited control over the parameters of the experiment (for example, the molecular weight of the diffusing species) prevented us from using more sophisticated theories.[89–92] Second, it allowed useful comparisons
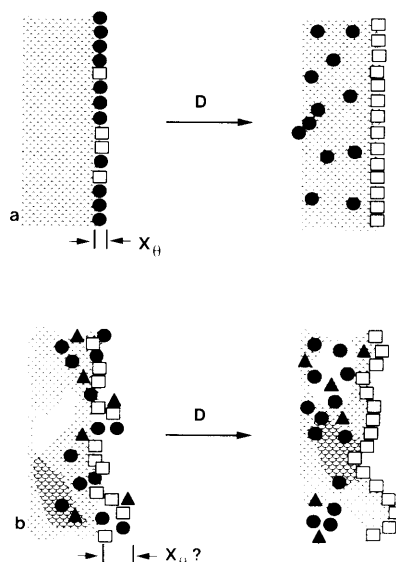
FIGURE 14. Schematic illustration of our model for the interfacial region of PE-CO$_2$H, and of the actual interfacial region. The filled symbols represent polar functional groups; the open symbols represent nonpolar ones. X_0 denotes the thickness of the θ interphase. The lower figure depicts the heterogeneity in morphology and in chemical composition, characteristic of the actual interface of PE-CO$_2$H. Reprinted with permission from reference 30. Copyright © 1987 American Chemical Society.

to previous work describing diffusion in bulk polyethylene.[93] We were interested, for instance, in how the energy of activation for diffusion ($E_{a,D}$) from a surface differed from that in the bulk.

We followed the diffusion of the polar functional groups away from the surface by measuring the advancing contact angle of water on the films as a function of the amount of time they had been heated at various temperatures. Since the θ interphase extends only a short distance into the polymer, these measurements selectively monitored diffusion in the interfacial region close to the surface (within 5 10 Å).

Deriving diffusion constants (D) from contact angles required several approximations. Figure 14 schematically compares the actual interface of PE-CO$_2$H to our model for the interface. First, we treated the system as if the surface were flat and composed of homogeneously distributed, noninteracting functional groups. The actual interface is rough, at least on the scale of 1000 Å, and there is no reason to believe that the functional groups are evenly distributed on the microscopic level.* The carboxylic acid groups may interact strongly via hydrogen bonding.[†] Second, we treated the θ interphase as a mixture of only two types of functionality: polar (P) groups and nonpolar (NP) groups. The actual interface, however, is a mixture of many types of polar (carboxylic acids and aldehydes–ketones) and nonpolar (predominantly methylene) groups. Third, we assumed that the bulk polymer was a homogeneous, isotropic medium. The bulk polymer is actually heterogenous and

* An added complication is that heating may change the roughness of the surface. There are no gross morphological changes on heating (as judged by SEM), but changes on a much smaller scale of length than is visible via SEM may be important. We note that the contact angle of water on reconstructed PE-CO$_2$H is the same as that on PE-H, a value lower than that on *unreconstructed* PE-CO$_2$C$_x$H$_{17}$.
[†] The ATR-IR spectra of these films were consistent with the presence of hydrogen-bonded dimers of the carboxylic acid groups.

locally anisotropic: there are crystalline and amorphous regions, and some polar functionality is distributed throughout the film. Finally, we assumed that all of the functional groups in the θ interphase affect the wetting behavior to the same extent, and that groups outside the θ interphase do not affect wetting. As the experiments with **1** showed, however, wetting can be affected strongly by subtle conformational changes within the θ interphase.

We treated $\cos \theta$ as a linear combination of molecular components, arising from the individual functional groups that make up the surface:[19]*

$$\cos \theta = \sum N_i \cos \theta_i \qquad (5)$$

where

$i = $ P (polar) or NP (nonpolar) functional group

$N_i = $ normalized, fractional area of the interface made
up of the ith functional group

This assumption is not correct, at least for interfaces composed of carboxylic acid and methyl groups;[94] it is, however, a useful first approximation and greatly simplifies the kinetic analysis.

By defining a normalized value of $\cos \theta$, $f_{\cos \theta}$ [Eq. 6], expressing it in terms of N_i, and combining it with the equation describing diffusion from a planar surface[‡] [Eq. 7], we extracted diffusion constants (D) for the interfacial reconstruction of PE-CO$_2$H at several temperatures:

$$f_{\cos \theta} = \frac{\cos \theta_t - \cos \theta_i}{\cos \theta_{t_0} - \cos \theta_i} \qquad (6)$$

$$\frac{N(x, t)}{N(x = 0, t = 0)} = (\pi D t)^{-1/2} \exp \left(\frac{-x^2}{4Dt} \right) \qquad (7)$$

Figure 15 shows the data plotted according to the Arrhenius equation from 20 to 100 C: they do not fit a single straight line. A least-squares fit to the data over the entire range of temperature gives an activation energy for diffusion, $E_{a, D}$, of 37 kcal/mol. A least-squares fit to the data in only the low-temperature regime gives a value for $E_{a, D}$ of 50 kcal/mol. The data at high temperatures may be suspect since significant reconstruction may have occurred in the time required for the films to equilibrate at these temperatures.

Other groups, who had previously found similar results, suggested alternative explanations associated with the onset of melting of the polymer. The lowest temperature at which Ter-Minassian-Saraga and co-workers observed reconstruction of

---

* This equation is based upon Cassie's model for heterogeneous interfaces [Eq. (3)].[6]

‡ The number of ith functional groups within the θ interphase is given by $\int_0^{x_0} N(x, t) \, dx$, where x_0 equals the depth of the θ interphase. For the calculations of diffusion constants, we approximated this value as 5 Å.[82]
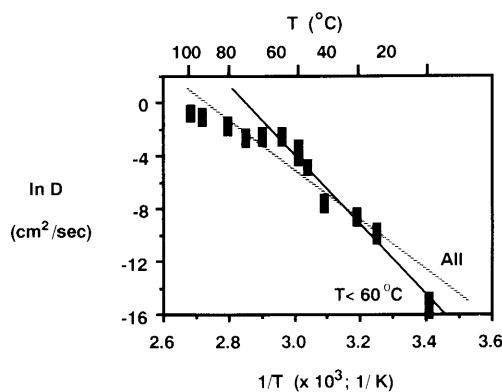
FIGURE 15. Arrhenius plot for the reconstruction of PE-CO_2H in the temperature range of 20–100 C. The solid line is a least-squares fit to the low-temperature ($\leqslant 60$ C) data; the dashed line is a least-squares fit to all of the data. Reprinted with permission from reference 30. Copyright c 1987 American Chemical Society.

the surface of their oxidized polyethylene (Section 2.2) coincided with the onset of the melting transition given by differential scanning calorimetry (DSC).[33]

Pennings and Bosman measured the rates of thermal "relaxation" of the surface free energy of polyethylene and other polymers that had been compression-molded against gold foil.[39] Their plot of the rate of relaxation for polyethylene. derived from the measurement of contact angles. as a function of 1 T. showed a discontinuity at 52 C; the data above this temperature fell on a straight line. and the data below it fell on a different straight line. The discontinuity occurred at approximately the same temperature as the onset of the melting peak given by DSC. Although the process that they were studying the conversion of crystalline to amorphous polymer is formally different from the reconstruction of PE-CO_2H. both processes involve conformational changes and diffusion of polymer chains in the interfacial region.

Klein and Briscoe reported a discontinuity in the plot of log D versus 1 T for diffusants with long alkyl chains in the bulk of branched. low-density polyethylene: the discontinuity occurred at 1 T_m (T_m = melting point of the polymer $\approx$ 107 C).[93] Above the melting point. the data fit a single straight line: below the melting point however. the data did not fit a straight line. The authors attributed the anomalous low temperature behavior to "complex morphological changes" associated with the onset of melting. They also cited dimerization of diffusants (stearamide in one case) as a potential complication at low temperature.

The values for $E_{a,D}$ derived from the plot in Fig. 15 are significantly higher than those reported by Klein and Briscoe for diffusion of molecules with long alkyl chains through the interior of polyethylene. The activation energy for diffusion of behenyl behenate, $CH_3(CH_2)_{20}CO_2(CH_2)_{21}CH_3$, through semicrystalline. low-density polyethylene is 23 kcal/mol.[93] The values of activation energy from the annealing experiments reported by Pennings and Bosman were 8 kcal/mol above 52 C and 31 kcal/mol below it. Baszkin and Ter-Minassian-Saraga did not report an activation energy for the thermal reconstruction of PE-H oxidized with sulfuric acid–potassium chlorate.

These differences in activation energy may be due, at least in part, to hydrogen bonding between carboxylic acid groups at the surface of PE-CO_2H. The enthalpy of dissociation for the H-bonded dimer of stearic acid in a solution of paraffin is

13.4 kcal/mol.[95] The contribution of the surface free energy (γ'_{sv}) of the polymer to the activation energy for diffusion away from the solid–vapor interface is small ($\leqslant 5\%$).*

3.4. Reconstruction of the Interface of Derivatives of PE-CO₂H

Although the contribution of γ_{SV} to $E_{a,D}$ is small *for* PE-CO₂H, the minimization of interfacial free energy is, we presume, an important driving force in the reconstruction of the interfaces of PE-CO₂H and its derivatives. A series of experiments with derivatives of PE-CO₂H that varied in their degree of hydrophobicity supported this hypothesis.

The hydrophobicity of a surface is a function of its interfacial free energy. The value of cos θ is proportional to the difference in interfacial free energies, $\gamma_{sv} - \gamma_{sl}$ [Eq. (1)]. These two terms are not separable using wetting data, but at extreme values of cos θ (large positive or negative), one of the two components is dominant. For contact angles of water on these surfaces, large positive values of cos θ (small values of θ) indicate polar surfaces with high surface free energies (mainly γ_{sv}); large negative values of cos θ (values of $\theta \gtrsim 90$) indicate nonpolar surfaces with low solid–vapor interfacial free energies (γ_{sv}).

Part a of Fig. 16 shows the advancing contact angle of water on surfaces with interfacial free energies lower than that of PE-H as a function of the amount of time the samples had been heated. Part b of Fig. 16 shows the advancing contact angle of water on surfaces with interfacial free energies higher than that of PE-H as a function of the amount of time the samples had been heated. These data show the expected results: (1) all of the surfaces approach the wetting behavior of PE-H on extended heating; and (2) surfaces with interfacial free energies lower than that of PE-H reconstruct more slowly than those with interfacial free energies higher than PE-H. A plot of D versus the cosine of the initial (i.e., before reconstruction) contact angle of water, $(\cos \theta_a)_i$, for PE-CO₂H and several of its derivatives illustrates this relation (Fig. 17).

The surface of PE[CH₂OCO(CF₂)₆CF₃] reconstructed very slowly relative to the other surfaces. To determine whether the slow rate was due, in part, to steric problems associated with diffusion of a large functional group, we monitored the reconstruction of several *high* energy surfaces [poly(ethylene glycol) esters of PE-CO₂H] as a function of the size of the interfacial functional groups. Figure 18 shows the rate of reconstruction for these interfaces, as measured by two quantities ($t_{1/2}$ and t_{100}), as a function of the number of monomer units in the ester. The quantity $t_{1/2}$ is the time required, at a given temperature, for $f_{\cos\theta}$ to reach 0.5 (i.e., "half reconstructed"); t_{100} is the time required for the advancing contact angle of water to reach 100°, that is, the point at which it is experimentally indistin-

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* The critical surface tension of PE-H is 31 ergs/cm²;[96] estimating that there are about 10^{15} "molecules"/cm² occupying the surface sites, γ_c is about 0.5 kcal/mol. Unfortunately, we do not know γ_c for PE-CO₂H; it is certainly higher than that of PE-H, but probably not by more than a factor of 2 or 3. The value of γ_c reported for a 20.7:79.3 mol% copolymer of acrylic acid and ethylene is 59 erg/cm².[97] The value of γ_c reported by Baszkin and Ter-Minassian-Saraga for surface-oxidized polyethylene is 39 erg/cm².[28]
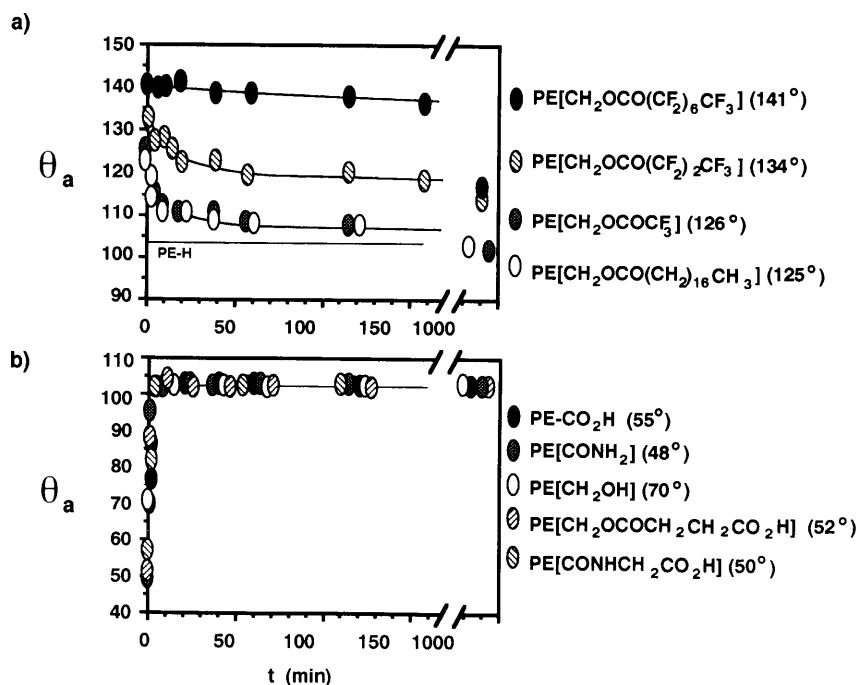
a)

b)

t (min)

FIGURE 16.   Thermal reconstruction of derivatives of $PE-CO_2H$ at 100 C in vacuum: (a) variation in contact angles of water (pH 1) for samples whose interfacial free energies are lower than PE-H as a function of the amount of time of heating; (b) variation in contact angles of water for samples whose interfacial free energies are higher than PE-H as a function of the amount of time of heating. The contact angles of water on these surfaces before reconstruction are given for reference. Reprinted with permission from reference 30. Copyright © 1987 American Chemical Society.

guishable from that on PE-H. The rate of reconstruction of longer esters ($n = 7$, 10, and 14) was significantly slower than that of the shorter esters ($n = 1$ 3). The differences, however, are not large enough to explain the slow rate observed for $PE[CH_2OCO(CF_2)_6CF_3]$. These data are consistent with the idea that the low interfacial free energy of the fluorinated surfaces impedes their reconstruction.

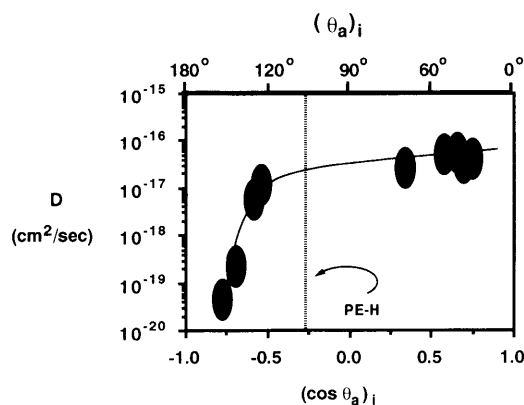The concentration of the fluorinated groups in the interfacial region of

FIGURE 17.   Diffusion constants (D) describing the reconstruction of PE-CO_2H and derivatives plotted as a function of ($\cos \theta_a)_i$, the cosine of the initial (before reconstruction) contact angle of water (pH 1). Reprinted with permission from reference 30. Copyright © 1987 American Chemical Society.
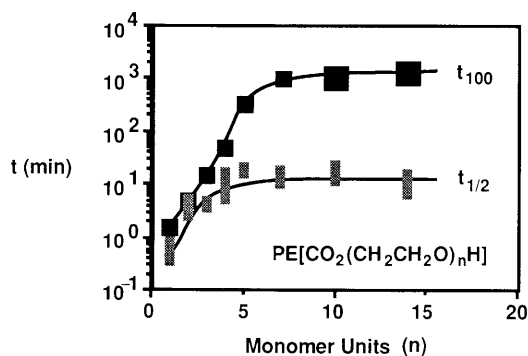
FIGURE 18. The quantities t_{100} and $t_{1\,2}$ for the esters, $PE[CO_2(CH_2CH_2O)_n)\,H]$, plotted as a function of the number (n) of ethylene glycol monomer units. The value of t_{100} is the time required for the contact angle of water (pH 1) to reach 100 upon heating at 100 C in vacuum. The value of $t^{1\,2}$ is the amount of time required for $f_{\cos\theta}$ (for water, pH 1) to reach 0.5 ("half reconstructed"). Reprinted with permission from reference 30. Copyright c 1987 American Chemical Society.

$PE[CH_2OCO(CF_2)_nCF_3]$ $(n = 2$ or 6) was significant even after extended heating. These surfaces remained more hydrophobic than PE-H, even after 1000 min at temperatures greater than 130 C. For $PE[CH_2OCO(CF_2)_2CF_3]$, about 60% of the original F_{1s} XPS signal remained after 1000 min of heating at 100 C under vacuum (Fig. 19). The low interfacial free energy of surfaces containing these functional groups apparently provides a thermodynamic preference for keeping a large concentration of these groups within the θ and XPS interphases. Similar results have been reported by others.[98, 102]

3.5. Reconstruction of the Interface of PE-CO₂H and Derivatives on Heating in Contact with Liquids

We were interested in the influence of a contacting liquid on the thermal reconstruction of the surface of PE-CO₂H and its derivatives, because the introduction of a solid–liquid interface allowed a systematic variation in interfacial free energy. This question also had practical significance, since the surfaces of these films reconstruct at room temperature when in contact with many organic solvents. Some solvents (e.g., methylene chloride, hexane) swell the interfacial region of polyethylene and its derivatives at room temperature; other solvents (e.g., toluene or hexadecane) dissolve the films at elevated temperatures. The advancing contact angle of water on the surface of PE-CO₂H, for example, changes from its initial
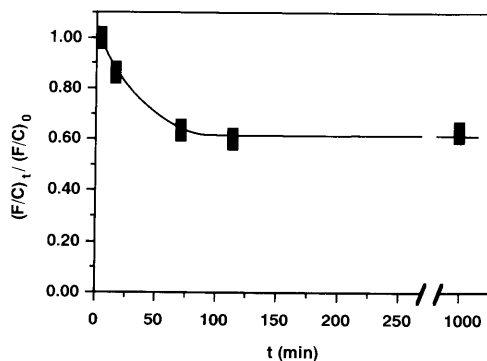

FIGURE 19. Surface concentration of fluorine, relative to that of carbon, by XPS for $PE[CH_2OCO(CF_2)_2CF_3]$ as a function of the amount of time the sample had been heated at 100 C in vacuum. Reprinted with permission from reference 30. Copyright C 1987 American Chemical Society.

value of 55° to 80° after soaking in methylene chloride at room temperature for 4 h. This behavior restricts the number of solvents useful for the synthesis of derivatives of PE-CO₂H; we have not, however, studied the process of swelling in detail.

The previous section described how solid–vapor interfacial free energy (γ_{sv}) can influence the rate at which a surface reconstructs; this section focuses on the influence of γ_{sl}. Surfaces bearing polar functional groups (e.g., PE-CO₂H) interact strongly with polar liquids (e.g., water) by dipolar and hydrogen bonding interactions in addition to dispersive forces. As a result, we expected that polar, hydrophilic surfaces would reconstruct slowly or not at all when in contact with a polar liquid. In the absence of these favorable polar interactions—that is, those when the film is in contact with a nonpolar liquid—we expected that PE-CO₂H and its polar derivatives would reconstruct relatively quickly.

To test these hypotheses, we monitored the reconstruction of PE-CO₂H, a nonpolar derivative (PE[CO₂C₈H₁₇]), and PE-H (as a control) with the films in contact with a polar or with a nonpolar liquid. The two liquids chosen for comparison in these experiments, water and perfluorodecalin, do not appear to swell the interfacial region of the polymer.

Figure 20a shows the dependence of the advancing contract angle of water on these surfaces as a function of the amount of time they had been heated in water (pH 6–7) at 100°C. The interfaces of PE-CO₂H and PE-H showed essentially no change in their wettability by water over the course of these experiments. We attribute the thermal stability of the PE-CO₂H–water interface to the favorable

a)

b)

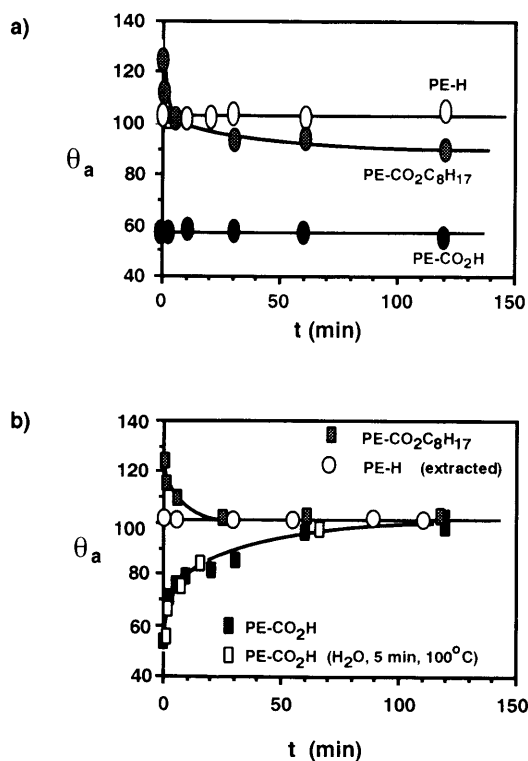FIGURE 20. Advancing contact angles of water (pH 1) on PE-H, PE-CO₂H, an PE-CO₂C₈H₁₇ as a function of the time the films had been heated at various temperatures (a) under water (pH 6–7) and (b) under perfluorodecalin. Plot (b) includes data for PE-CO₂H that had been heated in water for 5 min, then dried, prior to heating in perfluorodecalin. Reprinted with permission from reference 30. Copyright © 1987 American Chemical Society.

interactions between the hydrophilic functionality at the surface and the contacting aqueous phase.

The surface of $PE[CO_2C_8H_{17}]$ behaves differently: initially it is more hydrophobic than PE-H, but on heating in water it becomes more hydrophilic than PE-H. After 2 h of heating in water at $100°C$, its contact angle had decreased from the initial (unreconstructed) value of $124°$ to about $90°$. The contact angle dropped from $124°$ to about $93°$ in the first 30 min; it fell only slightly in the next hour. We infer from this behavior that, on heating in water, the interface of $PE[CO_2C_8H_{17}]$ reconstructs, exposes polar ester groups to the aqueous phase, and buries hydrophobic alkyl chains. This reconstruction minimizes the interfacial free energy of the system. These results are similar to the wetting behavior of the o-anthranilate amide of $PE-CO_2H$ (1), discussed in Section 2.5, and to work reported by others.[40, 45, 58, 60]

An alternative explanation for this behavior is that heating in water hydrolyzes some of the interfacial ester groups, leaving (more polar) carboxylic acid groups. We feel that this explanation is not correct, however, since the hydrolysis of $PE[CO_2C_8H_{17}]$ in 1 N NaOH proceeds to only approximately 30% completion (by ATR-IR) after a week at room temperature.[20]

We heated the same samples (PE-H, $PE-CO_2H$, and $PE-CO_2C_8H_{17}$) in the nonpolar solvent, perfluorodecalin. Figure 20b shows the contact angle of water on these surfaces as a function of the amount of time that they had been heated at $100°C$ in perfluorodecalin. The reconstructions under these conditions were qualitatively similar to those vacuum and under argon.

As with the reconstructions in vacuum or under argon, the surfaces of $PE-CO_2H$ and $PE-CO_2C_8H_{17}$ approached the hydrophobicity of PE-H: after 2 h, they were indistinguishable from PE-H in their wettability by water. The *rates* at which they approached this value, however, were slower than those under inert atmospheres. We believe that the slower rates reflect the difference in interfacial free energies between the two systems. The lower free energy of the polymer–perfluorodecalin interface, relative to that of the polymer–vacuum (or argon) interface, provides a smaller thermodynamic driving force to reconstruction (Fig. 21). These results are in agreement with the slow rate of reconstruction of the $PE[CH_2OCO(CF_2)_nCF_3]$–vacuum interface, relative to that of the $PE-CO_2H$–vacuum interface. As expected, the contact angle on PE-H did not change during the course of these experiments.
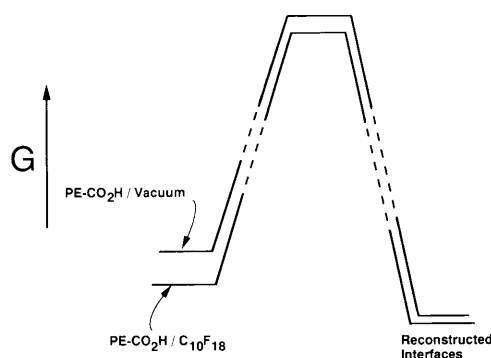

FIGURE 21. Hypothetical plot of free energy versus "reaction coordinate" for the thermal reconstruction of $PE-CO_2H$ in contact with vacuum and with perfluorodecalin.
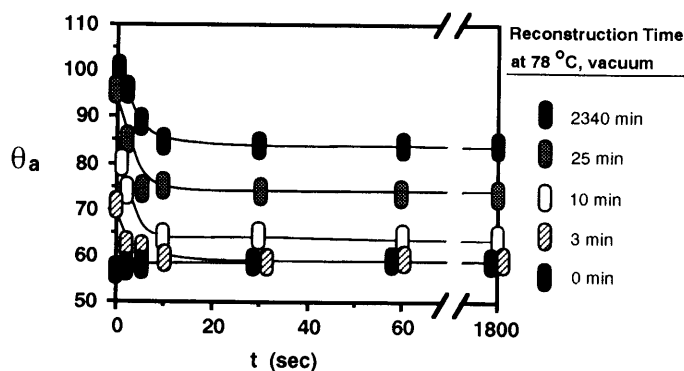
FIGURE 22. Advancing contact angles of water (pH 1) on PE-CO₂H that had been heated at 78 C in vacuum for various amounts of time, as a function of the amount of time the samples were then heated at 100 C in water (pH 6-7). Reprinted with permission from reference 30. Copyright C 1987 American Chemical Society.

3.6. Recovery of Polar Functional Groups from the Sub-θ Interphase

In the previous section, we attributed the stability of the interface of PE-CO₂H in water to a thermodynamic preference for having polar, hydrophilic functional groups in contact with the aqueous phase. To test this hypothesis further and to determine the degree of reversibility of the thermal reconstruction of these interfaces, we heated samples of *reconstructed* PE-CO₂H in water to try to "recover" polar functionality that had diffused out of the θ interphase.

Figure 22 shows the contact angle of water as a function of the amount of time samples had been heated in distilled water (pH 6-7) at 100 C. The PE-CO₂H had been reconstructed by heating at 78 C in vacuum for various periods of time. The reconstruction was only partially reversible for samples heated in vacuum for more than 3 min. In all cases however, the surfaces reached limiting contact angles within 30 s on heating in water; no further decrease had occurred after 30 min.

3.7. Depth Profiling of PE-CO₂H and Derivatives During the Thermal Reconstruction of Their Interfaces

The accessibility of functional groups in the sub-θ interphase to reagents in solution allowed us to follow the movement of polar functionality out of the θ interphase during reconstruction. Since the thickness of the θ interphase is small, direct measurement of the concentration of polar functionality as a function of depth into the polymer would require resolution on the scale of a few angstroms. Although collecting XPS data at various takeoff angles* can, in principle, be used for depth profiling of this sort,[51] the roughness of the surface of these films prevented us from collecting interpretable data. We followed the reconstruction of PE-CONHCH₂CO₂H by XPS, but found little difference between intensities using takeoff angles of 20° and 75°.

In the absence of a direct method for determining the depth profile of polar

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* A takeoff angle is the angle between the plane of the surface of the sample and the detector.

functionality, we turned to an indirect one. We treated partially reconstructed PE[CH$_2$OH] with perfluorinated n-alkyl anhydrides, [CF$_3$(CF$_2$)$_n$CO]$_2$O, of different lengths; we reasoned that if the hydrophobic perfluoroalkyl chains were sufficiently long, they would extend into the θ interphase and raise the contact angle of water (Fig. 23).

Figure 24 shows the contact angles of water on PE[CH$_2$OCO(CF$_2$)$_n$CF$_3$] as a function of the amount of time the PE[CH$_2$OH] had been heated at 100 C in vacuum. Data are presented for perfluoroalkyl groups of different lengths and for unacylated PE[CH$_2$OH] for comparison. Several points deserve comment. First, PE[CH$_2$OH] reconstructed quickly; within 5 min of heating at 100 C in vacuum the hydroxyl groups had migrated out of the θ interphase, and the contact angle of water was the same as that on PE-H.

Second, the perfluoro*methyl* ($n = 0$) ester derived from PE[CH$_2$OH] that had been reconstructed for 5 min was almost as hydrophobic as that derived from *unreconstructed* PE[CH$_2$OH]. Even the perfluoromethyl ester of PE[CH$_2$OH] that had been reconstructed for 20 min was more hydrophobic than PE-H. These results imply that the initial reconstruction (about the first 5 min) involves subtle conformational changes of the hydroxyl-containing groups, reminiscent of the pH-dependent behavior of **1**. After 5 min of heating, the hydroxyls had migrated
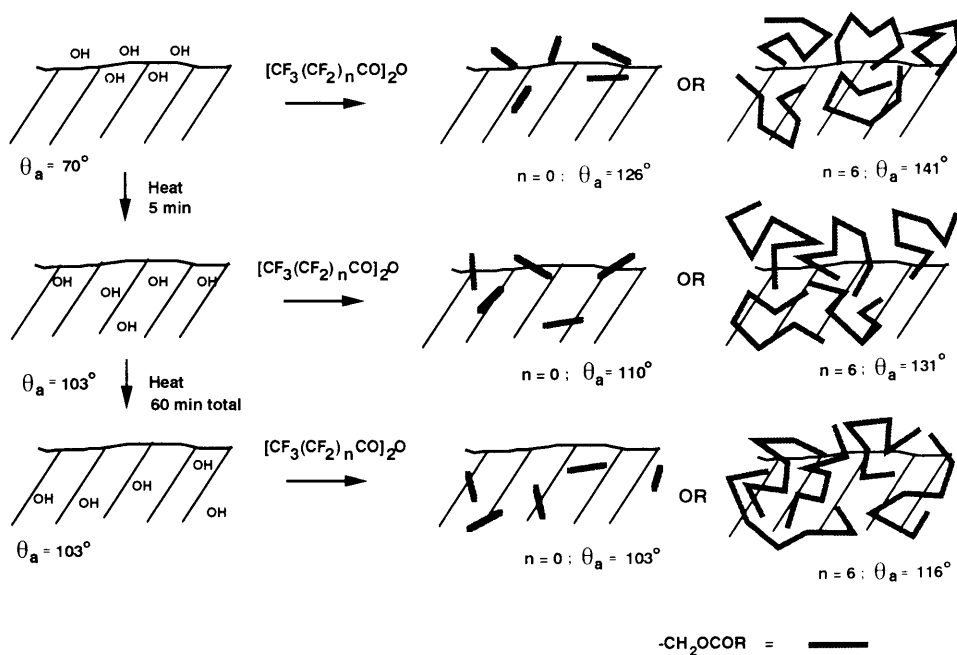

FIGURE 23. Schematic illustration of the interfacial region of PE[CH$_2$OH] and its derivatives, PE[CH$_2$OCO(CF$_2$)$_n$CF$_3$], before and after initial reconstruction of the PE[CH$_2$OH] at 100 C in vacuum. Reaction of perfluoroanhydrides with the hydroxyl groups in the sub-θ interphase produced surfaces whose wetting behavior provided information about the depth of the θ interphase. Contact angles of water (pH 1) are shown at each step of the reconstruction and functionalization. Reprinted with permission from reference 30. Copyright C 1987 American Chemical Society.
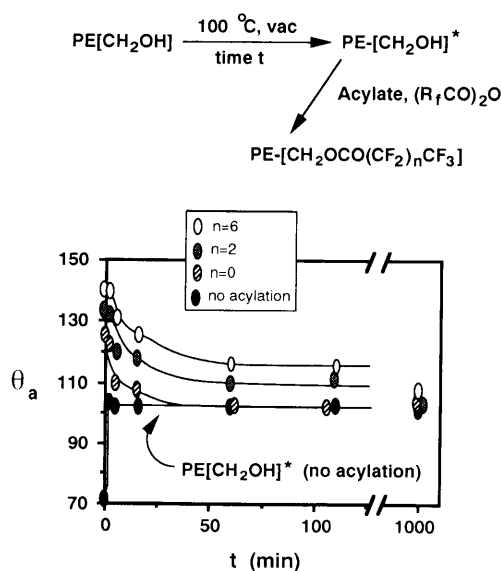
$$PE[CH_2OH] \xrightarrow[\text{time } t]{100\ {}^\circ C,\ vac} PE\text{-}[CH_2OH]^*$$

$$\searrow \text{Acylate, } (R_fCO)_2O$$

$$PE\text{-}[CH_2OCO(CF_2)_nCF_3]$$

FIGURE 24. Advancing contact angles of water (pH 1) on $PE[CH_2OCO(CF_2)_nCF_3]$ as a function of the amount of time that the $PE\text{-}CH_2OH$ had been heated at 100 C in vacuum prior to acylation. Data for unacylated $PE[CH_2OH]$ are shown for comparison. Reprinted with permission from reference 30. Copyright © 1987 American Chemical Society.

out of the θ interphase, but they remained close enough to the surface that the perfluoromethyl groups of the esters protruded into the θ interphase. These results also confirmed that the θ interphase is very thin (~ 5 10 Å).

Third, as the hydroxyl groups diffused away from the interface, the length of the perfluoroalkyl chains of the esters became important for determining the wettability of the interface. For samples at each point in the reconstruction, the hydrophobicity of the esters increased with increasing length of the perfluoroalkyl chains. After further heating (~ 1 h), the hydroxyl groups had diffused more than a few angstroms away from the interface, and the perfluoromethyl ester no longer influenced wetting. After extended heating (1000 min). the hydroxyl groups had diffused sufficiently far into the polymer that none of the esters influenced wetting. In each case. ATR-IR spectra confirmed the existence of esters outside of the θ interphase.

Treatment of the esters with 1 N NaOH regenerated reconstructed $PE[CH_2OH]$; that is, the wetting behavior of the product was indistinguishable from that of PE-H. Retreatment with the anhydride produced an esterified surface whose contact angle was the same as its original value. The reversibility exemplified in these experiments is important, because it rules out the possibility that the esterification or saponification reactions, themselves, reconstruct the surfaces.

3.8. Is Interfacial Strain a Driving Force for the Reconstruction of the Surface of PE-CO₂H?

By comparing the rates of reconstruction for samples annealed either in vacuum before oxidation or in water after oxidation to unannealed samples, we showed that mechanical stress in the films was not an important factor in these processes. Figure 25 compares annealed and unannealed samples in their rates of reconstruction at 65 C.
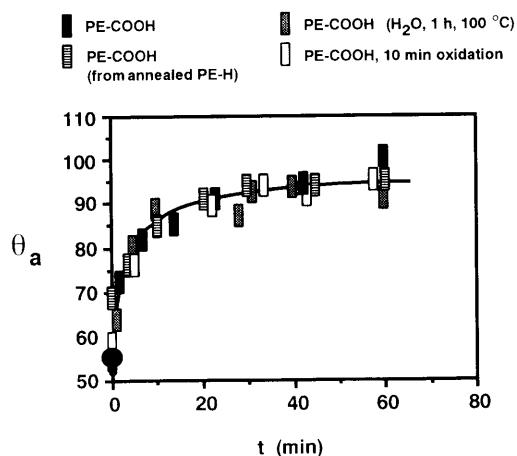
FIGURE 25. Advancing contact angles of water (pH 1) on various types of PE-CO$_2$H as a function of the amount of time the samples had been heated at 65 C in vacuum. The samples were PE-CO$_2$H prepared by oxidation of PE-H (solid box); PE-CO$_2$H prepared by oxidation of PE-H that had been annealed at 100 C under vacuum for five days (box with lines); PE-CO$_2$H prepared by oxidation of PE-H, then heated at 100 C for 1 h in water (pH 6–7) prior to reconstruction (stippled box); and PE-CO$_2$H prepared by oxidation of PE-H for 10 min instead of the usual 1 min (unfilled box). All of the samples had θ_a(water) = 54–57 before reconstruction. Reprinted with permission from reference 30. Copyright c 1987 American Chemical Society.

We heated a sample of PE-H in vacuum at 100 C for five days, a treatment longer by a factor of 10^3 than that required for all of the polar groups of PE-CO$_2$H to diffuse out of the θ interphase. The PE-CO$_2$H derived from this film reconstructed at the same rate as PE-CO$_2$H derived from unannealed PF-H. We heated another sample of PE-CO$_2$H in distilled water at 100 C for 1 h; this treatment allowed extensive annealing of the interface while keeping the hydrophilic CO$_2$H groups within the θ interphase. As expected, the contact angle of water (pH 1) on this sample was the same before and after treatment. The rate of reconstruction of the annealed sample was indistinguishable from that of unannealed PE-CO$_2$H.

It is possible that the oxidation itself has an important effect on the thermal reconstruction of these films: treatment of PE-H with hot chromic acid may reveal underlying mechanical strain or *introduce* strain in the interfacial region of the polymer films. Oxidation with chromic acid could produce strain by inducing reactions (i.e., of radicals)[103] that cross-link the methylene chains at the surface. In addition, oxidation could lower the density of the interfacial region of the polymer, relative to that of the bulk, by selectively etching amorphous portions of the interface. The initial reconstruction might then be driven by relaxation to an "equilibrium density" in the interfacial region.[27,29]

To test these hypotheses, we oxidized a sample of PE-H with chromic acid at 72 C for 10 min, instead of the usual 1 min, to produce PE-CO$_2$H with a deeply etched surface (Fig. 2). The interface of this sample reconstructed at the same rate as PE-CO$_2$H produced by a 1 min oxidation, indicating that the oxidation neither reveals nor introduces strain into the polymer films. This result does not, however, rule out the possibility that the oxidation introduces strain into the interfacial region in a quickly established ($\leqslant$ 1 min) steady-state process.

CONCLUSIONS

The unique feature that chemistry offers materials and surface science is the ability to manipulate systems of interest at the molecular level. Synthetic chemistry

provides versatile methods for the modification of existing organic surfaces and for the creation of new ones. This versatility makes it possible to address the following question: what are the relations between molecular identity and orientation at a surface and the macroscopic, interfacial (especially liquid–solid) behavior of that surface? Initial oxidation of PE-H with chromic acid introduces carboxylic acid moieties into the solid–liquid interface that serve as starting points for further chemical elaboration. This approach allows access to a wide range of functional group types. The relative orientation of these groups can be systematically varied: syntheses of surfaces bearing amides derived from each isomer (*o*, *m*, and *p*) of anthranilic acid provide examples.

Most of our studies have focused on wetting of solids by liquids. Wetting measurements probe the chemical composition, structure (orientation and order), and dynamics at the surface of solids. An example of the last of these areas—the dynamics of polymer-bound functional groups at or near the surface of PE-X—is the focus of this review.

Surface-modified polyethylene provides a challenging "real" system for studying the relations between interfacial structure and wetting: its surface is rough, chemically and morphologically heterogeneous, and penetrable by many liquids and reagents. Since the surface of PE-X is nonideal, the molecular details of its reconstruction are not amenable to study by conventional spectroscopic techniques alone. For instance, changing the takeoff angle in XPS experiments does not significantly change the surface sensitivity of the measurements. Despite these complexities, convenient experimental protocols can give useful information about the location and environment of the surface-bound functional groups.

The work described in this review illustrates the usefulness of combining spectroscopic and nonspectroscopic experiments to infer interfacial structure. This combination allows resolution on the scale of a few angstroms in experiments designed to locate functional groups at or near the surfaces of the polymer. The analytical techniques discussed—measurement of contact angles, XPS, and ATR-IR—each probe a different portion of the polymeric interphase. These techniques give complementary information about the thermal reconstruction of the interfacial region.

Our ability to interpret data from contact angles and from XPS was aided by reference to model systems. Zisman's method for producing ordered monolayers by molecular self-assembly at the surface of a solid,[71] applied in the system comprising alkanethiols and gold, allows production of structurally well-defined organic surfaces. Modification of the molecular precursors of the SAMs—an activity entirely within the field of synthetic organic chemistry—provides routes to a range of model organic surfaces.

These model systems make it possible to address specific questions about the relations between interfacial structure and wettability. One conclusion from our work with these systems is that wetting is the most surface-sensitive technique available to us: wetting by water senses only the outermost 5–10 Å of a solid. Since wetting is surface sensitive, the degree of order in the interfacial region of systems composed of terminally functionalized alkyl chains is important in determining contact angles; that is, the *orientation* of interfacial functional groups can profoundly affect contact angles on the surfaces bearing these groups.

One of the most generally useful methods for examining the surface of PE-X is contact angle titration, the measurement of the variation in the contact angle of water on a surface with the pH of the contacting drop. The contact angle titration of the o-anthranilate amide of PE-CO_2H illustrates the relationship between wetting and microreconstruction of a polymer surface. The results of this study show that (1) subtle conformational changes within the θ interphase of a polymer can strongly influence the contact angle of water on its surface, and (2) even in this disordered system, a small nonpolar group (containing six carbon atoms) is sufficient to shield a polar group(s) from a contacting drop of water. We use the word "shield" *only* within the context of the measurement of contact angles for solid–liquid interfaces at quasi-equilibrium. This "shielding" does not apply to *kinetic* phenomena; for instance, polar groups in the sub-θ interphase are still accessible to reagents in aqueous solution.

We studied in detail the thermal reconstruction of PE-CO_2H and several of its derivatives. The main conclusions from these studies are as follows:

1. The initial reconstruction involves conformational changes close to the surface, akin to those inferred in the PE-anthranilate system, driven by the tendency to minimize the interfacial free energy of the system.

2. In a slower process, functional groups passively diffuse into the bulk of the polymer. This process is presumably driven by entropy.

3. The rate of reconstruction and the composition of the interface at equilibrium depend on the initial composition of the interface. Surfaces with inter-facial free energies higher than PE-CO_2H reconstruct quickly to give interfaces indistinguishable from PE-H in their wettability by water. Surfaces with interfacial free energies lower than PE-CO_2H reconstruct more slowly than does PE-CO_2H; surfaces bearing long perfluoroalkyl groups (even PE[$CH_2OCO(CF_2)_2CF_3$]) retain significant concentrations of fluorine in XPS interphase (and even in the θ interphase) after extended heating.

4. Interfacial strain, introduced either in the manufacture of the films or in their surface functionalization, does not seem to be an important factor in deter-mining the kinetics and thermodynamics of reconstruction.

Our experimental value for the activation energy of reconstruction of PE-CO_2H is higher than those measured for related processes (diffusion of large monomers in bulk polyethylene, or breakdown of the crystalline lamellae at the surface of low-density polyethylene). These differences add emphasis to the claim that the interfacial reconstruction of PE-CO_2H is complex, and we believe that several factors are probably important in determining the rate of this process. Aside from the inherent difference between a value of $E_{a,D}$ derived directly from the measure-ment of contact angles on a complex solid and those derived from infrared spectro-scopy or from measurements of critical surface tension, these factors may include hydrogen bonding to form dimers of the carboxylic acid moieties in the interfacial region of PE-CO_2H and preferential etching of amorphous regions of the poly-ethylene interphase in its synthesis.

ACKNOWLEDGMENTS

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