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Wetting of Functionalized Polyethylene Film Having Ionizable Organic Acids and Bases at the Polymer–Water Interface: Relations between Functional Group Polarity, Extent of Ionization, and Contact Angle with Water[1]

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This paper examines the wetting by water of low-density polyethylene film modified at the polymer–water (air) interface by introduction of polar organic functional groups (carboxylic acids, amines, and others). Water/polymer contact angles were determined for each of these interfaces; for interfaces containing acidic or basic functional groups, the contact angle was determined as a function of the pH. The observed contact angle was related to the hydrophilicity of these functional groups: as the hydrophilicity (as measured by Hansch π parameters) increased up to a certain point, the contact angle decreased. Beyond that point, increased hydrophilicity had little additional influence on the contact angle. This result is interpreted in terms of water adsorbed on the polar interfacial functional groups; extensive hydration of interfacial groups having large negative π parameters moderates their effective hydrophilicity. The influence of a functional group on wettability was related to the normalized fraction of the area of the interface occupied by that type of functional group; in some instances this area fraction appears more useful in describing interfacial properties than the simpler mole fraction. Interfaces containing ionizable functional groups usually showed a contact angle that varied with pH, with the lower contact angle observed at values of pH for which the interfacial groups were in the more polar, charged form; interfaces without ionizable functional groups did not display a change in contact angle with pH. The paper rationalizes the change in contact angle with pH in terms of the relative areas of the interface occupied by the functional groups in different ionization states and in terms of the extent of ionization of acidic and basic groups. The interfacial values of pK_a are compared with the values of pK_a for similar functional groups in aqueous solution. In all cases, it is more difficult to generate the charged form of the functional group at the interface than it is in aqueous solution, probably due in major part to the lower dielectric constant of the interface.

Introduction

Treatment of low-density polyethylene film with aqueous chromic acid solution yields "polyethylene carboxylic acid" (PE–CO_2H), a material containing carboxylic acid and ketone and/or aldehyde groups concentrated in a thin oxidatively functionalized interfacial region.[4] We are using this material, and other materials derived from it by *modification of its constituent functional groups*, to study the relation between the molecular-level characteristics of the interfacial region—structure, polarity, reactivity, location, and concentration of functional groups—and macroscopic material properties of the functionalized polymer such as wettability and adhesion strength.[4-9] Previous papers have demonstrated that the wettability of PE–CO_2H by water changes with the pH of the water and that this change correlates with the state of ionization of the carboxylic acid groups.[4] Examination of changes in the contact angle of water on PE–CO_2H as a function of pH is a technique we call "contact angle titration". It provides a particularly convenient (if indirect) method for examining the state of ionization of functional groups influencing the wetting of the functionalized polymer. Empirically, results obtained by using this technique correlate well with estimates of the extent of ionization obtained by direct spectroscopic measurements using ATR-IR spectroscopy[4] and fluorescence spectroscopy[5] and by conventional titration.[4] We have previously proposed a qualitative justification for this correlation,[4] but the more detailed examination of this paper suggests that the basis of contact angle titration is not simple.

This paper has four objectives: The first objective is to survey a range of organic functional groups on the surface of polyethylene for their influence on wettability and to search for a correlation between some appropriate measure of polarity of the individual functional groups in solution and the wettability of an interface incorporating them. Second, we wish to confirm that changes in wettability with pH of interfaces having acidic or basic groups reflect protonation or deprotonation and to examine *how* such ionizations influence wetting. The third objective is to compare the proton acidities of functional groups in the interfacial region with their acidities in solution. Finally, we wish to clarify the physical chemical basis of the technique of contact angle titration.

As we have done previously,[5,6] we refer to that part of the functionalized interface of PE–CO_2H and its derivatives that determines the wettability of the polymer as the "contact angle interphase" or "θ interphase" and to parts of the interface lying below the θ interphase and having no influence on contact angle as the "sub-θ interphase". Although the structural features that determine whether an interfacial group influences wetting are not yet precisely established, we believe that the groups in the θ interphase must be within angstroms of the outermost part of the polymer.[10-13]

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$PE-CO_2H$ and Its Derivatives. Background. The morphology of the interface of $PE-CO_2H$ at ~1000-Å resolution is not detectably different from that of the unfunctionalized polymer.[4] The only important functional groups present are carboxylic acid and ketone and/or aldehyde moieties in an approximately 3:2 ratio. $PE-CO_2H$ has a relatively low interfacial free energy and resists contamination by adsorption of contaminants from the air. It can be handled briefly in air without special precautions. We have not yet been able to establish by direct observation the thickness of the functionalized interface or the distribution of functional groups, but it appears that ~30% of the carboxylic acid groups determines the wettability of this material, and the remainder of these carboxylic acid groups have little or no influence on wettability.[6] Indirect evidence suggests that the functionalized interface in $PE-CO_2H$ is thin—that is, probably <20 Å in thickness.[6]

All carboxylic acid groups in the functionalized interface are accessible to aqueous base[4] and are converted to carboxylate ions at values of solution pH ≥12. The polarity experienced by a fluorophoric reporter group (the dansyl moiety) incorporated in the interface is uniform and, when placed in contact with water, is similar to that of methylene chloride.[5] The functionalized interface is reasonably stable: the functional groups do not migrate away from the θ interphase at room temperature or under reaction conditions used in forming derivatives, although migration is rapid at 100 °C.[7]

The interface of $PE-CO_2H$ and its derivatives is composed of a number of types of organic groups including methyl, methylene, ketone/aldehyde, carboxylic acid, and possibly others. We use several nomenclatural devices to simplify discussion of the interfacial chemistry of $PE-CO_2H$. Groups present anywhere in the oxidatively functionalized interfacial region are indicated with square brackets [ ], following the name of the polymer; for example, $PE[>C{=}O][CO_2H][CONH_2]$ is polyethylene containing ketone/aldehyde, carboxylic acid, and amide groups in its functionalized interface. With this nomenclature, the material $PE-CO_2H$ made in the initial oxidation reaction can be described more accurately as $PE[>C{=}O][CO_2H]$. Since the majority of the reactions that we use to introduce functionality into the interfacial region involve derivatization of the interfacial carboxylic acid groups rather than the ketones, we often omit the $[>C{=}O]$ from the name and assume that, unless otherwise specified, there is a background of ketone/aldehyde (and, of course, methylene groups) in the interface of all samples. Thus, if the nature of the group derived from the ketone/aldehyde groups is not specified, these groups are assumed to be unchanged: $PE[CONH_2]$ is $PE[>C{=}O][CONH_2]$, not $PE[>CHOH][CONH_2]$.

Theory

Contact Angle Titration. Figure 1 shows representative advancing contact angles θ_a of buffered water on $PE-CO_2H$ and several of its derivatives as a function of pH. Much of the work in this paper is directed toward understanding three features of these data. First, only surfaces containing ionizable functionality ($RCO_2H \rightleftharpoons RCO_2^-$; $RNH(CH_2)_4^+ \rightleftharpoons RN(CH_2)_4$) show a pH dependence of the contact angle. Why? Second, the magnitude of θ_a decreases as the polarity of the functional group in the interface increases. What is the relation between the polarity of a functional group (a concept that is intuitively clear if not quantitatively uniquely defined) and its influence on wetting characteristics of an interface? Third, all of the interfaces show pronounced hysteresis in contact angle. What physical model should we use in discussing this hysteresis?

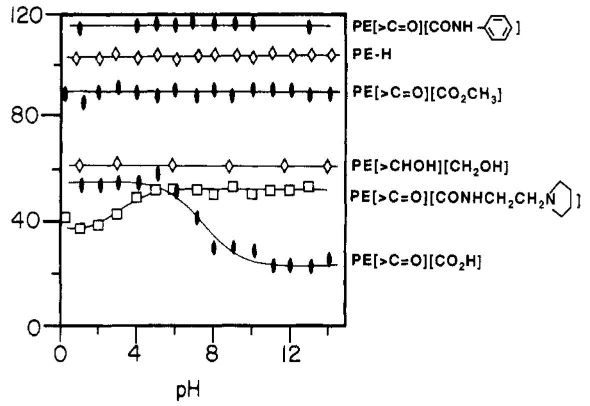

Figure 1. Advancing contact angle θ_a (obtained by using sessile drops) as a function of the pH of the drop for several derivatives of $PE-CO_2H$. Solutions were buffered (0.05 M).

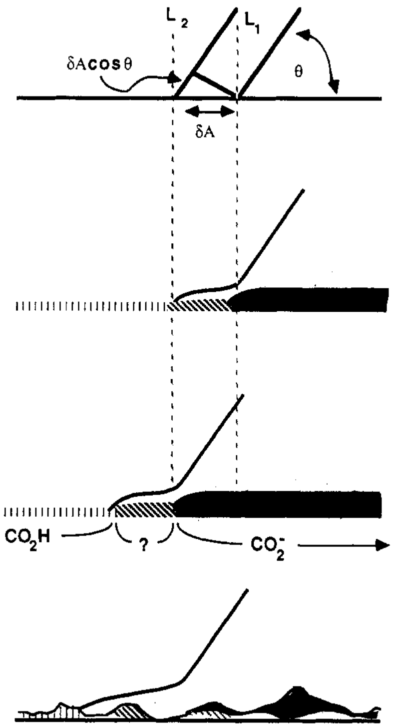

Figure 2. Schematic illustration of the edge of a drop as it moves from position L_1 to position L_2. The edge of the drop makes an angle of θ with the interface. As the drop advances, it sweeps over an area δA and the liquid experiences an increase in interfacial area of $\delta A \cos \theta$ (top). The nature of the interface may change as the drop moves over it due to, for example, ionization of carboxylic acid groups on contact with basic water (middle). The real polymer surface is rough and heterogeneous (bottom).

The theoretical discussion that follows suggests a simplified physical model for the wetting of $PE-CO_2H$ and its derivatives. In particular, we note that the assumption (below) that the functional groups in the interface contribute independently to the interfacial free energy is inaccurate but leads to a tractable and physically reasonable picture. We start with an analysis similar to one used in discussions of equilibrium wetting (Young's equation, Figure 2, eq 1).[13-15] Consider the free energy, ΔG, of a

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$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

system composed of a drop of water on a homogeneous solid containing only one type of interfacial functional group as the edge of the drop moves from a position L_1 to a position L_2 with a corresponding change in the area δA of the solid under the drop (eq 2). If the solid interface

$$\Delta G/\delta A = \gamma_{LV}\cos\theta + \gamma_{SL}^{pH} + \eta_R^{pH} - \gamma_{SV} \tag{2}$$

contains groups reactive toward water (for example, carboxylic acid or amine moieties), the free energy of reaction (η_R^{pH}, in units of energy per area) must be included. All of our experiments involve the wetting of interfaces under air saturated with water vapor, that is, "moist" spreading. We assume that polar functional groups in the interface are to some extent hydrated and believe that the water molecules adsorbed at the interface have a significant influence on the solid–vapor interfacial free energy (γ_{SV}, see below).

The type of reactivity in which we are most interested is the reaction between acids (bases) in the θ interphase and bases (acids) present in the aqueous drop. In this instance, both η_R^{pH} and γ_{SL}^{pH} depend on the nature of the functional groups present and on the pH of the drop.[16] In general, we expect η_R^{pH} and γ_{SL}^{pH} to be related, in the sense that if a reaction occurs when the solid comes in contact with the liquid, γ_{SL} should also change. We discuss in greater detail the relation between η_R^{pH} and γ_{SL}^{pH} later; here we combine them in a single term $\gamma_{SL}{}^*$.

The equilibrium contact angle defined in eq 1 can be modified to take into account the influence of reaction of interfacial groups, by deriving an expression (eq 3) analogous to Young's equation (eq 1) starting with eq 2. If $\gamma_{SV} - \gamma_{SL}{}^*$ is less than or equal to γ_{LV}, and if there are no kinetic barriers to movement of the drop edge, the equilibrium contact angle should be given by eq 3. If $\gamma_{SV} - \gamma_{SL}{}^*$ is greater than γ_{LV}, the system is not at equilibrium. The term S^* (eq 4) is defined by analogy with the classical spreading pressure: for the system to be at equilibrium, $S^* \leq 0$.[13]

$$\cos\theta = \frac{\gamma_{SV}^{pH} - (\gamma_{SL}^{pH} + \eta_R^{pH})}{\gamma_{LV}} = \frac{\gamma_{SV}^{pH} - \gamma_{SL}{}^*}{\gamma_{LV}} \tag{3}$$

$$S^* = \gamma_{SV} - \gamma_{SL}{}^* - \gamma_{LV} \tag{4}$$

For a material such as PE–CO_2H having a number of different interfacial groups, we can postulate eq 5 and 6 in estimating γ_{SV}^{pH} and $\gamma_{SL}{}^*$. In these equations, $A_{SV,i}$ is the normalized function of the *area* of the solid–vapor interphase occupied by the functional group i.[17] These equations are based on the assumption that each functional group contributes to the interfacial free energy independently of other interfacial groups according to the normalized fraction A_i of the interfacial area it occupies. We note three features of these equations. First, the assumption of independence of functional groups is certainly incorrect in detail. Second, the concept of the "area fraction" of an interfacial group is not exactly defined. Nonetheless, it is evident that for a very large group (for example, an oligosaccharide) the area fraction and the more familiar mole fraction (χ_i) will be equite different. Third, the values of $A_{SV,i}$ and $A_{SL,i}$ are not necessarily the same: the interface might reconstruct or hydrate on contact with water to minimize its free energy and thereby change the value of A_i. PE–CO_2H itself provides a probable example of a system in which the θ interphase reconstructs on contact with bulk water.[6]

$$\gamma_{SV}^{pH} = \sum A_{SV,i}\gamma_{SV,i}^{pH}$$
$$i = \text{interfacial groups} \tag{5}$$

$$\gamma_{SL}{}^* = \sum A_{SL,i}\gamma_{SL,i}{}^*$$
$$i = \text{interfacial groups} \tag{6}$$

The principal objective of this section is to generate a qualitative understanding of the response of the contact angle to changes in the polarity of the interface. To this end, we ignore the difference between $A_{SV,i}$ and $A_{SL,i}$ and write eq 7 as a description of an interface having mixed functionality. An analogous expression (eq 8) gives the spreading pressure S^* in terms of contributions from independent functional groups. In a well-behaved case ($\cos\theta_i \leq 1$; $S_i{}^* \leq 0$) this equation carries the useful indication that $\cos\theta$ for the interface can be thought of in terms of area-weighted contributions from each constituent type of functional group. A more complex case arises when some or all of the $S_i{}^*$ are greater than zero and especially when $S^* \leq 0$ but with some $S_i{}^* > 0$. This case includes PE–CO_2^- (and perhaps PE–CO_2H itself).

$$\cos\theta \simeq \sum_i A_i \frac{\gamma_{SV,i}^{pH} - \gamma_{SL,i}{}^*}{\gamma_{LV}} = \sum_i A_i \cos\theta_i$$
$$\text{for } A_{SL,i} = A_{SV,i} \tag{7}$$

$$S^* = \sum_i S_i{}^* \tag{8}$$

We are primarily interested in systems in which the interface includes both polar (especially ionizable polar) groups and nonpolar, nonionizable groups. As a limiting case, we consider a system containing only one type of polar and one type of nonpolar group (eq 9) with A_P describing the area fraction occupied by the polar group.

$$\cos\theta \simeq A_P\cos\theta_P + (1 - A_p)\cos\theta_{NP} \tag{9}$$

For sufficiently polar, hydrophilic functional groups at 100% relative humidity, these groups will be covered with hydrating water molecules. In such a case, we hypothesize that the polar groups are functionally "buried" under a layer of water. Equation 9 can then be simplified by assuming that $\gamma_{SV,P}$ (interfacial free energy of the solid–vapor interface with an equilibrium coverage of adsorbed water) is equal to γ_{LV}. This equality follows from the fact that the solid interface is in thermodynamic equilibrium with the vapor: if $\gamma_{SV,P}$ were greater than γ_{LV}, water would condense on the interface; if $\gamma_{SV,P}$ were less than γ_{LV}, water would evaporate from it. It also follows that, in this limiting case, $\gamma_{SL,P} \simeq 0$, because the interface generated under the drop as it advances (Figure 2) is an interface between

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(16) It is also possible that γ_{SV} may change due to a reaction between the drop and the functional groups on the interface but beyond the drop edge. We have evidence that protons, for example, can migrate beyond the edge of a drop of aqueous acid and protonate basic species in the "solid–vapor" interface. Thus, formally, we should treat the functional groups on the outside of the drop (those that determine γ_{SV}) as being also capable of reaction with reagents in the drop and consider the possibility that ${}_{SV}^{pH}$ might to some extent also be a function of pH for interfaces with acidic or basic groups (such as PE–CO_2H). This phenomenon is intrinsically a nonequilibrium one and is difficult to treat realistically at the elementary level of this paper. We note that the possibility of reaction between groups in the interface beyond the edge of the drop and reagents in the drop may not be general. Details concerning this phenomenon will be reported in a separate paper.

(17) The term A_i is not precisely defined. The average projected area of a functional group might be suitable at this level of complexity. In this paper, A_i takes the place of β_i, which we used in previous papers.[4-6] For related discussions see: Cassie, A. B. D. *Discuss. Faraday Soc.* **1948**, *3*, 11–16.

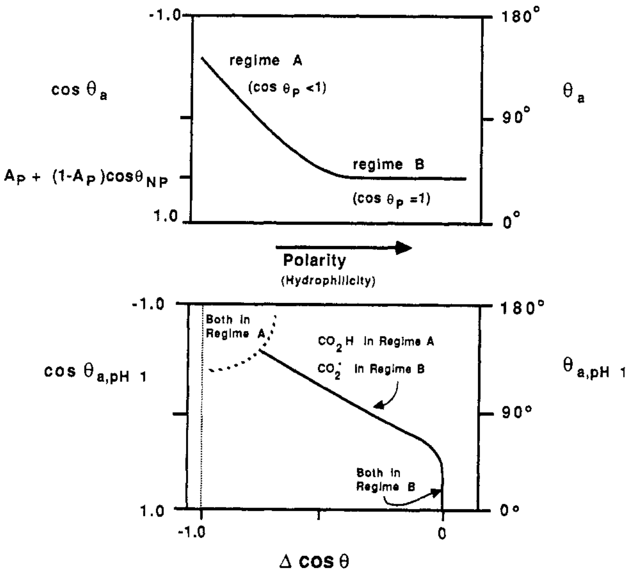


Figure 3. Top: Qualitative correlation between the contact angle (plotted as cos θ) and the polarity (hydrophilicity) of interfacial groups. Less polar groups fall into regime A. An increase in the polarity of a group in this regime results in an increase in cos θ (eq 7). Very polar groups fall into regime B. These groups are effectively buried by adsorbed, hydrating water at 100% humidity. Since these hydrated clusters present an interface similar to that of bulk water, increasing the hydrophilicity of the focal polar groups does not result in a further increase in cos θ (eq 8). Bottom: Qualitative relationship between the polarity of an unionized carboxylic acid group (described b cos $\theta_{\mathrm{a,pH1}}$) and the *change* in contact angle upon ionization of this group (Δ cos θ, eq 11). The relationship can be classified according to the regimes (top) into which the carboxylic acid and carboxylate groups fall (eq 12b–d). If both groups were to fall into regime B, for example, the difference in hydrophilicity between CO_2H and CO_2^- would have no influence on θ.

adsorbed water and bulk water. Thus, it follows from eq 1 that cos $\theta_P = 1$, and eq 9 can be simplified to

$$\cos\theta \simeq A_P + (1 - A_P)\cos\theta_{NP} \qquad (10)$$

for groups P sufficiently hydrophilic that cos $\theta_P = 1$. Our interest in this type of equation stems from the fact that the interfaces generated from PE–CO_2H contain nonpolar regions (unreacted methylene groups) and polar regions (derived from the carboxylic acid and ketone groups). The polar region of these interfaces varies in polarity as the nature of the interfacial groups changes (and can, in fact, become less hydrophilic than the nonpolar regions, as with fluorinated carboxylic acid esters). As the polarity of the polar region changes, the change in contact angle should follow eq 7. In the low polarity limit the contact angle responds to the polarity of the polar region through changes in cos θ_P. As the groups in the θ interphase become more hydrophilic, cos θ_P increases and the contact angle decreases (Figure 3, regime A). When the interfacial groups become sufficiently polar and hydrophilic, water vapor begins to adsorb on and hydrate them. At some value of hydrophilicity, the interfacial groups will be completely hydrated and cos θ_P will approach 1 (i.e., eq 10 will apply). In this model, additional increases in hydrophilicity will not result in a change in θ because cos θ_P remains unchanged at 1 and cos θ_{NP} is not influenced by the polar groups (Figure 3, regime B). As an initial hypothesis, we suggest that eq 9 and 10 provide a qualitative rationalization for the experimental data we observe for PE[R].

We note that the hypothesis that the hydrophilicity of very polar groups is "leveled" by adsorption of water from the vapor onto these groups does not explicitly involve reaction of these groups (protonation or deprotonation): these equations apply to both nonionizable groups and to PE–CO_2H and PE–NR_2H^+. Assuming that Figure 3 (top) qualitatively describes the relationship between the polarity of groups in the the interface and the resulting contact angle with water, we can predict a relationship between the contact angle on an interface that contains carboxylic acid groups and the change in contact angle expected when those carboxylic acid groups are ionized. For example, if the carboxylic acid group is already very polar prior to ionization (Figure 3, top, regime B), an increase in polarity upon ionization of the groups in the θ interface should not result in a significant decrease in θ. On the other hand, if the carboxylic acid group were initially fairly nonpolar (Figure 3, top, regime A), then an increase in polarity should result in a decrease in θ. The experimental data in Figure 1 suggest that the latter description applies to carboxylic acids and tertiary amines; data described later suggest that the former description applies to primary amines.

A more quantitative expression connects the difference in cos θ between the fully ionized (e.g., PE–CO_2^-) and fully unionized form (e.g., PE–CO_2H), Δ cos θ, and the value of cos θ in the unionized form (eq 11). In the specific case in which the polar functional groups of interest are CO_2H and CO_2^- groups, we measure the contact angle at pH 1 to ensure that all of these groups are protonated and at pH 13 to ensure that all are deprotonated (eq 11). We

$$\Delta\cos\theta = \cos\theta_{\mathrm{pH1}} - \cos\theta_{\mathrm{pH13}} \qquad (11)$$

can imagine three types of behavior for Δ cos θ, depending on whether the CO_2H and CO_2^- groups fall in regime A or B of Figure 3 (top). In regime A, cos $\theta_P < 1$. Assuming for eq 7 that $A_P = A_{CO_2H} = A_{CO_2^-}$, we write the general expression eq 12a:

$$\Delta\cos\theta = A_P(\cos\theta_{CO_2H} - \cos\theta_{CO_2^-}) \qquad (12a)$$

$$\Delta\cos\theta = 0(\cos\theta_{CO_2H} = \cos\theta_{CO_2^-} = 1) \qquad (12b)$$

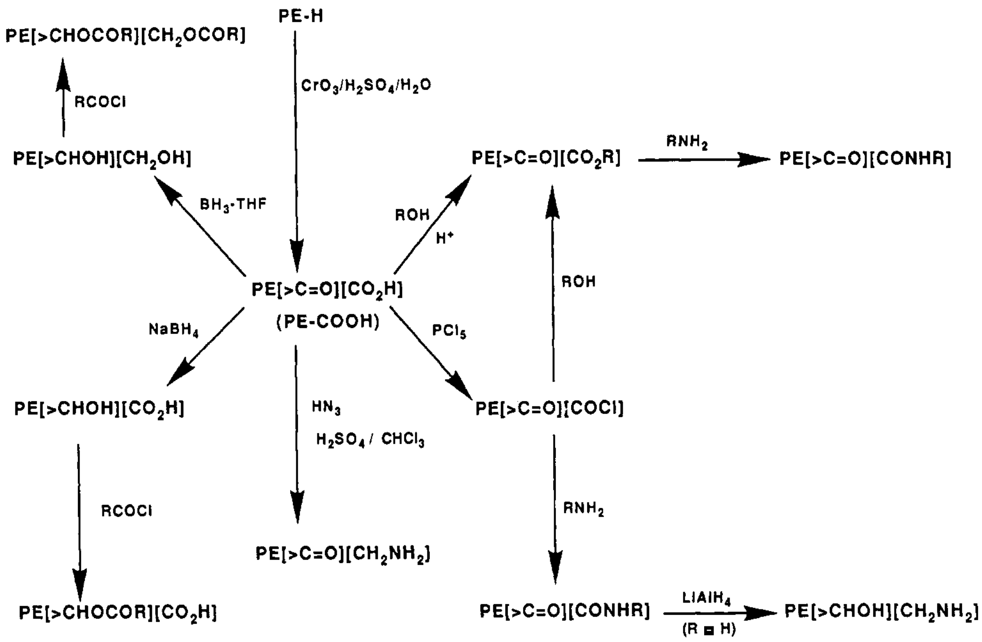
$$\begin{aligned}\Delta\cos\theta &= \cos\theta_{\mathrm{pH1}} - [A_P + (1 - A_P)\cos\theta_{NP}] \qquad (12c)\\ &= A_P(\cos\theta_{CO_2H} - 1)\\ &\qquad (\cos\theta_{CO_2H} < 1;\quad \cos\theta_{CO_2^-} = 1)\end{aligned}$$

$$\begin{aligned}\Delta\cos\theta &= A_P(\cos\theta_{CO_2H} - \cos\theta_{CO_2^-}) \qquad (12d)\\ &(\cos\theta_{CO_2H} < 1;\quad \cos\theta_{CO_2H} < \cos\theta_{CO_2^-} < 1)\end{aligned}$$

In this equation, cos θ_{CO_2H} is the contact angle of water on an interface containing only CO_2H groups ($A_{CO_2H} = 1$) and cos $\theta_{CO_2^-}$ is the contact angle on an interface containing only CO_2^- groups. If both CO_2H and CO_2^- groups are in regime B, eq 12b holds; if the CO_2H group is in regime A and the CO_2^- group in regime B, eq 12c holds; and if both groups are in regime A, eq 12d holds. This treatment predicts that as cos θ_{pH1} decreases Δ cos θ should also decrease (eq 12c) and should, for sufficiently polar groups, go to zero (eq 12b). Figure 3 (bottom) summarizes these equations schematically.

We note that the relations (eq 12a–d) neglect both changes in A_P that might result from the ionization of the interfacial groups and contributions from the energy of reaction η_R^{pH}. Both of these parameters are expected to influence the contact angle (eq 3 and 9). While potential changes in A_P are difficult to evaluate, we can estimate the contribution to the contact angle from η_R^{pH} by quantifying the relationship between η_R^{pH} and pH. The free energy of ionization of an interfacial acid, ΔG_i, is given by eq 13. In order to determine the total amount of energy resulting from the partial ionization of n surface groups at any given

Scheme I. Reactions Used To Modify the Interface of Polyethylene Film



pH (η_R^{pH}), we integrate this value from no ionization of interfacial groups ($\alpha = 0$) to the extent of ionization existing at equilibrium under the drop (α_i; eq 14).[18]

$$\Delta G_i = -RT \ln K_a + RT \ln \frac{[H^+][A^-]}{[HA]} = -RT \ln K_a + RT \ln \frac{[H^+]\alpha}{1-\alpha}; \quad \text{where } \alpha = [A^-]/([A^-] + [HA]) \quad (13)$$

$$\eta_R^{pH} = \int_0^{\alpha_i} \Delta G_i \, d\alpha = nRT \ln (1 - \alpha_i) \quad (14)$$

If we assume that γ_{SV} and γ_{SL} are independent of pH, eq 14 can be combined with eq 3, resulting in eq 15 and 16. This assumption is probably incorrect, but it will allow the contribution to changes in θ_a due to η_R^{pH} to be distinguished easily from changes due to γ_{SV} and γ_{SL}.

$$\cos \theta_{pH} = [\gamma_{SV}^{pH} - \gamma_{SL}^{pH} - nRT \ln (1 - \alpha_i)]/\gamma_{LV} \quad (15)$$

$$\cos \theta_{pH}^{\eta} = \cos \theta_{pH1} - [nRT \ln (1 - \alpha_i)]/\gamma_{LV} \quad (16)$$

Using eq 16, we can predict changes in θ_a as a function of pH due solely to the free energy of ionization.[19] This prediction is discussed further after presentation of relevant experimental data.

These discussions are based on the assumption of a system showing no kinetic barriers to the advance or retreat of the drop edge. In fact, all of the derivatives of polyethylene examined showed pronounced hysteresis. For example, although water at low pH reaches a stable, reproducible advancing angle on PE–CO_2H ($\theta_a \simeq 55°$), the receding angle is $\theta_r \simeq 0°$; that is, the drop edge is completely pinned and cannot be withdrawn. The interface of PE–CO_2H is rough and certainly chemically heterogeneous. It also may swell in contact with water. The position of the drop edge and the value of the contact angle may thus be influenced by kinetic factors; we discuss this problem of disentangling kinetic and thermodynamic determinants of cos θ later.

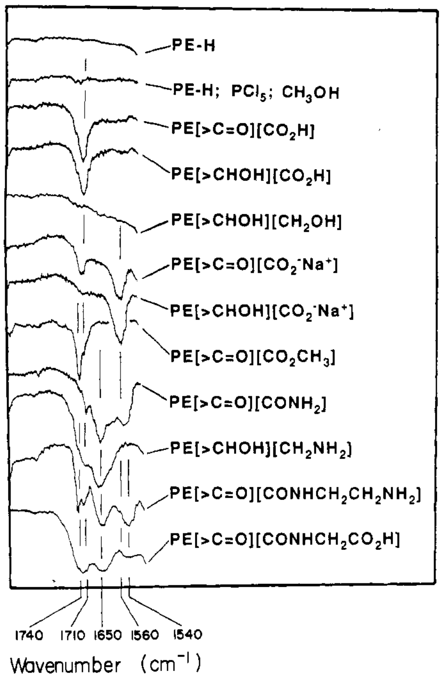


Figure 4. ATR-IR spectra of the carbonyl region of several derivatives of surface-modified polyethylene. Wavenumbers indicated are those representative of esters (1740 cm^{-1}), carboxylic acids and ketones (1710 cm^{-1}), amides (1650 cm^{-1} (C=O) and 1540 cm^{-1} (NH)), and carboxylate anions (1560 cm^{-1}). The peak at 1640 cm^{-1} for PE[>CHOH][CH_2NH_2] results from an NH_2 scissoring vibration. Because absolute absorbances are influenced by many experimental parameters (e.g., the extent of contact between the film and the KRS-5 crystal), only *relative* peak intensities within a single spectrum can be compared quantitatively.

Results and Discussion

Preparation and Characterization. The polyethylene film samples were first extracted in refluxing methylene chloride to remove antioxidants and other film additives. The samples were oxidized in aqueous chromic acid (Scheme I).[4] Scheme I summarizes pathways used to

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(18) The result of this integration [$nRT \ln (1 - \alpha_i)$] assumes that the interfacial acid groups follow the relation $pK_a = pH - \log \alpha_i/(1 - \alpha_i)$. PE–$CO_2H$ has been shown not to follow this simple relation.[4] It also assumes no change in bulk pH on ionization; that is, the pH of the drop is buffered.

(19) To formulate a prediction from eq 16, three parameters must be known or estimated: cos θ_{pH1}; n, the number of surface groups/cm^2; α_i, the extent of ionization as a function of pH.[18]

derivatize the functionalized interface. Using the analytical methods described in previous papers (XPS, ATR-IR, wetting), we estimate that the yields in conversion of carboxylic acid groups into esters or amides exceed 90%. In most of our work, the ketone groups originally generated by oxidation are left unchanged. They may also be reduced to alcohols and derivatized. Figure 4 shows typical ATR-IR spectra. For example, PE–CO_2H has a peak at 1710 cm^{-1} (carboxylic acid and ketone/aldehyde functionality). Following treatment with aqueous base two peaks are present, one at 1710 cm^{-1} (ketone/aldehyde) and a second at 1560 cm^{-1} (carboxylate anion). When the CO_2H groups in the interface are esterified and form PE-[CO_2CH_3], a new peak appears at 1740 cm^{-1} (carboxylic acid ester); the spectrum of this material is unchanged when it is treated with base.

These spectra are for the most part self-explanatory. The spectrum of PE[>CHOH][CH_2NH_2] may require some discussion. We attribute the absorbance at 1640 cm^{-1} to the NH_2 scissoring vibration and believe that the absence of a significant peak at 1540 cm^{-1} indicates that most of the amide NH groups have disappeared. The presence of NH_2 groups in this interface is confirmed by reaction of PE[>CHOH][CH_2NH_2] with dansyl chloride (see below). The resulting material, PE[>CHOH][CH_2NH_2–dansyl], is fluorescent[5] and exhibits a curve in contact angle titration similar to other interfaces that contain dansyl groups (see below). Dansyl chloride does not react with aliphatic alcohols,[20] and, when allowed to react with PE-[>CHOH][CH_2OH], no fluorescence or inflection in contact angle titration is observed.

All of the methods used to characterize the derivatives of PE–CO_2H are only semiquantitative, but on their basis we believe that most of the transformations used here proceed in yields sufficiently high that the functional groups introduced by the transformation are the primary functionality present on the surface. We have endeavored to ensure that when other species are present in the interface as contaminants (due to low yields or side reactions) they are not ionizable species. For example, the reaction of PE[CO_2CH_3] with $NH_2CH_2CH_2NH_2$ generates a material that shows primarily amide absorption in the ATR-IR spectrum (1650 cm^{-1}) although some methyl ester (1740 cm^{-1}) remains (Figure 4). These remaining esters are probably below the θ interphase of the polymer. Even if they are present in the θ interphase, we do not expect them to influence the pH dependence of the contact angle (see below). They can, of course, influence the magnitude of the pH-*independent* component of the contact angle.

Contact Angle Titration. The experimental techniques used in measuring the advancing contact angle (θ_a) as a function of pH on PE–CO_2H and derivatives have been described elsewhere.[4] We emphasize the importance of using buffered solutions and of carrying out measurements in an atmosphere maintained at 100% relative humidity.

Certain of the contact angle titrations involved interfaces having relatively small values of $\Delta\theta_a$ between the ionized and unionized forms. To provide a sense for the reproducibility of contact angle measurements, we performed a contact angle titration on a single type of surface, PE-[CONHCH(CO_2H)CH_2CO_2H], which was synthesized and examined on four different occasions. Figure 5 shows the individual contact angle measurements determined at pH 1 and pH 13 (all integral values of pH between 1 and 14 were examined and had similar reproducibility) on the four different samples. From the statistics obtained from this (Figure 5) and other experiments, we conclude that contact angle measurements are reproducible from sample to sample to ±5° and on a given sample to ±3°. The advancing angles were reproducible and surprisingly stable. The contact angle of a number of aqueous drops on the surface of PE–CO_2H was constant for more than 1 h when the chamber in which the sample was examined was maintained at 100% relative humidity.[4] Tapping the sample to jar the drop had no significant effect. Even tilting the sample had only a small influence on contact angle (Figure 6). The drops used in all our work (1 μL, $R \sim 1$ mm) were small compared with the capillary length,[13] $\kappa^{-1} \simeq 3$ mm; for these drops, gravitational effects are not important. For larger drops (10–50 μL), the advancing contact angle (pH 1) on PE–CO_2H was still relatively unchanged (±5°).

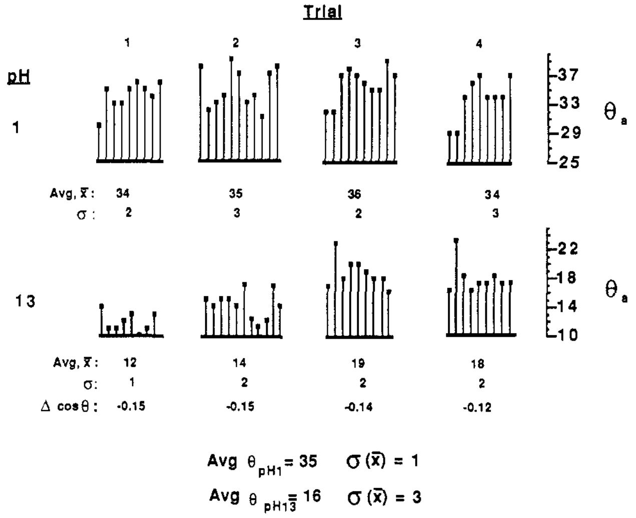

Figure 5. Examination of the types of errors observed in contact angle measurements. The contact angle (pH 1 and pH 13) was determined on four samples of PE[>C=O][CONHCH(CO_2H)-CH_2CO_2H] independently synthesized and examined on four different occasions. Each point represents a separate measurement of contact angle using a new drop of water and a new region of the interface. The average and the associated error for each trial, along with the change in cos θ between pH 1 and pH 13, are also indicated for each trial. The overall average and associated error are also reported for each pH. Measurements of θ_a at other values of pH between 1 and 14 had similar reproducibility, as did measurements using different samples.

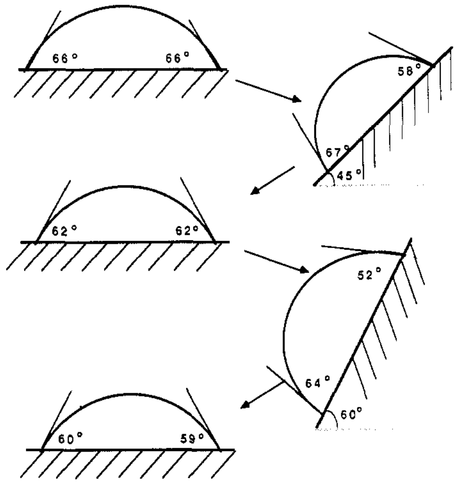

Figure 6. Influence of tilting the sample (PE[>CHOH][CH_2OH]; pH 1) on the contact angle θ. Drops were tilted while under 100% humidity. The drop did not move along a surface tilted to 45° or 60° from normal.

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[20] Seiler, N. In *Methods of Biochemical Analysis*; Glick, D., Ed.; Wiley: New York, 1970; Vol. 18, p 260.

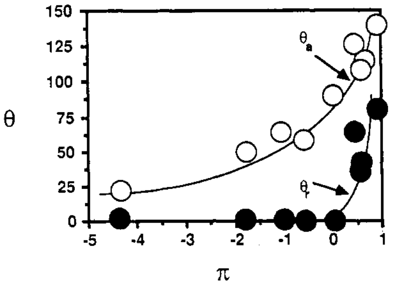

Figure 7. Advancing (θ_a) and receding (θ_r) contact angles of water (pH 1 except for PE[CO$_2^-$] (pH 13)) on samples of functionalized polyethylene with a range of polarities in the contact angle interphase. Samples shown: PE[CO$_2^-$], $\pi = -4.4$; PE[CONHNH$_2$], $\pi = -1.92$; PE[>CHOH][CH$_2$OH], $\pi = -1.13$; PE[CO$_2$H], $\pi = -0.72$; PE[CO$_2$CH$_3$], $\pi = -0.01$; PE–CO$_2$C$_8$H$_{17}$, $\pi = 0.55$; PE–[>CHOCOR][CH$_2$OCOR], R = C$_{17}$H$_{35}$, $\pi = 0.55$; R = CF$_3$, $\pi = 0.5$ (estimate); R = C$_7$F$_{17}$, $\pi = 0.88$.

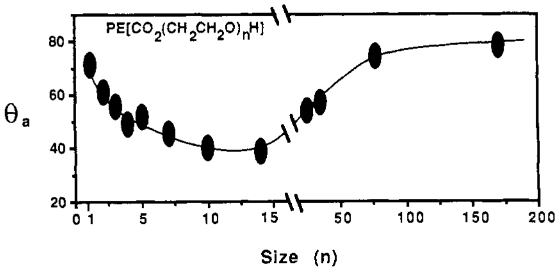

Figure 8. Influence of the size of the polar group A_P on the contact angle (pH 1). All samples were esters of poly(ethylene glycol), PE[CO$_2$(CH$_2$CH$_2$O)$_n$H], with the size determined by the length of the ether chain, n. Note: The abscissa undergoes a change in scale after $n = 15$. The interfaces were prepared by reaction of PE[COCl] with the appropriate oligomer or polymer. For $n = 1$–4, the pure, neat liquids were used as reactants; for $n > 4$, molecular weight mixtures were used, with n indicative of the average molecular weight; and for $n > 14$, the reaction between PE[COCl] and the polymer was carried out in acetone since the polymers were solids.

We have surveyed the hysteresis[14] of a range of samples representing different polarities by drawing liquid back into a syringe in contact with the drop and reading θ_r when the drop edge was stopped receding. We have arbitrarily plotted these results against the Hansch π parameter (see below) characteristic for that substituent (Figure 7).[21] All samples, including those with nonpolar interfaces, show hysteresis.

Nonionizing Functionalities. Table I gives advancing contact angles for a range of functional groups R in the contact angle interphase of PE[R]. None of these groups changes its state of ionization over the pH range 1–13. Even incorporation of very polar, hydrophilic groups such as *N*-acylglucosamine, sulfate, and sulfonate into the interphase does not yield systems showing complete wetting.

Equations 9 and 10 provide a rationalization for this lower limit to the contact angle as well as an interesting implication for efforts to design fully wettable surfaces derived from PE–CO$_2$H. In the plateau region of Figure 3 (top), increasing the polarity of R has no influence on θ (although it might influence behavior in "dry spreading").[13] The only practical method to increase the wetting of the interface beyond the plateau value appears to be to increase A_P, either by increasing the extent of functionalization of the interface or by increasing the size of the polar substituents R so that they occupy a larger area fraction of the interface sensed by the wetting liquid.

Table I. Contact Angle of Water on Interfaces That Contain No Functional Groups and Whose State of Ionization Changes with pH[a,b]

code	sample	θ_a
1	PE–H (unoxidized)	103
	Amides	
2	PE[CONH–glucose]	20
3	PE[CONHCH$_2$CH$_2$OH]	40
4	PE[CONH$_2$]	50
5	PE[CONHCH$_3$]	49
6	PE[CON(CH$_3$)$_2$]	53
7	PE[CONHCH(CH$_2$CH$_2$CH$_3$)$_2$]	91
8	PE[CONHCH(CH$_2$(CH$_3$)$_2$)$_2$]	100
9	PE[CONHCH$_2$(*c*-C$_6$H$_{11}$)]	103
10	PE[CONHNHCOC$_{11}$H$_{23}$]	110
11	PE[CONHC$_6$H$_5$]	113
12	PE[CONHC$_8$H$_{17}$]	114
	Alcohol Derivatives[a]	
13	PE[CH$_2$OH] (PE[>CHOH][CH$_2$OH])	68
14	PE[CH$_2$OCO(CH$_2$)$_{16}$CH$_3$]	123
15	PE[CH$_2$OCOCF$_3$]	126
16	PE[CH$_2$OCO(CF$_2$)$_2$CF$_3$]	134
17	PE[CH$_2$OCO(CF$_2$)$_6$CF$_3$]	141
	Esters	
18	PE[CO$_2$CH$_3$]	90
19	PE[CO$_2$CH$_2$CH$_2$Br]	97
20	PE[CO$_2$CH$_2$CH$_3$]	103
21	PE[CO$_2$(CH$_2$)$_2$CH$_3$]	107
22	PE[CO$_2$CH(CH$_3$)$_2$]	110
23	PE[CO$_2$(CH$_2$)$_3$CH$_3$]	116
24	PE[CO$_2$CH(CH$_3$)CH$_2$CH$_3$]	115
25	PE[CO$_2$(CH$_2$)$_5$CH$_3$]	123
26	PE[CO$_2$(CH$_2$)$_7$CH$_3$]	125
	Others (Always Ionized)	
27	PE[CONHCH$_2$CH$_2$SO$_3^-$]	32
28	PE[CONHCH$_2$CH$_2$OSO$_3^-$]	36

[a] The alcohol-derived surfaces actually contain esters formed from primary and secondary hydroxy groups derived from the reduction of carboxylic acid and ketone groups, respectively. [b] Amides were prepared either by reaction of PE–COCl with RNH$_2$ (NH$_3$ and methyl-, dimethyl-, and octylamines) or by reaction of PE–CO$_2$CH$_3$ with RNH$_2$; esters were prepared by acid-catalyzed esterification of PE–CO$_2$H; alcohol derivatives were obtained by reaction of PE–CH$_2$OH with acid chlorides or anhydrides.

Figure 8 shows the contact angle on a series of interfaces modified by formation of esters with oligomeric polyethylene glycols PE[CO$_2$(CH$_2$CH$_2$O)$_n$H]. These experiments are designed to test the hypothesis that large groups have a larger influence on θ_a than do small groups with similar hydrophilicity. As the length of the poly(ethylene glycol) (PEG) chain increases over the interval $n = 1$–14, θ_a decreases. Above $n = 14$, however, θ_a increases slowly with n. We attribute the decrease in θ_a between $n = 1$ and $n = 14$ to the effects of size: A_P increases as n increases, and the contact angle drops as nonpolar regions of the interface are covered by the polar chains. We suggest that the increase in θ_a for $n > 14$ can be attributed to a slight decrease in the average polarity of the PEG group as n increases. The OH group at the end of each chain is appreciably more hydrophilic than the ether units,[21] and increasing the chain length lowers the overall polarity. For small values of n the increased area A_P is more important, but as n increases the predominance of the ether groups outweighs the increase in area.[22]

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(21) Hansch, C.; Rockwell, S. D.; Jow, P. Y. C.; Leo, A.; Steller, E. E. *J. Med. Chem.* **1977**, *20*, 304–306. Hansch, C.; Leo, A.; Unger, S. H.; Kim, K. H.; Nikaitani, D.; Lien, D. *J. Med. Chem.* **1973**, *16*, 1207–1216. See also: Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley: New York, 1979.

(22) The relationship between the MW of attached polymers and A is decidedly unclear. Whether A even increases as the MW increases depends on whether the polymeric chains are extended into the solution or coiled up into a ball.

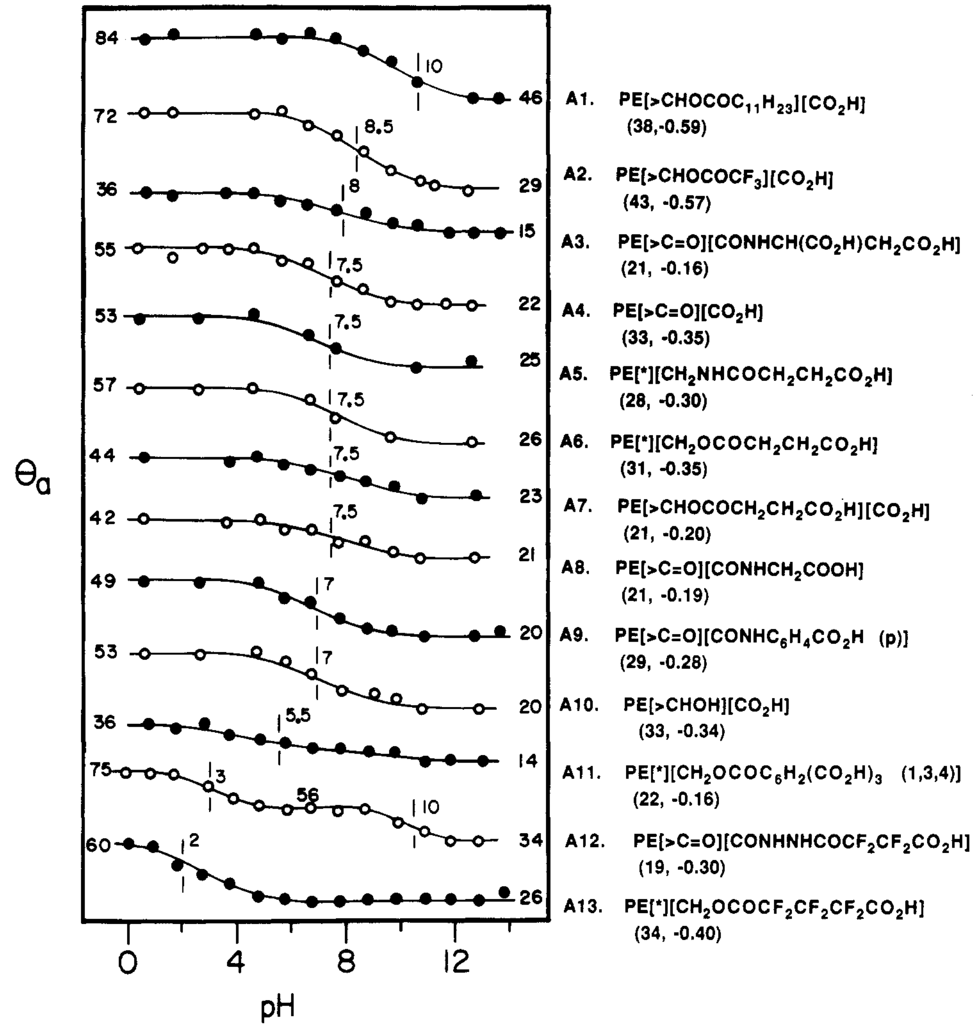

Figure 9. Contact angle titration for interfaces containing carboxylic acid groups. All curves are to the same vertical scale. The limiting values of the contact angle and the values of $pK_{1/2}$ are shown for each interface. Following the structures summarizing the functional groups in the interface are values for the changes in θ_a on ionization and for $\Delta \cos \theta_a$. The inflection at pH 10.5 for PE[>C=O]-[CONHNHCOCF$_2$CF$_2$CO$_2$H] is due to ionization of the N*H*COCF$_2$ proton. The number to the left of the structure is used for identification in later figures. Structures derived from PE[>CHOH][CH$_2$OH] are abbreviated with an *: PE[*][CH$_2$OR] = PE[>CHOR][CH$_2$OR].

From these and other experiments, it appears that it is possible to reduce the contact angle on these types of interfaces by increasing the effective area covered by polar molecules. We have not been able to generate a surface from PE-CO$_2$H that has θ_a = 0, even when large, polar polymers (such as poly(acrylic acid)) have been attached to the interface.[23] This failure may be due in part to crystalline, oxidation-resistant regions of the interface having dimensions of 0.01–0.1 μm.[24] If (relatively) unfunctionalized regions of this geometry are present in the interface, it would be difficult or impossible to cover them completely with individual molecules attached to the polar regions of the interface.

Carboxylic Acids. Figure 9 summarizes contact angle titrations of a number of derivatives of PE-CO$_2$H having carboxylic acid groups in the functionalized interface. All of these materials having monocarboxylic acid functionalities show a pH dependence of the contact angle that is qualitatively similar to that of PE-CO$_2$H. The width of the inflection (4–5 pH units) is similar for all monoacids (although di- and triacids are broader); the magnitude of the difference between the low and high values of pH is also similar.

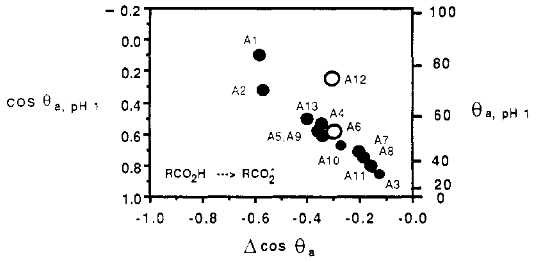

Figure 10. Correlation between $\theta_{a,pH1}$ (the contact angle on the unionized surface) and $\Delta \cos \theta_a$ for the interfaces listed in Figure 9. The labels correspond to the labels used in Figure 9. The solid points (●) represent interfaces made in two or fewer synthetic steps; open symbols (○) represent surfaces made in four or more synthetic steps. These latter points may have a lower surface density of CO$_2$H groups due to low yields in the syntheses.

The acidity of carboxylic acid groups is low on interfaces that have low polarity as a result of intentional inclusion of nonpolar functions: examples of representative values of $pK_{1/2}$ (the value of solution pH at which the contact angle has a value midway, in terms of cos θ_a, between those of the high and low pH plateaus) include PE[>CHOH]-

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(23) PE[>CHOH][CH$_2$NH$_2$] was allowed to react with poly(acrylic acid chloride) in acetone solution containing triethylamine for 18 h, followed by rinsing in basic water. Observed values of θ_a were pH 1, 53°; pH 13, 30°; $pK_{1/2}$ = 7.

(24) For SEM micrographs, see ref 4. For information on crystalline and noncrystalline regions in polyethylene, see: Bassett, D. C. *Principles of Polymer Morphology*; Cambridge University Press: Cambridge, 1981.

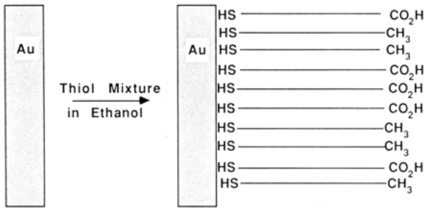

Figure 11. Schematic illustration of the formation of monolayers from $HS(CH_2)_{15}CH_3$ and $HS(CH_2)_{15}CO_2H$. Monolayers were formed by the spontaneous adsorption of the thiols onto the gold surface from ethanol solution.

$[CO_2H]$, 7.5; PE[>C=O][CO_2H], 7.5; PE[>$CHOCOCF_3$][CO_2H], 8.0; and PE[>$CHOCOC_8H_7$][CO_2H], 10. This effect can be attributed in major part to an increase in the difficulty of ionization (and thus an increase in $pK_{1/2}$) of the CO_2H groups as the local polarity they experience decreases.[5]

The relationship between θ_{pH1} (that is, the contact angle on the protonated form of the interface) and $\Delta \cos \theta_a$ is instructive (Figure 10): as θ_{pH1} decreases, $\Delta \cos \theta_a$ also decreases. This relationship is consistent with eq 12c.

We note that $\Delta \cos \theta_a$ changes significantly for interfaces in which the nature of the ionizing group is unchanged (PE[>CHOH][CO_2H], $\Delta \cos \theta_a = -0.34$; PE[>$CHOCOCF_3$][$CO_2H$], $\Delta \cos \theta_a = -0.57$; PE[>$CHOCOC_{11}H_{23}$][$CO_2H$], $\Delta \cos \theta_a = -0.59$). This observation indicates that the nature of the functional groups surrounding the carboxylic acid group influences the magnitude of $\Delta \cos \theta_a$ and that the contributions of functional groups to interfacial free energies are cooperative, rather than independent, as assumed in eq 7.

Model Systems: Oriented Organic Monolayers. PE–CO_2H is a complex system: interpretation of its wetting behavior is difficult because evidence concerning the molecular-scale structure of its θ interphase is inferential. We have, in a related project,[25] examined in detail the properties of oriented organic monolayers of thiols having the structures of $HS(CH_2)_nCO_2H$ and $HS(CH_2)_nCH_3$ adsorbed on thin gold films. Here we summarize several conclusions concerning their structure and describe a number of data relevant to their behavior in contact angle titration. These data are useful in interpreting the more extensive data for PE–CO_2H and its derivatives.

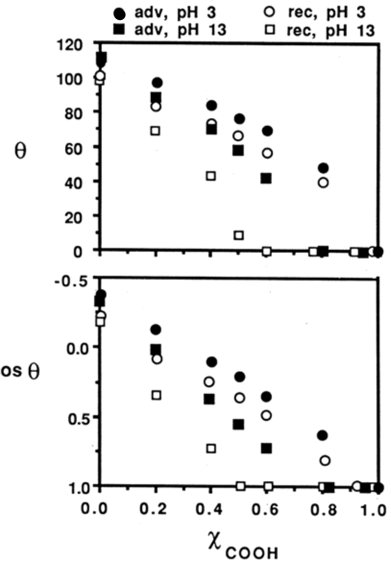

Figure 12. Contact angle as a function of χ_{CO_2H}. Advancing and receding angles were determined at pH 1 and pH 13.

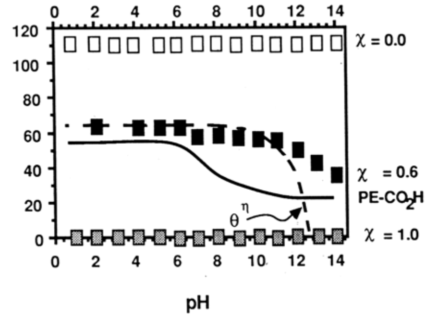

Figure 13. Contact angle titrations of monolayer surfaces containing methyl and carboxylic acid groups (χ_{CO_2H} = 0.0, □; 0.6, ■; 1.0, ▨; Figure 12). The contact angle titration obtained for PE–CO_2H is shown as a solid line for comparison. The dashed line is the behavior expected on the basis of eq 16 with the following assumptions: $pK_a = 11$; $\theta_{a,pH1} = 62$ °; $n = 3 \times 10^{14}$ cm^{-2} (see text).

Long-chain alkanethiols functionalized in the ω-position with a number of organic groups adsorb spontaneously on gold and form oriented monolayer films (Figure 11). The packing density of these films is high, and the component thiols are highly oriented.[26-29] The oxidation state of the sulfur when adsorbed is still not unambiguously established; here we write it simply as thiol (SH).[29] We and several other groups working on these systems have concluded that the alkyl chains are fully extended, with densities similar to that expected for a crystalline sheet,[30] and have significant crystalline order.[31] They provide the most highly ordered system presently applicable to the study of the physical–organic chemistry of interfaces. Figure 12 summarizes observations made on the wettability of films prepared by adsorption of mixtures of $HS(CH_2)_{15}CO_2H$ and $HS(CH_2)_{15}CH_3$ on gold. The mole fraction χ of the carboxylic acid component in this mixture refers to the *solution* value. (X-ray photoelectron spectra suggest that the surface acid mole fraction in mixed monolayers is less than the solution value; however, the exact surface composition is not critical in our analysis below.) Because CH_3 and CO_2H groups are similar in size,[31] $\chi_i \simeq A_i$ (eq 9). Several observations are relevant to the behavior of PE–CO_2H. First, when $\chi_{CO_2H} = 1$, the interface is completely wettable at *both* pH 1 and 13. Thus, an interface composed of closely packed CO_2H groups is completely wetted ($\cos \theta_{CO_2H} = 1$, eq 10). For intermediate values of χ, the contact angle at pH 13 is lower than the contact angle at pH 1, the difference presumably being due to ionization of the interfacial carboxylic acid groups at high pH. Second, the hysteresis in

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(25) We will shortly publish details of the characterization of these thiol monolayers.

(26) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481–4483.

(27) Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 1233–1239. Li, T. T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107–6109.

(28) Sagiv, J., unpublished results.

(29) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358–2368. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. L. *J. Am. Chem. Soc.* **1987**, *109*, 3559–3568.

(30) Alexander, A. E.; Hibberd, G. E. In *Techniques of Chemistry*; Weissberger, A.; Rossiter, G. W., Eds.; Wiley-Interscience: New York, 1972; Vol. 1, p 575.

(31) Strong, L.; Whitesides, G. M. *Langmuir*, in press.

(32) We believe that the extended all-trans methylene chains of these monolayers each occupy approximately 20–25 Å^2 of the surface and that the volume at the terminal end of the chain is occupied by the methyl or carboxylic acid group. Thus, the effective area occupied by each of these groups is similar, even though a carboxylic acid group is slightly larger than a methyl group.

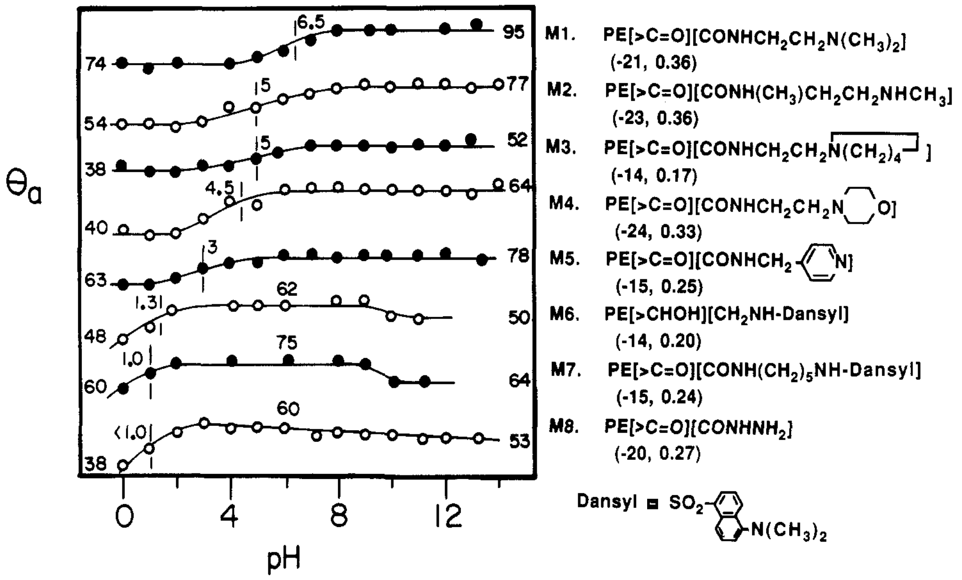

Figure 14. Advancing contact angle θ_a as a function of pH for interfaces containing amine moieties. Each curve shows values of θ_a at high and low pH, and the values of $pK_{1/2}$. Following the structure summarizing the functional groups in the interface are values for the change in θ_a on ionization and for Δ cos θ_a. The number to the left of the structure is for identification in later figures.

this system, although large, is significantly less than that observed for PE–CO_2H. Tilting the sample, however, still does not cause the drop to roll down the plate, as with PE–CO_2H. The magnitude of the hysteresis for measurements at pH 1 appears to be independent of the polarity of the interface: $\cos\theta_a - \cos\theta_r \simeq 0.15$ at $\chi = 0$ and at $\chi = 0.8$. For measurement at pH 13, the hysteresis increases as χ_{CO_2H} increases, until the receding angle is zero. Third, the contact angle titration curve at $\chi = 0.6$ (Figure 13, selected because $\theta_{a,pH1}$ is approximately equal to that for PE–CO_2H) is, in some respects, similar to that observed for PE–CO_2H. In particular, the values of θ_{pH1} and θ_{pH13} are similar for the two systems. The carboxylic acid groups in the monolayer are, however, significantly less acidic than those for PE–CO_2H ($pK_{1/2} > 11$). It is also unclear whether the contact angle reaches a plateau at high pH.[33]

To help evaluate the importance of contributions from η_R^{pH} to the change in θ_a on this interface, Figure 13 also includes a plot of θ_a as a function of pH derived by using eq 16 assuming the interfacial $pK_a = 11$. This plot also assumes that the density of carboxylic acid groups in the θ interphase is equivalent to that in a close-packed stearic acid crystal,[30] 5×10^{14} cm^{-2}, reduced by the mole fraction of acid groups present in the monolayer (assumed to be equal to the mole fraction in solution, 0.6) to yield $n = 3 \times 10^{14}$ cm^{-2}. In this analysis, the drop in θ_a as the pH increases is due solely to the entropy of dilution of the proton that is released upon ionization. Although eq 16 clearly does not describe quantitatively the behavior of either PE–CO_2H or the monolayer system, it does indicate that the free energy of ionization is in principle sufficiently large to influence θ_a.

It is important to later discussions to note that $\cos\theta_{CO_2H} \rightarrow 1$ only close to $\chi_{CO_2H} = 1$, while $\cos\theta_{CO_2^-} \rightarrow 1$ at $\chi_{CO_2^-} \simeq 0.7$. The difference between these two intercepts is that expected qualitatively on the basis of hydrophilicity. Moreover, the question of whether $\cos\theta_{CO_2H} = 1$ (eq 12) in the environment provided by PE–CO_2H is not unambiguously answered from these experiments, since the polarity experienced by CO_2H in a monolayer and on a hypothetical perfectly functionalized polyethylene interface may not be the same.

The data in Figure 12, in conjunction with data from PE–CO_2H, raise certain questions about the model used in deriving eq 2–12, especially about the assumption that the contributions of functional groups to interfacial free energies are linearly independent (eq 4 and 5). An ordered monolayer interface composed only of CO_2H groups (Figure 12, $\chi = 1.0 \simeq A_{CO_2H}$) has $\theta_a = 0°$. This result suggests that this interface has a significant amount of adsorbed water, that is, $\gamma_{SV} \simeq \gamma_{LV}$.[34] Thus, the carboxylic acid groups on this interface fall into the range of functional group hydrophilicity where increased hydrophilicity should have no influence on θ_a or cos θ_a (Figure 3, regime B). In fact, however, the observed value of θ_a on interfaces with $\chi_{CO_2H} < 1$ is lower at pH 13 than at pH 1. There are two possible explanations for this behavior. First, the decrease in θ_a at high pH is due to the energy of ionization (Figure 13, θ_a), a possibility that we cannot presently disprove. Second, the amount of water adsorbed on the CO_2H groups is less when surrounded by hydrophobic methyl groups than when surrounded by CO_2H groups. Thus, when $\chi_{CO_2H} < 1$, the carboxylic acid groups may not, in fact, be polar enough to have a thick layer of adsorbed water. Conversion of these carboxylic acid groups into carboxylate anions could then result in the observed decrease in θ_a. We note that this second explanation is consistent with data from PE–CO_2H and derivatives.

We conclude from the similarities between the contact angle titration curves for PE–CO_2H and the oriented thiol

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[33] These differences may stem from different causes of the change in θ_a with pH. A_P, γ_{SV}^{pH}, γ_{SL}^{pH}, η_R^{pH}, and interfacial swelling may all contribute, in different proportions, to the change in θ_a on ionization in these surfaces.

[34] A contact angle of 0° on a pure CO_2H surface should be accompanied by the adsorption of a significant amount of water at the interface, a prediction confirmed by measurement of hexadecane contact angles. At 100% relative humidity, hexadecane beads on a CO_2H surface (θ_a = 35–40°) even though it wets the surface at ambient humidity (30–70%). If the relative humidity is allowed to decrease, a point is reached where the adsorbed aqueous film evaporates and the hexadecane drop suddenly spreads. Since hexadecane wets neither a pure methyl surface (θ_a = 47°) nor a pure acid surface ($\theta_a \simeq 35°$) at 100% RH, the model developed for polyethylene would predict that hexadecane should bead at all intermediate surface compositions. In fact, an 80% acid surface is wet by hexadecane at all relative humidities. This result militates strongly against island formation and suggests that for monolayer systems the different components of the interface cannot be treated entirely as being independent.

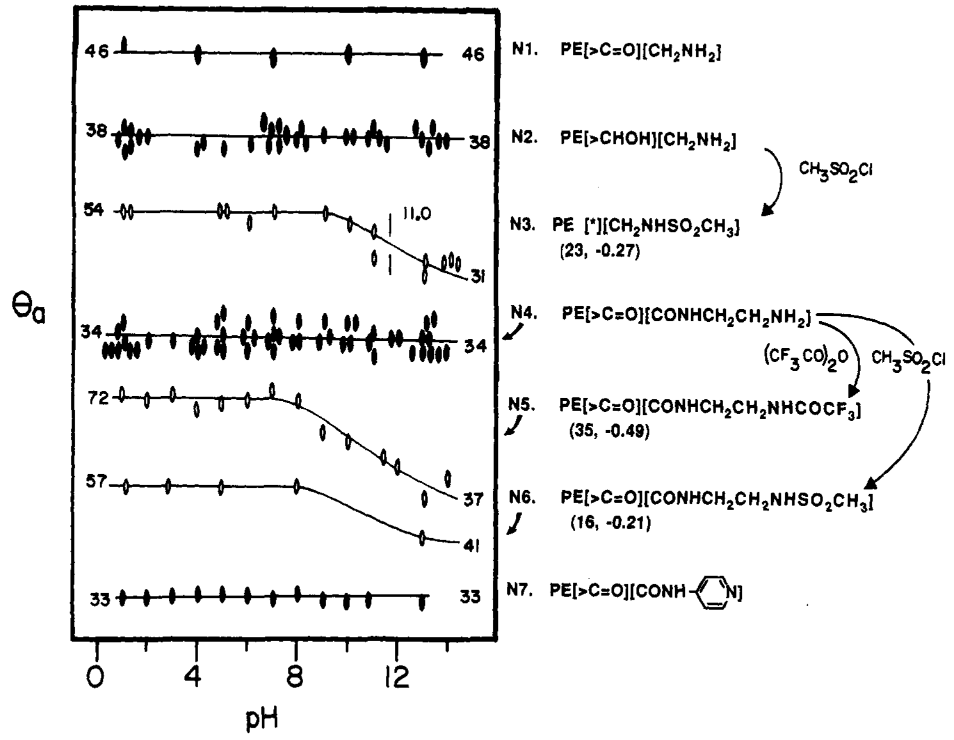

Figure 15. Contact angle titration of four amine- and pyridine-containing interfaces that show no dependence of θ_a on pH, together with contact angle titrations for derivatives of these substances. The data for PE[>CHOH][CH_2NH_2] and PE[>C=O][$CONHCH_2CH_2NH_2$] summarize data both from a number of replicate titrations and for materials prepared by different synthetic methods (seven titrations and one synthetic method for the former; nine titrations and two different synthetic methods for the latter). The scatter in the data shown for these two samples is indicative of the magnitude of the variation in different experiments, rather than the smaller scatter in one experiment. Individual experiments gave data of the sort shown for PE[>C=O][CH_2NH_2], but the plot shifted up or down for different samples. A second derivative of PE[>CHOH][CH_2NH_2] was made by reacting it with dansyl chloride, a material that does not react with aliphatic alcohols.[20] The titration curve for this interface is shown in Figure 14 (M6). The structure shown as PE[*][CH_2NHR] is an abbreviation for PE[>CHOR][CH_2NHR].

monlayers that the behavior of the former is not unexpected for an interface containing a mixture of ionizable CO_2H and nonionizable, nonpolar functionality and is not predominantly an artifact of swelling or reconstruction in the complex polymer interface (although these phenomena probably are important in determining hysteresis). The important observation that the values of θ_a are similar on rough, heterogeneous PE–CO_2H and on relatively flat, homogeneous monolayer systems that plausibly simulate the mixture of functionality present in the polymer interface ($\chi \simeq 0.5$), *but that hysteresis is relatively much smaller on the monolayer than on the polymer*, implies that the observed values of contact angle on the polymer are close to equilibrium values. How it is possible to obtain quasi-equilibrium values from a system in which high hysteresis implies important nonequilibrium determinants to wetting and what combination of thermodynamic and kinetic factors (in detail) fixes the observed values of θ_a remain to be established.

Amines. Figure 14 summarizes the results of contact angle titration on amine-containing interfaces. All of the interfaces in this figure (and most simple secondary or tertiary amines) yield changes in the contact angle as a function of pH; interfaces containing other types of amine groups (especially primary amines) do not (see below). The form of the curve of θ_a vs pH is the reverse of that obtained with interfaces containing carboxylic acid groups: the contact angle increases on going from low to high pH. This result is expected for an interface containing basic species that are more hydrophilic in the charged, protonated form (NHR_3^+) than in the neutral, deprotonated form (NR_3).

The $pK_{1/2}$ of each of the interfaces summarized in Figure 14 is significantly lower than the pK_a of the corresponding soluble species. This result is the opposite of that for the carboxylic acid interfaces, for which the $pK_{1/2}$ was always higher than the pK_a of the soluble analogue. We attribute the shift in $pK_{1/2}$ relative to the analogous solution pK_a in the interfaces containing both carboxylic acids and amines to the difficulty associated with creating a charged group at the interface (due to a low local dielectric constant and perhaps to charge–charge interactions).

The four amine-containing interfaces that did not display any change in the contact angle with water as a function of pH (Figure 15)—three containing CH_2NH_2 groups and one a pyridine—were made by independent methods (Scheme I) to minimize the chance that a synthetic artifact (failure of a synthesis, interfacial reconstruction during synthesis) was responsible for the surprising absence of an inflection in the titration curves. All have a relatively low contact angle that is independent of pH. PE[>C=O][CH_2NH_2] was prepared by reaction of PE[>C=O][CH_2CO_2H] with HN_3 in sulfuric acid–chloroform. The interface of this material may have reconstructed partially under the conditions employed ($CHCl_3$, 50 °C, 1 h); reconstruction would result in a decrease in A_P.[17] PE[>CHOH][CH_2NH_2] was prepared by initial reaction of PE[COCl] with NH_4OH to form PE[>C=O][$CONH_2$], followed by reduction of both amide and ketone groups.[5] PE[>C=O][$CONHCH_2CH_2NH_2$] was made either by esterifying PE[>C=O][CO_2H] in methanol and forming PE[>C=O][CO_2CH_3] and allowing this interface to react with ethylenediamine or by causing PE[COCl] to react with ethylenediamine. The ketone groups are probably still present after these transformations, but we have not characterized them explicitly. The interfaces made by these two synthetic routes are indistinguishable. PE[>C=O][CONHpyr] was prepared by reaction of PE[>C=O][COCl] with *p*-aminopyridine.

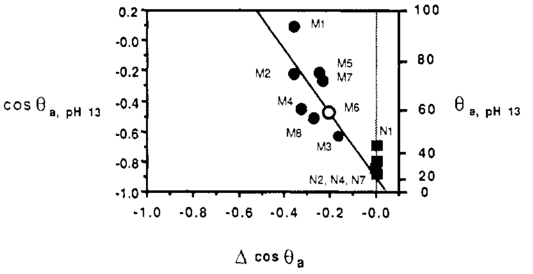

Figure 16. Correlation between the contact angle at pH 13 (the contact angle on the unionized interface) and the change in contact angle upon ionization for amine-containing interfaces shown in Figures 14 and 15. The labels correspond to the labels used in those figures. The solid line represents a least-squares fit to only those samples that showed a change in θ_a with pH ($\Delta \cos \theta_a \neq 0°$; ●, ○). The open symbol represents an interface requiring four synthetic steps, and thus this interface may have a lower interfacial density of amine moieties than the other interfaces. The value of $\cos \theta_{pH6}$ was used in place of $\cos \theta_{pH13}$ for the interfaces that contained an acidic group in addition to the amine function (M6, M7, Figure 14).

The fact that none of these samples shows a pH dependence of the contact angle establishes that this property is not simply an artifact of a single synthetic method. ATR-IR spectra of samples containing CH_2NH_2 groups suggest that amine functionalities comprise a significant portion of the functional groups present in the functionalized interfaces (based on the ATR-IR peaks at 3350 cm^{-1} (NH and OH), 1640 cm^{-1} (NH_2 scissor; Figure 4), and 1120 cm^{-1} (C-N).[35] In order to prove, however, that the amine groups are present in the θ interphase and actually do not influence the contact angle (although secondary and tertiary amines do so), we converted them to new functionalities (CH_2NHSO_2R and $CH_2NHCOCF_3$), both sufficiently acidic to deprotonate in an accessible range of pH. The resulting amides display the expected dependence of contact angle on pH (Figure 15). In addition, $PE[>C=O][CH_2NH_2]$ was allowed to react with lauroyl chloride. The resulting interface was hydrophobic ($\theta_a > 100°$), presumably as a result of forming $PE[>C=O][CH_2NHCOC_{11}H_{23}]$. Thus, unless these interfaces reconstructed during these reactions to bring "buried" amine groups into the θ interphase, we conclude that amines *are* present in the θ interphase but do not change hydrophilicity with pH. We believe reconstruction of the interface during reaction to be unlikely: CH_3SO_2Cl does not appreciably swell polyethylene at room temperature, and even in solvents that swell polyethylene (methylene chloride, toluene) reconstruction typically results in the *loss* of functionality from the contact angle interphase to the interior.[7]

Why is the wetting of the three interphases containing CH_2NH_2 groups independent of pH? We propose that these groups have reached a limit in hydrophilicity and that conversion of CH_2NH_2 to $CH_2NH_3^+$ does not appreciably increase the hydrophilicity of the interface (that is, that $\cos \theta_P \simeq 1$ for both CH_2NH_2 and $CH_2NH_3^+$ (eq 8 and 9)). This proposal is justified in detail below. We note here, however, that a plot of $\Delta \cos \theta_a$ vs $\cos \theta_{pH13}$ for all the amine-containing interfaces examined (Figure 16) shows a general trend similar to that observed for carboxylic acid containing interfaces (Figure 10): $\Delta \cos \theta_a$ decreases with $\cos \theta_a$ for the unionized interface.

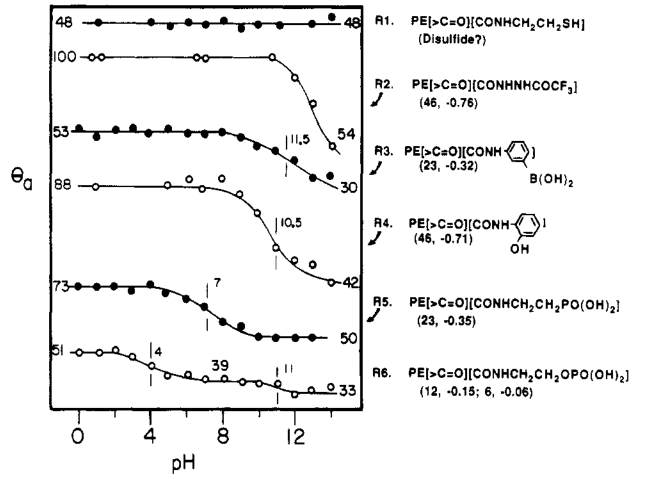

Figure 17. Advancing contact angle θ_a as a function of pH for interfaces containing a variety of ionizable functional groups. Each curve shows values of θ_a at low and high pH and the values of $pK_{1/2}$. Following the structure summarizing the functional groups in the interface are values for the change in θ_a on ionization and for $\Delta \cos \theta_a$. The number to the left of the structure is for identification in later figures.

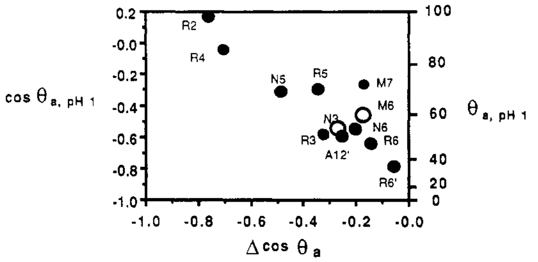

Figure 18. Correlation between $\theta_{a,pH1}$ on the unionized (or less ionized in the case of multiple ionizations) surface and $\Delta \cos \theta_a$ for interfaces containing various functional groups. Data plotted are for interfaces shown in Figure 17 and for the sulfonamides and fluorinated amides shown in Figures 9 and 15. The labels correspond to the labels used in those figures; A12′ and R6′ represent the second (high pH) ionization of interfaces A12 and R6 with difunctional acid groups. The value of $\cos \theta_{pH8}$ was used in place of $\cos \theta_{pH1}$ for A12′ and R6′. The open symbols (○) represent interfaces requiring four or more synthetic steps which therefore may have lower interfacial concentrations of the particular functional group concerned.

Other Ionizing Functional Groups. We have surveyed interfaces containing several other ionizable functional groups (Figure 17). All of these samples, except that containing a thiol group,[36] show a pH dependence for the contact angle that is qualitatively consistent with the solution ionization of these functional groups. For comparison with previous data, Figure 18 plots $\Delta \cos \theta$ on ionization against $\cos \theta_{pH1}$ of the unionized surface. As for interfaces containing carboxylic acid and amine moieties, the change in contact angle decreases as the contact angle on the unionized surface decreases.

Correlations between the Contact Angle of Water on Functionalized Interfaces and Functional Group Hydrophilicity. We have defined the hydrophilicity of functional groups in terms of their Hansch π parameters.[21] The π parameter is given by eq 17 and is defined as the

$$\pi = \log([c]_{\text{octanol}}/[c]_{H_2O}) - 2.13 = (2.303RT)^{-1}(G°_{H_2O} - G°_{\text{octanol}}) \quad (17)$$

log of the partition coefficient (octanol/water) of the functional group attached to a benzene ring minus the log

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[35] Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 2nd ed.; Wiley: New York, 1958.

[36] We have not performed contact angle titrations on this sample under inert atmosphere or with aqueous drops containing thiol reducing agents to determine whether the thiol-compromising interface might have been oxidized to disulfides.

of the partition coefficient of benzene itself (2.13). Thus, π is a parameter that measures the relative stability of a functional group in water and in a low-polarity medium (octanol). In an ideal system having only one type of interfacial functional group, Young's equation (eq 1) could be interpreted similarly as measuring the relative stability of that group at the interface between polymer and water (relatively high polarity) and at the interface between polymer and air saturated with water vapor (relatively low polarity). Because both π and θ_a are measures of the relative stability of a functional group in polar and nonpolar environments, we postulate that π and $\cos\theta_a$ are linearly related (eq 18 and 19).

$$K_{IL}(\gamma_{S,H_2O} - \gamma_{SV}) = \sigma_{IL}(G°_{H_2O} - G°_{octanol}) \quad (18)$$

$$\cos\theta_a = -\sigma_{IL}\left(\frac{2.3RT}{K_{IL}\gamma_{LV}}\right)\pi \quad (19a)$$

$$\cos\theta_a = C\pi \quad (19b)$$

Equation 18 hypothesizes a linear free energy relationship between corresponding interfacial and solution free energy terms: σ_{IL} is a dimensionless constant of proportionality between interfacial and solution terms, and K_{IL} is a constant that converts interfacial free energy (in erg/cm^2) into free energies (in kcal/mol of surface groups).[37] Simplification of eq 19a yields eq 19b, where C is simply a dimensionless combination of constants (for experiments at constant T). An obvious extension of eq 19 to interfaces with more than one functional group yields eq 20.

$$\cos\theta_a = \sum_i A_i C\pi_i \quad (20)$$

$$\pi^* = \sum_i A_i\pi_i \quad (21)$$

As indicated previously, we have no method to measure A_i experimentally, but we have estimated χ_i, the mole fraction of the different functional groups present in the interface. We assume that $\chi_i = A_i$ for most of the interfaces considered. We have previously estimated that for the starting material PE[>C=O][CO$_2$H] $\chi_{CO_2H} = 0.3$, $\chi_{C=O} = 0.2$, and $\chi_{CH_2} = 0.5$.[4] For PE[>C=O][CO$_2$CH$_3$], the corresponding values would be $\chi_{CO_2CH_3} = 0.3$, $\chi_{C=O} = 0.2$, and $\chi_{CH_2} = 0.5$; for PE[>CHOCOCF$_3$][CH$_2$OCOCF$_3$] in which both carboxylic acid and ketone moieties are reduced to alcohols before acylation, the values would be $\chi_{CHOCOCF_3} = 0.5$ and $\chi_{CH_2} = 0.5$. Values of π for the functional groups were obtained from the literature[21] or estimated following the procedure outlined in the Experimental Section.

Figure 19 is the first of two plots relating the hydrophilicity of the interfacial functional groups to the wettability of the interface. It is simply a plot of the observed values of θ_a (or $\cos\theta_a$) as a function of π_i for the major functional group involved. This plot makes no correction for the functional groups derived from the ketones (whether in the form of a ketone or alcohol) nor does it take into account the presence of CH$_2$ groups. It does, however, establish the important qualitative point that the wettability of the interface does not seem to respond to decreases in π below −2 (that is, to increases in hydrophilicity beyond the level represented approximately by PE[CONHNH$_2$], PE[CONH-glucose], or PE-[CONHCH$_2$CH$_2$SO$_3^-$]).

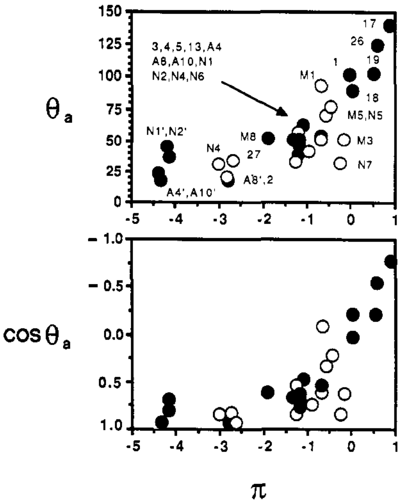

Figure 19. Correlation between θ_a (top) and $\cos\theta_a$ (bottom) and the π value of the functional groups attached to PE–R. The π values were obtained directly from the literature (●)[21] or were estimated (○; see Experimental Section). The π values for the open symbols should be considered less accurate than those for the solid symbols. Interfaces shown contain either >C=O or >CHOH groups and CH$_2$/CH$_3$ groups; these were not taken into account. Larger (more positive) π values indicate lower hydrophilicity. The data points labeled with a ′ (e.g., A4′) represent θ_a on the ionized form of the appropriate surface (e.g., A4).

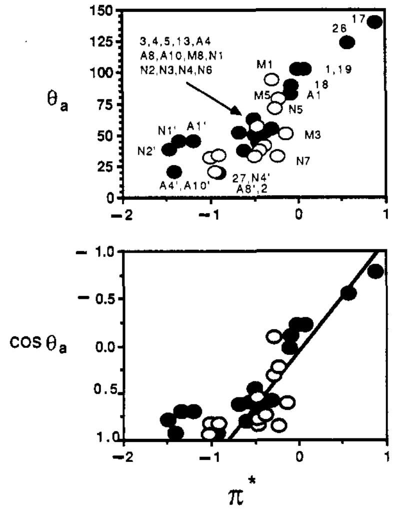

Figure 20. Correlation between θ_a (top) and $\cos\theta_a$ (bottom) and π^* (eq 21; π^* takes into account all of the functional groups believed to be present in the interface) determined for each interface in Figure 19 and others. The π values used to determine π^* were obtained directly from the literature (●)[21] or were estimated (○; see Experimental Section). The π^* values for the open symbols should be considered less accurate than those for the solid symbols. The data points labeled with a ′ (e.g., A4′) represent θ_a on the ionized form of the appropriate surface (e.g., A4). The line is a best fit to the linear portion of the graph ($\pi^* > -0.8$).

The second plot (Figure 20) follows eq 21 in determining the π^* value for each interface and thus takes into account the hydrophilicity of all of the functional groups on the surface. Again, there is a strong suggestion of the influence of the hydrophilicity on the contact angle, as anticipated by eq 9 and 10 (Figure 3). This figure also shows the predicted relationship between $\cos\theta_a$ and π^* (eq 18b) using π^* in place of π. The constant C was determined from a best fit to the data with $\pi^* > -0.8$: $C = -1.1$.[37] At lower

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[37] This empirical value for C also allows σ_{IL} to be evaluated if K_{IL} is known. If we assume the interface contains 10^{15} groups/cm^2 (equivalent to the packing density in a stearic acid crystal multiplied by a roughness factor of 2),[30] then $K_{IL} \simeq 0.0144$ (kcal/mol)(erg/cm^2)$^{-1}$. Using $K_{IL} = 0.0144$ and $C = -1.12$, we calculate (eq 19) $\sigma_{IL} = 0.9$. This value is within our expected error (arising primarily in assuming a value for the surface roughness) of 1. The change in the interfacial free energy, γ_{SL}, between pH 1 and pH 11 is only 0.4 kcal/mol if γ_{SV} is assumed to be pH independent. This energy change is small compared with the free energy of ionization, ΔG_i, for RCO$_2$H (pH 1) → RCO$_2^-$ (pH 11) + H$^+$: approximately 5 kcal/mol for pK_a of 7.5.

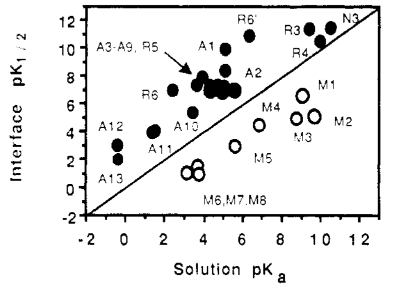

Figure 21. Correlation between $pK_{1/2}$ determined by contact angle titration and the pK_a for similar functional groups in solution. Open symbols represent basic species (amines), and solid symbols represent acidic species (carboxylic acids, phenols, fluorinated amides, sulfonamides, phosphonic acids, alkyl phosphates, boronic acids). The data point labeled R6′ represents the second (more basic) $pK_{1/2}$ and pK_a of interface R6 (Figure 17).

π^*, cos θ_a becomes unresponsive to changes in π^* and the data deviate significantly from this line.

Correlations between Values of Interfacial $pK_{1/2}$ and Solution pK_a. Figure 21 summarizes the data obtained for all the ionizable species as a plot of the observed values of $pK_{1/2}$ vs the pK_a of the relevant functional group in aqueous solution. In some instances the pK_a values reported for the solution analogues are literature values (e.g., $pK_a = 3.24$ for $CH_3CONHNH_2$ as an appropriate soluble analogue for PE[$CONHNH_2$]).[38] In other cases the pK_a values are predictions based on the widely recognized relationships between the various functional group interactions in a molecule and the resulting pK_a.[39] A datum falling along the diagonal line in this plot would have the same values of $pK_{1/2}$ and pK_a; that is, the value of solution pH required to achieve half-ionization would be the same for that group at the interface and in solution. In fact, all of the data examined fall in groups above and below the line. Those falling above the line, with the surface $pK_{1/2}$ larger than solution pK_a, are all acidic species, while those falling below the line are all basic species. The origin of the difference between acidic and basic species is certainly the difficulty in generating either positively or negatively charged functional groups from neutral groups in the interfacial region.

Conclusions

We summarize the conclusions from this work.

1. *The advancing contact angle of water on PE-CO_2H and its derivatives correlates with the hydrophilicity of the functional group in the interface.* The quality of the correlation between cos θ_a and π is remarkably good (Figure 20). We emphasize one hidden similarity: in both "moist" wetting of the polymer interface by water and in partitioning of organic molecules between octanol and water, the nonpolar phase (air or octanol, respectively) is saturated with water. Hence, polar groups are free to solvate with water both at the solid–vapor interphase and in the octanol phase, provided that their affinity for water is sufficiently high.

2. *The influence of increased hydrophilicity on contact angle appears to reach saturation for very hydrophilic substituents* ($\pi \lesssim -2$). The chemical potential of water is constant throughout the system (liquid water is in equilibrium with water vapor and with water adsorbed on the functionalized interface). Sufficiently hydrophilic groups will be solvated (that is, strongly associated with adsorbed water) on the moist interface used to determine θ_a (Figure 22). These water-solvated groups will resemble water itself from the vantage of additional water molecules. Hence, all interfacial groups that are sufficiently polar to be highly associated with adsorbed water at 100% relative humidity should give rise to an interface having roughly the same interfacial free energy (that is, roughly that of the surface tension of liquid water). Under the moist conditions employed to determine contact angles, the specific hydrophilicity of the groups attached to the interface is therefore, to a first approximation, irrelevant as long as the groups are sufficiently hydrophilic to be fully solvated. Our data suggest that functional groups with π values less than −1 to −2 are sufficiently polar as to be fully solvated at 100% humidity. This range of π values includes such functional groups as CO_2^- (−4.36), NH_3^+ (−4.19), SO_3^- (−4.76), glucose (−2.84), and $CONHNH_2$ (−1.92). Groups that fall into the transition region between full and partial coverage by water (i.e., those at the inflection in the relationship between π and cos θ_a, Figure 19) include CO_2H (−0.72), NH_2 (−1.23), $CONH_2$ (−1.23), OH (−1.13), and $NHSO_2CH_3$ (−1.18). Groups that collect little water (i.e., those in the linear portion of the relationship between π and cos θ_a, Figure 19) include CO_2CH_3 (−0.01), CH_2OCOCF_3 (0.55, estimate), CH_2 (0), CH_3 (0.56), and CF_3 (0.88).

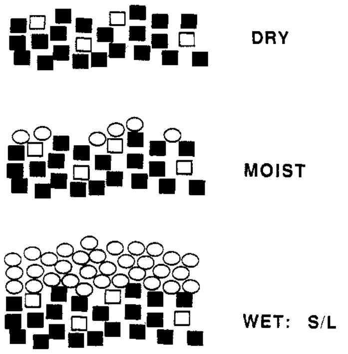

Figure 22. Schematic representation of a solid composed of hydrophilic (□) and hydrophobic (■) functional groups, dry, in equilibrium with water vapor (○) and in contact with liquid water.

3. *An important parameter in determining the influence of a functional group on the wetting of these types of interfaces appears to be the surface area that this group covers.* The "area fraction" is probably more important in determining the influence of a functional group on wetting than is the mole fraction of that group in the interface. In particular, in cases where some of the interfacial functional groups are significantly larger than others, the larger groups will probably make more important contributions to the interfacial free energy. Definition of the area covered by a functional group is not a simple procedure. For example, long functional groups attached at the interface (such as $-(CH_2CH_2O)_n-$) could extend out into the bulk water and thus, in principle, occupy a relatively small fraction of the interfacial area, or they might condense onto the surface and cover a large area.

The increase in interfacial area coverage upon ionization of functional groups might also have a significant influence on wetting. A carboxylate anion in an interface in contact with water vapor might, for example, collect a larger "pool" of associated water than would an unionized carboxylic acid group. The resulting increase in the effective A_i would result in a decrease in contact angle, even in the absence of a change in $\gamma_{SV,i}$ or $\gamma_{SL,i}$; the possibility that A_i might

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[38] Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*: Butterworths: London, 1965.

[39] Perrin, D. D.; Dempsey, D.; Serjeant, E. P. *pK_a Prediction for Organic Acids and Bases*; Chapman and Hall: New York, 1981.

be a function of the ionization state of the group i could significantly influence interpretation of relationships between θ_a and π (a parameter whose sensitivity to size is probably due more to functional group surface area than to projected area on an interface). The increase in A_i upon ionization of the carboxylic acid groups of PE–CO_2H may, in fact, be one reason why the contact angle decreases at high pH. Similar arguments would apply to the contact angle titrations of all of the interfaces tested in this paper.

4. *Contact angle titration provides a convenient method for measuring the ionization of functional groups on an interface*: the conversion of an uncharged (less hydrophilic) to a charged (more hydrophilic) group is often accompanied by an increase in wettability and a decrease in contact angle. It is something of a puzzle why this technique works as well as it does. Results obtained with contact angle titration are internally consistent and physically reasonable. The values of $pK_{1/2}$ inferred from this technique and from direct observation using ATR-IR[4] and fluorescence[5] spectroscopies (and occasionally using direct titration[4]) are in good agreement. Systems derived from PE–CO_2H are, however, not at thermodynamic equilibrium: hysteresis is large, the drop does not move on a tilted sample, and the drop edge appears to be pinned. Model monolayer systems show less hysteresis, but values of contact angle that are compatible with those observed for PE–CO_2H and derivatives are also obtained with these structurally better-defined systems. Thus, θ_a for PE[R] is apparently not determined solely by the same factors that result in the large observed hysteresis. We presume that the hysteresis reflects some combination of interfacial heterogeneity (e.g., roughness or uneven distribution of functional groups) and reaction on contact with the bulk water (swelling and/or ionization). Although the values of contact angles can only be considered approximations to those that would be observed for a system in true thermodynamic equilibrium, we presently believe that the differences between the nonequilibrium or quasi-equilibrium values obtained with the polymer interfaces and equilibrium values that would be obtained on an ideal system containing the same functional groups are (hysteresis notwithstanding) small.

Several factors might, in principle, cause a decrease in θ_a on ionization of the interfacial groups in PE–CO_2H. These include an increase in A_P, an increase in γ_{SV}, a decrease in γ_{SL}, swelling of the interfacial region, and processes making a contribution to η_R^{pH} (eq 3), such as the free energies of ionization or swelling. We draw upon the comparison of PE–CO_2H to the structurally better-defined monolayer systems based on organic thiols absorbed on gold to suggest that interfacial swelling is relatively unimportant in determining θ_a. Since these monolayer systems are not expected to swell significantly in either the ionized or unionized state, and since their behavior in wetting is qualitatively similar to that of the functionalized polymer, we conclude that swelling of the interfacial region of PE–CO_2H is not essential for a decrease in θ_a.

We do not currently know whether the energy of reaction (η_R^{pH}) is important in determining the contact angle as a function of pH for PE–CO_2H. One fact suggests, however, that it is not: if the energy of ionization were driving the movement of the drop to lower contact angles, the contact angle would be expected to continue to drop beyond the pH of full ionization (eq 16, Figure 13). For example, even if the interface were fully ionized at pH 10, the free energy of ionization at pH 14 would be greater than that at pH 11 by the entropy of dilution of the protons ($RT\Delta pH = 1.4$ kcal/mol), and the contact angle would be lower at pH 14 than at 11. This continued drop in θ_a above the point of full ionization is not observed for PE–CO_2H or any material derived from it.

The remaining factors that might plausibly contribute to the decrease in θ_a on ionization may all be important. Changes in A_P on ionization of an interfacial group are likely to be important for many of the materials studied. Changes in γ_{SV} and γ_{SL} on ionization may also be important, although the monolayer studies indicate that cos $\theta_{CO_2H} = \theta_{CO_2^-} = 1$, and our first-order analysis (eq 3–10) suggests that interfaces containing these two functional groups should not be distinguishable by contact angle. In fact, the relationship between π and θ_a (Figure 19) and the relationship between cos $\theta_{a,pH1}$ and Δ cos θ_a (Figures 10, 16, and 18) suggest that the influence of a particular functional group on the interfacial free energy may depend on its environment, and conclusions drawn from the monolayer system may not be directly applicable to PE–CO_2H. Certainly, qualitatively the hydrophilicity of the CO_2^- group is greater than that of a CO_2H group, and the wettability of the interface follows the same order.

5. *The supposition that in an interface containing a number of different functional groups the contribution of each group toward the wetting properties can be considered additive and independent (eq 5 and 6) provides a valuable starting point for analysis and leads to a qualitatively revealing physical model of wetting, but this supposition may be incorrect in many situations.*

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 on a Physical Electronics Model 548 spectrometer (Mg Kα X-ray source, 100-eV pass energy, 10^{-8}–10^{-9} Torr, instrument calibrated according to ASTM STP 699).

ATR-IR Measurements. Pieces of polyethylene film 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 aqueous solution were dried under vacuum (60 min, 0.01 Torr, room temperature) prior to contact with the KRS-5 crystal to prevent crystal damage and to eliminate peaks due to excess water from the spectrum. 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. Spectra were obtained on a Perkin-Elmer Model 598 spectrometer.

Contact Angle Measurements. Contact angles were determined on a Ramé-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 values were determined 5–20 s 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 25 °C. The volume of the drop used was always 1 μL. Polyethylene samples were cut to a size of 0.5 × 2 cm and attached by the back of the sample to a glass slide by using two-sided Scotch tape to keep the sample flat. All values reported are the average of at least eight measurements taken at different locations on the film surface and have a maximum error in the mean of ±3°. The pH profiles were fully reversible on the interfaces after the drops were removed from the interfaces by washing with distilled water and drying in air. Some samples, such as PE[$CONHNHCOCF_3$], could be imagined to hydrolyze at high pH. None of the titration curves are dominated by such reactions, as shown by treating the interfaces with base for a few seconds (the time necessary to determine θ_a) and then redetermining θ_a at low pH. The buffers used (0.05 M) were as follows: pH 1, 0.1 N HCl; pH 2, maleic acid; pH 3, tartaric acid; pH 4, succinic acid; pH 5, acetic acid; pH 6, maleic acid; pH 7 and 8, HEPES; pH 9 and 10, CHES; pH 11, 4-aminobutyric acid; pH 12, phosphate; pH 13, 0.1 N NaOH;

other buffers[4] were substituted with no apparent differences in θ_a.

π Values for Interfacial Functional Groups. The functional group π values used in determining the π^* values for the interfaces were obtained from the literature.[21] In many cases, the π values for the exact functional groups were not available. In some cases, estimates were made for π based on the functional groups present. This averaging was only used for interfaces of the type PE-[$CONHCH_2CH_2R$]. The π value estimated for this functional group was the numerical average of π for the secondary amide (−1.27) and the functional group R. While the results of this averaging are probably only approximations to the values that would be obtained in actual experiments, the values appeared to be useful in understanding the wetting properties of these types of surfaces. A second type of deviation from the strict use of π values for the functional groups was used in the case of the very long hydrocarbon or fluorinated hydrocarbon chains of surface esters. Although the length of an ester would clearly influence π, it would probably not influence θ_a above a certain length because only a portion of the chain would be exposed at the edge of the surface. For this reason, π was estimated to be 0.55 for the methyl surface resulting from PE[$CO_2C_8H_{17}$] ($\pi = 0.55$ for CH_3). Similarly, π was estimated to be 0.88 for PE[$CH_2OCOC_7F_{15}$] ($\pi = 0.88$ for CF_3). Other values of π used in this work were as follows: CO_2CF_3, 0.55 (estimate); $CO_2CH_2CH_3$, 0.51; CH_2, 0; CO_2CH_3, −0.01; $CONHCH_2CH_2N(CH_2)_4$, −0.19 (avg); $CONHCH_2$–pyridine, −0.48 (avg); CONH–pyridine, −0.48 (avg); C=O, −0.55; OH, −1.13; $CONHCH_2CH_2NHCOCF_3$, −0.60 (avg); CO_2H, −0.72; OSO_2CH_3, −0.88; $CONHCH_2CO_2H$, −1.0 (avg); $NHSO_2CH_3$, −1.18, $CONHCH_2CH_2OH$, −1.2 (avg); $CONH_2$, −1.23; NH_2, −1.23; $CONHCH_2CH_2NHSO_2CH_3$, −1.23 (avg); $CONHCH_2CH_2NH_2$, −1.25 (avg); $CONHCH_3$, −1.27; $CONHNH_2$, −1.92; $CONHCH_2CH_2NH_3^+$, −2.73 (avg); glucose, −2.8; $CONHCH_2CO_2^-$, −2.82 (avg); $CONHCH_2CH_2SO_3^-$, −3.02 (avg); NH_3^+, −4.19; CO_2^-, −4.36; SO_3^-, −4.8.

Polyethylene (PE–H) (Film 1). Low-density biaxially blown polyethylene film (100 μm thick, $\rho = 0.92$ g/mL) was a gift from Flex-0-Glass, Inc (Flex-0-Film DRT-600B). The film was cut into 10 × 10 cm squares. These were extracted by suspending the film in refluxing CH_2Cl_2 for 24 h to remove antioxidants and other additives present in the film. The removal of additives could be monitored with the carbonyl region of the ATR-IR spectrum. Prior to extraction, a peak at 1650 cm^{-1} was present. This peak was eliminated by the extraction. The samples were dried under vacuum (20 °C, 0.01 Torr, 4 h) or in air (20 °C, 4 h) prior to oxidation to allow residual solvent to evaporate. Samples that were not oxidized immediately were stored under dry argon. In all cases, experiments were performed on the side of the film facing the inside of the stock roll.

PE–CO_2H (PE[>C=O][CO_2H]; Film A4). PE–H was oxidized by floating on $H_2SO_4/H_2O/CrO_3$ (29/42/29; w/w/w) at 72 °C for 60 s. These 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 at 1710 cm^{-1}.

PE[>CHOH][CO_2H] (Film A10) and Derivatives. A solution of 4 g of $NaBH_4$ (98%, Alfa) in 100 mL of 0.1 N NaOH was heated to 50 °C. PE–CO_2H was added, stirred for 2 h, removed, and immersed in 1 N HCl for 10 min. The film was rinsed in water, in 1 N HCl, 3 times in distilled water, and once each in methanol and methylene chloride. At the resolution employed, the XPS spectrum was indistinguishable from that of PE–CO_2H. The contact angle with water (pH 1) was 54°, and the sample had a new ATR-IR peak at 3350 cm^{-1}. In order to form PE[>CHOCOR][CO_2H], PE[>CHOH][CO_2H] was treated with neat trifluoroacetic anhydride (or lauroyl chloride, both Aldrich) for 18 h at room temp. The films were then rinsed in water (4 times) and methanol (twice) and dried in the air to form PE[>$CHOCOCF_3$][CO_2H] (film A2) or PE[>$CHOCOC_{11}H_{23}$][CO_2H] (film A1). To generate PE[>$CHOCOCH_2CH_2CO_2H$][CO_2H] (film A7), PE[>CHOH][CO_2H] 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 air-dried.

PE[>CHOH][CH_2OH] (PE[CH_2OH]; Film 13) and Derivatives. PE–CO_2H was treated with excess 1 M BH_3–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}. In order to keep the nomenclature as brief as possible, derivatives of PE[>CHOH][CH_2OH] are often shown as derivatives of PE[CH_2OH], and it should be assumed that the secondary hydroxy groups are similarly derivatized. In order to generate PE[$CH_2OCO(CF_2)_nCF_3$] (films 15–17), PE-[CH_2OH] was allowed to react with neat [$CF_3(CF_2)_nCO]_2O$ (Lancaster Synthesis, just enough to cover the film) for 18 h at room temperature. The films were rinsed 5 times in methanol, twice in acetone, and twice in water. The ATR-IR spectrum ($n = 0$) showed new peaks at 1790 (CF_3CO_2R), 1165, and 1226 (C–F) cm^{-1}. PE[CH_2OH] was allowed to react with stearic acid chloride (Fluka, 5 g) in acetone (50 mL) containing 5 mL of triethylamine for 18 h. The film was removed, rinsed in methanol, water, acetone, and hexane, and dried in air to form PE[$CH_2OCO(CH_2)_{16}CH_3$] (film 14). Alternatively, to form PE-[$CH_2OCOCH_2CH_2CO_2H$] (film A6), PE[CH_2OH] 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. PE[CH_2OH] was allowed to react with a saturated acetone solution of 1,2,4,5-benzenetetracarboxylic acid anhydride for 2 h at room temperature. The film was removed, rinsed in acetone, methylene chloride, 0.1 N NaOH for 10 min, water, and acetone, and dried in air to form PE[$CH_2OCOC_6H_2(CO_2H)_3$ (1,3,4)] (film A11). Finally, PE[CH_2OH] was allowed to react with neat perfluoroglutaric anhydride (Lancaster Synthesis, just enough to cover the film) for 1 h at room temp. The film was removed, rinsed in methanol (3 times) and water, and dried in air to form PE-[$CH_2OCOCF_2CF_2CF_2CO_2H$] (film A13).

PE[COCl]. PE–CO_2H 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.

PE[$CO_2(CH_2CH_2O)_nH$]. For $n \leq 14$, PE[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 mixtures of different molecular weight, 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. For $n > 14$ the reactions were carried out similarly in 20% polymer (Aldrich)/80% acetone mixtures.

PE[$CONH_2$] (Film 4). PE[COCl] was put directly into concentrated NH_4OH for 20 min, rinsed in water (5 times) and methanol (twice), and then dried in air. ATR-IR showed new peaks at 1400 (C–N stretch), 3150 (NH), 1560 (NH), and 1660 cm^{-1} (C=ONH); XPS N/O ratio = 0.58.

PE[>CHOH][CH_2NH_2] (Film N2) and Derivatives. PE-[$CONH_2$] was treated with 1 M $LiAlH_4$ in refluxing diethyl ether (Aldrich, 1 M $LiAlH_4$ in ether) for 18 h. After the film was rinsed in water (4 times) and methanol (once), its surface appeared cloudy. The film was soaked in concentrated HCl for 10 min and rinsed in water (3 times) and methanol (twice). After the HCl treatment was repeated, the film was again clear. ATR-IR showed new peaks at 3350 cm^{-1} (NH_2 and OH) and 1640 cm^{-1} (NH_2). The peak at 1560 cm^{-1} (NH of $CONH_2$) had disappeared. (Note: This film has a foul, fishy smell. This smell may be PH_3 or some other toxic phosphorus compound derived from the reaction between residual PCl_5 in the film and $LiAlH_4$. Appropriate caution should be exercised.) In order to generate PE[>$CHOSO_2CH_3$][$CH_2NHSO_2CH_3$] (film N3), PE[>CHOH][CH_2NH_2] was treated with 5 mL of neat CH_3SO_2Cl containing 1 mL of triethylamine for 1 min (the triethylamine was added slowly and carefully). The film was rinsed several times in water and once in methanol and dried in air. PE[>$CHOCOCH_2CH_2CO_2H$][$CH_2CONHCH_2CH_2CO_2H$] (film A5) was generated by reacting PE[>CHOH][CH_2NH_2] with succinic anhydride (10 g) in acetone (50 mL) containing 1 mL of triethylamine for 1 h at room temp. The film was removed, rinsed in acetone (3 times), water, and acetone, and dried in air. PE[>CHOH][CH_2NH_2] was allowed to react with 100 mg of dansyl chloride (Sigma) in acetone (10 mL) for 10 s. At that point 0.5 mL of aqueous Na_2CO_3 (saturated) was added, and the film was removed after 30 s. The film was rinsed in methanol (5 times), water, and acetone and dried in air to form PE[>CHOH][CH_2NH-dansyl] (film M6).

PE[>C=O][CH_2NH_2] (Film N1). PE–CO_2H was put into a mixture of 100 mL of chloroform, 25 mL of concentrated sulfuric acid, and 1 g of NaN_3 (Kodak). The mixture was stirred at 50 °C for 1 h, and the film was removed. The sample was rinsed in water, acetone, water, acetone, and ether and dried in air. ATR-IR peaks: 1120 (C–N); 1640 (NH_2); 3350 cm^{-1} (NH). Upon reaction with lauroyl chloride (3 min in neat reagent) the film become hydrophobic ($\theta_a > 100°$).

PE[CO_2CH_3] (Film 18). The methyl ester has been made by three different methods, with the resulting interfaces being indistinguishable.[4] Here, PE–CO_2H was stirred for 18 h in 500 mL of anhydrous methanol containing 75 mL of sulfuric acid at 40 °C. The film was rinsed twice in methanol, 3 times with distilled water, and once in acetone. For all three methods, ATR-IR spectra showed a new peak at 1740 cm^{-1} and no CO_2^- peak (1560 cm^{-1}) after treatment with 1 N NaOH, indicating complete reaction.

PE[CO_2R]. The ethyl, 2-bromoethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, *n*-hexyl, and *n*-octyl esters (films 19–26) were made by soaking PE–CO_2H in the appropriate anhydrous alcohol (50 mL) containing sulfuric acid (10 mL) at 40 °C for 18 h (for ethyl and bromoethyl) or 72 h. The films were worked up as for PE[CO_2CH_3]. Alternatively, the propyl ester was made by putting PE[COCl] in propan-1-ol for 30 min and rinsing once with methanol, twice with water, and once with acetone.

PE[$CONHNH_2$] (Film M8) and Derivatives. PE[CO_2CH_3] was heated at 50 °C in 95% NH_2NH_2 (Eastman) for 1 h. The film was rinsed 3 times in methanol and twice in water. The ATR-IR spectrum showed a new peak at 1650 cm^{-1}. This material (PE[$CONHNH_2$]) was put into 50 mL of THF containing 10 mL of lauroyl chloride and 0.2 mL of triethylamine. After 42 h, the film was removed, rinsed in methanol, water, acetone, and hexane, and dried in air to form PE[$CONHNHCOC_{11}H_{23}$] (film 10). Alternatively, PE[$CONHNH_2$] was stirred for 18 h in 10 mL of THF containing 0.2 g of tetrafluorosuccinic anhydride (K and K Chemicals) at room temperature. The film was removed, rinsed in THF, methanol, water, and acetone, and dried in air to form PE[$CONHNHCOCF_2CF_2CO_2H$] (film A12). In order to form PE[$CONHNHCOCF_3$] (film R2), PE[$CONHNH_2$] was stirred in 10 mL of THF containing 0.5 mL of $[CF_3CO]_2O$ and 0.2 mL of triethylamine for 18 h at room temperature, followed by rinsing in THF, methanol, water, and acetone and drying in air.

PE[CONHR]. PE[CO_2CH_3] was soaked in the appropriate, neat, commercially obtained amine for 4 weeks at room temperature. The samples were soaked for several hours in water and/or methanol to remove excess amine reactant from the film. The samples were then rinsed in methanol and dried in air. Samples made in this manner were those derived from 2-aminoethanol (MCB, film 3), *N*-(2-aminoethyl)morpholine (Lancaster Synthesis, film M4), *N*-(2-aminoethyl)pyrrolidine (Lancaster Synthesis, film M3), 4-(aminomethyl)pyridine (Alfa, film M5), aminomethylcyclohexane (Lancaster Synthesis, film 9), *N*,*N*-dimethylethylenediamine (Aldrich, film MI), *N*,*N*′-dimethylethylenediamine (Alfa, film M2), 1,7-dimethyl-4-heptylamine, Lancaster Synthesis, film 8), 2-aminoethanol (MCB, film 3), ethylenediamine (Fisher; this reaction is one approach to film N4), and 4-heptylamine (Lancaster Synthesis, film 7).

PE[CONHR′]. PE[COCl] was put into aqueous solutions (unless otherwise specified) containing the appropriate amine-containing substances for 5 min. The samples were rinsed in water (4 times) followed by methanol (once) and dried in air. Surfaces made in this manner include those derived from commercially obtained *p*-aminobenzoic acid (Eastman, film A9, 50 mL of acetone containing 5 mL of triethylamine), aminoethanethiol (Aldrich, film R1, 30%, pH 8.8), (2-aminoethyl)phosphonic acid (Sigma, film R5, 50 mg (saturated) in 5 mL of methanol with 0.2 mL of triethylamine), 2-aminoethyl phosphate (Alfa, film R6, 1 g in 5 mL of methanol with 0.5 mL of triethylamine), 2-aminoethyl hydrogen sulfate (Sigma, saturated in 5 mL of methanol with 0.5 mL of triethylamine, film 28), *o*-aminophenol (Baker, film R4, saturated); (*m*-aminophenyl)boronic acid (film R3, 0.5 g of free base (Alfa) in 5 mL of methanol with 0.5 mL of triethylamine), 4-aminopyridine (Sigma, film N7, saturated solution), aniline (Fisher, neat, film 11), aspartic acid (film A3, 0.5 M at pH 10 (NaOH)), dansylcadaverine (Sigma, film M7, 50 mg in 10 mL of methanol with 0.5 mL of triethylamine), ethylenediamine (Fisher, this reaction is one approach to film N4, neat; the CF_3CO and CH_3SO_2 derivatives of this surface (N5 and N6) were made as for PE[>CHOH][CH_2NH_2]), glucosamine hydrochloride (Sigma, 2 M adjusted to pH 10 (NaOH), film 2), glycine hydrochloride (Aldrich, film A8, 2 M at pH 10 (NaOH)), methylamine (Eastman, 40% in H_2O, film 5), dimethylamine hydrochloride (Baker, 30% in 1 N NaOH, film 6), *n*-octylamine (Eastman, neat, film 12), taurine (Aldrich, $H_2NCH_2CH_2SO_3^-$, saturated, pH 9.5, film 27).

Monolayers. Monolayers were formed by adsorption of mixtures of $CH_3(CH_2)_{15}SH$ (0–1 mM) and $HO_2C(CH_2)_{15}SH$ (0–1 mM) from degassed absolute ethanol solution (20 mL) onto freshly evaporated gold surfaces for 12 h at room temperature. These gold surfaces were made by thermal evaporation of a 2000-Å-thick layer of gold onto a 3-in. silicon wafer, with a thin (200 Å) interveing layer of chromium to increase adhesion between the gold and silicon. The monolayers were rinsed in water and ethanol prior to determination of θ.