Size of Alkyl Group R: Principal Factor Determining Wettability of Surface-Functionalized Polyethylenes (PE-CO\textsubscript{2}R and PE-CO\textsubscript{2}NR) by Water\textsuperscript{1}

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Received May 22, 1989  
Revised Manuscript Received November 16, 1989

The wetting of solids by liquids is dominated by short-range (van der Waals, dipolar, hydrogen bonding) interactions.\textsuperscript{2a} This paper examines the relationships between the wettability by water of surface-functionalized, low-density polyethylene film and the size and structures of the organic functional groups present at the solid–liquid interface. Polyethylene is a particularly instructive system, because it is a structurally heterogeneous, "nonideal" solid, in which the interfacial functional groups are disordered in both position and orientation. Its disordered structure contrasts with the more ordered self-assembled monolayers obtained by chemisorption of organic thiols on gold.\textsuperscript{3,4} and comparisons of these systems should help to indicate the importance of interfacial order on wetting.

We have examined the wetting by water of polyethylene films having surfaces containing amide (PE-CO\textsubscript{2}NR) or ester (PE-CO\textsubscript{2}R) functionalities (1–3) and have determined the size of a nonpolar group R required to mask these small polar groups from contact with the water.\textsuperscript{5} This masking doubtless reflects weakening of electrostatic and hydrogen-bonding interactions between the contacting water and the polar functional group (P).

We have described elsewhere the preparation of surface-oxidized polyethylene ("polyethylene carboxylic acid", PE-CO\textsubscript{2}H) and the conversion of its carboxylic acid moieties to amides and esters via acid chlorides.\textsuperscript{6,7} Here we note that (i) the functional groups in these materials are restricted to a thin interfacial layer (<1–2 nm thick); (ii) approximately 30% of the organic groups present in that part of the functionalized interface that determines wetting are CO\textsubscript{2}H groups (the remainder being methylene and ketone/alkyl groups); (iii) the conversion of CO\textsubscript{2}H to CONHR and CO\textsubscript{2}R groups occurs in high yields; and (iv) the interfacial region is rough and chemically heterogeneous.

The interfaces presented by PE-CO\textsubscript{2}R and PE-CO\textsubscript{2}H to a contacting liquid are disordered, but are similar to one another in their morphologies and in their surface densities of functional groups. Figure 1 summarizes relevant measurements of advancing contact angles of water \( \theta (H_2O) \) on these surfaces.\textsuperscript{10} The contact angles on the interfaces having R = H (PE-CO\textsubscript{2}H, \( \theta_a = 55^\circ \), PE-CO\textsubscript{2}NR, \( \theta_a = 43^\circ \)) provide reference values. For small n-alkyl amides and esters (n = 1, 2), surfaces having amides are more hydrophilic than surfaces having the corresponding esters. This order—amide more wettable (hydrophilic) than ester—is in accord with other values of relative hydrophilicity such as Hansch \( \pi \) parameters.\textsuperscript{11} As R increases in size through a series of n-alkyl groups, n-C\textsubscript{n}H\textsubscript{2n+1}, \( \theta_a \) increases and reaches a constant value for \( n \geq 6 \).\textsuperscript{12} The limiting hydrophobicities achieved by esters and amides are very similar.\textsuperscript{13} Thus, incorporation of even small, nonpolar alkyl groups into ester or amide groups at the polyethylene–water or polyethylene–vapor interface is sufficient to shield the core functionality from the interactions with water.

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\textsuperscript{1} This work was supported in part by the Office of Naval Research, the Defense Advanced Projects Research Agency, and the National Science Foundation under the Engineering Research Center Initiative to the Bio-technology Process Engineering Center (Cooperative Agreement CDR-88-03014). M.D.W. was an IBM Predoctoral Fellow in Polymer Science for 1986–1987. G.S.F. was a NIH Postdoctoral Fellow for 1988–1989.


\textsuperscript{4} We have previously studied wetting of oriented, self-assembled monolayer films formed by chemisorption of \( \omega \)-mercapto ethers (HS(CH\textsubscript{2})\textsubscript{n}OR) or gold (Bain, C. D.; Whitesides, G. M. J. Am. Chem. Soc. 1988, 110, 5897–5902). The density of polar functional groups in the interfacial region is higher for these monolayers than for PE-CO\textsubscript{2}R. We are still defining the size of a nonpolar group R required to mask these small polar groups from contact with the water.\textsuperscript{5} Here we note that (i) the functional groups in these materials are restricted to a thin interfacial layer (<1–2 nm thick); (ii) approximately 30% of the organic groups present in that part of the functionalized interface that determines wetting are CO\textsubscript{2}H groups (the remainder being methylene and ketone/alkyl groups); (iii) the conversion of CO\textsubscript{2}H to CONHR and CO\textsubscript{2}R groups occurs in high yields; and (iv) the interfacial region is rough and chemically heterogeneous.

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For all esters and amides, the values of \( \theta_a \) are an average of values at pH 1 (0.1 M HCl), pH 7 (0.05 M phosphate buffer), and pH 13 (0.1 M NaOH). All values reported are independent of pH. For PE-CO\textsubscript{2}H, the value is for pH 1. These data are for sessile drops: The drop was placed on the surface by using a hypodermic needle, the drop edge allowed to advance by adding liquid, the needle withdrawn, and the contact angle measured. All measurements were made at 100% relative humidity and room temperature. The hystereses in the angles were high (40–90°) in all cases, indicating that these systems are not at equilibrium: for further discussion on hysteresis in these systems, see ref 7.


For unfunctionalized polyethylene, \( \theta_a = 103^\circ \). The oxidation used to introduce the carboxylic acid groups in PE-CO\textsubscript{2}H roughens the surface. This roughness is responsible for some part of the apparent hydrophobicity of the long-chain esters and amides. Another source of hydrophobicity may be the higher concentration of methyl groups near the surface of the esters and amides relative to that of PE–H (Fox, H. W.; Zisman, W. A. J. Colloid Sci. 1952, 7, 428–442).

We believe that the slightly higher values of \( \theta_a \) observed for the amides than for the esters reflects slightly higher yields in their formation from PE-CO\textsubscript{2}Cl. An alternative explanation is that hydrogen bonding between the amide groups (a phenomenon that occurs in the bulk of polyurethane blends: Coleman, M. M.; Skrowaczek, D. J.; Hu, J.; Painter, P. C. Macromolecules 1988, 27, 59–65) concentrates the nonpolar alkyl groups at the organic-air interface.
that determine wetting. These results imply that, to exhibit effective shielding, the functional groups need not be preoriented at the interface in a way that optimizes the presentation of the group R to the water.

We have carried out a limited investigation of structural isomers of the alkyl group (R) attached to N and O. The differences in contact angle with changes in structure are small; for example: C_4-C_6 groups R on CONHR, \( \theta_a = 125^\circ \) for (CH_2)_4CH_3, 123° for CH(CH_2CH_3)_2, 125° for c-C_5H_{11}, and 123° for CH(CH_2CH_3)_2. 125° for c-C_5H_{11}, and 123° for C(CH_3)_3. Thus, the contact angle depends primarily on the size of the group that is a part of the ester or amide moiety rather than on the structural details of the group.

XPS data provide qualitatively useful information concerning

the proximity of the ester or amide group to the solid–vacuum interface, and this information supplements that obtained from wetting. The ratio of the intensities of N 1s to C 1s peaks (normalized to the value for the unsubstituted amide CONH_2) and that of the O 1s to C 1s peaks (normalized either to the value for PE–CO_2H or for PE–CONH_2) decrease by only approximately a factor of 2 from \( n = 0 \) to \( n = 18 \). As the alkyl group becomes larger, the N or O nucleus in the polar functionality should be increasingly buried beneath the hydrocarbon of the R group, and the ratios of N or O to C should, in principle, decrease (ultimately to 0 for sufficiently large alkyl groups). The attenuation length of photoelectrons is \( \sim 40 \) Å in these systems. The relatively small decrease in these ratios thus indicates that the hydrocarbon structures overlying the amide and ester groups are thin. The conclusion of these experiments—that the size of the alkyl groups required to mask polar functionality in wetting is small compared to the thickness of hydrocarbon required to significantly attenuate XPS signals—is compatible with the proposed structures for the interfacial functional groups. These experiments also emphasize the high sensitivity of wetting as a probe of interfacial structure, relative to XPS. 15

These results confirm that the interfacial region responsible for wetting, inferred to be thin in studies of well-ordered systems, is also thin in these disordered systems, at least for solvents that do not swell this region. 16, 17 The efficiency with which small groups R in the disordered solid–water interface of derivatives of PE–CO_2H mask the influence of polar functionality (especially primary amides) on wetting is remarkable. 18, 19 The ability of a given alkyl group to mask a polar group in these disordered interfaces is similar to that observed previously for monolayers of alkyl thiocyanates on gold, 20 systems we believe to be more ordered than PE–CO_2H and its derivatives. Establishing whether this similarity reflects intrinsic insensitivity of wetting to details of local structure around the polar group, or whether the monolayers are less ordered (or the polyethylene is more ordered) than we have assumed, is a subject of continuing investigation.


(15) Changing the take-off angle in the XPS measurements on these systems does not significantly change the surface sensitivity. We attributed this insensitivity to roughness of the interfaces.

(16) For early work pointing to the same conclusion, see: Zisman, W. A. In Contact Angles, Wettability, and Adhesion; Fowkes, F. M., Ed.; Advances in Chemistry 43; American Chemical Society: Washington, DC, 1964: pp 1–51.


(18) We cannot presently compare the data from self-assembled monolayers and surface-functionalized polymers in a way that provides a useful description of the structures and degree of order of the alkyl groups overlying the polar functional groups in these two types of surfaces.

(19) The dependence of wettability on pH for PE–CONH–C_6H_4–CO_2H is large (Wilson, M. D.; Whitesides, G. M. J. Am. Chem. Soc. 1988, 110, 8718–8719). We have rationalized this observation, assuming that polar groups are easily masked by overlying nonpolar groups, and that reorganization of the solid–liquid interface occurs readily.