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Communications to the Editor

Size of Alkyl Group R: Principal Factor Determining Wettability of Surface-Functionalized Polyethylenes (PE–CONHR and PE–CO_2R) by Water[1]

Mark D. Wilson, Gregory S. Ferguson, and
George M. Whitesides*

Harvard University, Department of Chemistry
Cambridge, Massachusetts 02138

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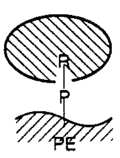
The wetting of solids by liquids is dominated by short-range (van der Waals, dipolar, hydrogen bonding) interactions.[2-4] This paper examines the relationships between the wettability by water of surface-functionalized, low-density polyethylene film and the size and structures of the organic functional 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,[4,5] 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–CONHR) or ester (PE–CO_2R) 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.[6] 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_2H) and the conversion of its carboxylic acid moieties to amides and esters via acid chlorides.[6-9] 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_2H groups (the remainder being methylene and ketone/aldehyde groups);[6] (iii) the conversion of CO_2H to CONHR and CO_2R groups occurs in high yields; and (iv) the interfacial region is rough and chemically heterogeneous.



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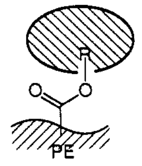

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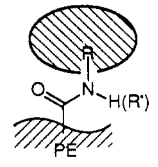

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The interfaces presented by PE–CO_2R and PE–CONHR to a contacting liquid are disordered, but are similar to one another in their morphologies and in their surface densities of functional groups. Figure 1 summarizes relevant measurements of advancing contact angles of water $\theta_a(H_2O)$ on these surfaces.[10] The contact angles on the interfaces having R = H (PE–CO_2H, $\theta_a = 55°$; PE–$CONH_2$, $\theta_a = 43°$) 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 π parameters.[11] As R increases in size through a series of *n*-alkyl groups, $n\text{-}C_nH_{2n+1}$, θ_a increases and reaches a constant value for $n \geq 6$.[12] The limiting hydrophobicities achieved by esters and amides are very similar.[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 polar core functionality from the interactions with water

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(4) We have previously studied wetting of oriented, self-assembled monolayer films formed by chemisorption of ω-mercapto ethers ($HS(CH_2)_{16}OR$) on gold (Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897–5898). The density of polar functional groups in the interfacial region is higher for these monolayers than for PE–CO_2R. We are still defining the order in these systems. The $(CH_2)_{16}$ units seem ordered (predominantly trans extended); the R groups are significantly less ordered (Laibinis, P. E.; Nuzzo, R. G.; Whitesides, G. M. Unpublished results).

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(6) We note, however, that the term "contact" can only be defined with respect to a given technique (e.g., measurement of contact angles) for probing the interaction. We have found previously that carboxylic acid and ester groups too deeply embedded in the polymer to be sensed by measurement of contact angles were still accessible to aqueous base (Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1987**, *3*, 62–76).

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(8) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1986**, *2*, 266–281.

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(10) For all esters and amides, the values of θ_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_2H, 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.

(11) Hansch, C.; Leo, A.; Ungar, S. M.; Kim, K. H.; Nikaitani, D.; Lien, E. J. *J. Med. Chem.* **1973**, *16*, 1207–1216.

(12) For unfunctionalized polyethylene, $\theta_a \approx 103°$. The oxidation used to introduce the carboxylic acid groups in PE–CO_2H 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).

(13) We believe that the slightly higher values of θ_a observed for the amides than for the esters reflects slightly higher yields in their formation from PE–COCl. An alternative explanation is that hydrogen bonding between the amide groups (a phenomenon that occurs in the bulk of polyurethane blends: Coleman, M. M.; Skrovanek, D. J.; Hu, J.; Painter, P. C. *Macromolecules* **1988**, *21*, 59–65) concentrates the nonpolar alkyl groups at the organic–air interface.

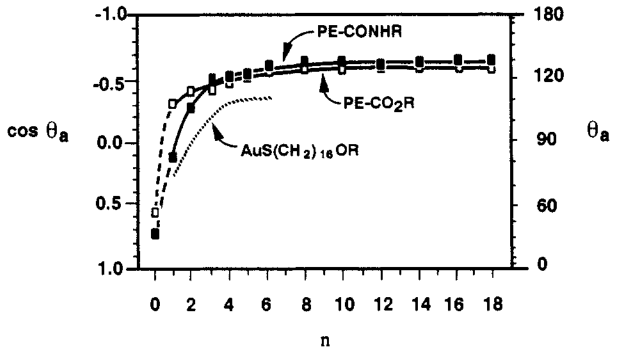

Figure 1. Values of advancing contact angles of water on polyethylene film functionalized at the surface with esters, PE–CO_2R (□), and amides, PE–CONHR (■); R = n-C_nH_{2n+1}. The cross-hatched line represents advancing contact angles for self-assembled monolayers of ω-mercapto ethers $HS(CH_2)_{16}O$-n-C_nH_{2n+1} on gold (taken from ref 4). The height of the symbols indicates the uncertainty in the measurement.

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_5 groups R on CONHR, θ_a = 125° for $(CH_2)_4CH_3$, 123° for $CH(CH_2CH_3)_2$, 125° for c-C_5H_9, and 123° for $C(CH_3)_3$; for CO_2R, θ_a = 123° for $(CH_2)_4CH_3$, 115° for $CH(CH_2CH_3)_2$, 117° for c-C_5H_9, and 117° 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 (λ) of photoelectrons is ~40 Å in these systems.[14] 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 thiolates on gold,[4,5] 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[19]) than we have assumed, is a subject of continuing investigation.

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(14) Roberts, R. F.; Allara, D. L.; Pryde, C. A.; Buchanan, D. N. E.; Hobbins, N. D. *SIA, Surf. Interface Anal.* **1980,** *2,* 5–10. Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1989,** *93,* 1670–1673.

(15) Changing the take-off angle in the XPS measurements on these systems does not significantly change the surface sensitivity.[9] 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.

(17) Kessaissia, Z.; Papirer, E.; Donnet, J.-B. *J. Colloid Interface Sci.* **1981,** *82,* 526–533.

(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.

Trigonal-Planar $[M(SR)_3]^{1-}$ Complexes of Cadmium and Mercury. Structural Similarities between Mercury–Cysteine and Cadmium–Cysteine Coordination Centers

Eric S. Gruff and Stephen A. Koch*

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794

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Mercury–cysteine coordination has recently been indicated in the mercury metalloregulatory protein (MerR), mercuric ion reductase, and related proteins.[1-4] The details of the coordination geometries of the metal centers in these proteins remain to be determined. The coordination of cysteine to the other group 2B metals, Zn and Cd, is well precedented in metalloproteins.[5] The unique occurrence of two- and three-coordinate thiolate complexes in the chemistry of mercury[6,7] has suggested the possibility that a low-coordinate metal–cysteine center could provide a structurally based method for preferential binding of mercury to Hg–cysteine proteins. We present the first evidence that low-coordinate complexes exist in the thiolate chemistry of cadmium as well as mercury and to emphasize the close structural similarity of monomeric Cd and Hg thiolate complexes.

We have recently structurally characterized the first example of a trigonal-planar thiolate complex of zinc, $[Zn(S\text{-}2,3,5,6\text{-}Me_4C_6H)_3]^{1-}$.[8] An attempt to prepare the Cd analogue gave the dimeric compound $[(n\text{-}Pr_4N)]_2[Cd_2(S\text{-}2,3,5,6\text{-}Me_4C_6H)_6]$. Increasing the steric hindrance of the thiolate ligand resulted in the

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