

The Anthranilate Amide of "Polyethylene Carboxylic Acid" Shows an Exceptionally Large Change with pH in Its Wettability by Water¹

Mark D. Wilson and George M. Whitesides*

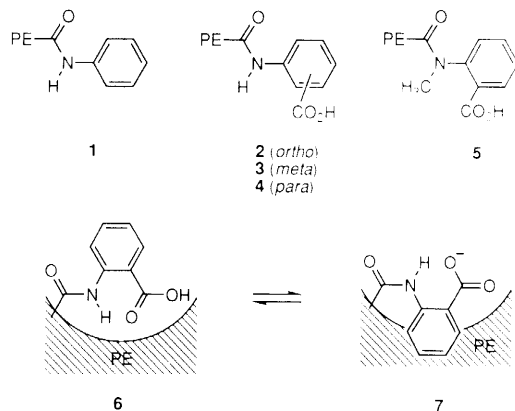
Harvard University, Department of Chemistry
 Cambridge, Massachusetts 02138

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"Polyethylene carboxylic acid" (PE-CO₂H) is a material prepared from low-density polyethylene film (PE-H) by generating carboxylic acid groups in a thin (≤ 2 nm) interfacial region by using chromic acid solution as oxidant.²⁻⁶ This material is a convenient substrate with which to explore the physical-organic chemistry of organic surfaces. One interesting and analytically useful characteristic of PE-CO₂H is that its wettability by water depends on pH: for pH ≤ 4 , the carboxylic acid groups are protonated and the surface relatively hydrophobic (the advancing contact angle, θ_a , is $\sim 55^\circ$); for pH ≥ 10 , the carboxylic acid groups are present as the more hydrophilic carboxylate anions, and the contact angle drops to $\theta_a \approx 20^\circ$. Other acidic, surface-functionalized derivatives of PE-CO₂H also show a pH-dependent contact angle. In most cases the magnitude of the changes in $\cos \theta_a$ with pH are limited by the fact that derivatives of PE-CO₂H seldom show a value of θ_a less than $\sim 20^\circ$ (independent of the relative hydrophilicity of the functional groups present at the polymer-water interface)⁶ and that most potentially ionizable derivatives are relatively hydrophilic at low values of pH.⁷

Here we report that the material **2** formed by reaction of PE-COCl with anthranilic acid⁸ shows a very large change in contact angle with pH: from $\theta_a \approx 110^\circ$ (more hydrophobic than unfunctionalized PE-H) at low pH to $\theta_a \approx 33^\circ$ at high pH (Figure 1).⁹

The value of $\theta_a \approx 119^\circ$ for the reference material **1** is independent of pH and is also higher than that of PE-H. The difference in θ_a for **1** and PE-H cannot be interpreted directly in terms



(1) The work was supported in part by the Office of Naval Research and the Defense Advanced Projects Research Agency. M.D.W. held an IBM Predoctoral Fellowship in Polymer Science (1986-1987).

(2) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725-740.

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

(4) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1987**, *3*, 62-76.

(5) Holmes-Farley, S. R.; Reamey, R. H.; Nuzzo, R. G.; McCarthy, T. J. *Langmuir* **1987**, *3*, 799-815.

(6) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921-937.

(7) $\cos \theta_a$ is proportional to interfacial free energy by Young's equation ($\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$) and is thus a more useful parameter in physical-organic studies of wetting than is θ_a : Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed.; Wiley Interscience: New York, 1982.

(8) PE-COCl was placed in a flask containing a saturated solution (~ 0.2 M) of 2-aminobenzoic acid in dry diethyl ether under an atmosphere of N₂. After ~ 12 h the film was removed and soaked for 10 min alternately in acetone and water (four alternations). The material was dried in air (≥ 30 min) before measuring θ_a .

(9) All of the surfaces studied here show pronounced hysteresis. Values for receding contact angles θ_r are (at pH 1) PE-H 85° ; **1**, 15° ; **2**, 0° ; **3**, 0° ; **4**, 0° ; **5**, 0° . Although the origin of this hysteresis remains uncertain,^{3,5,6} it is clear that the values of θ_a do not reflect interfaces at thermodynamic equilibrium.

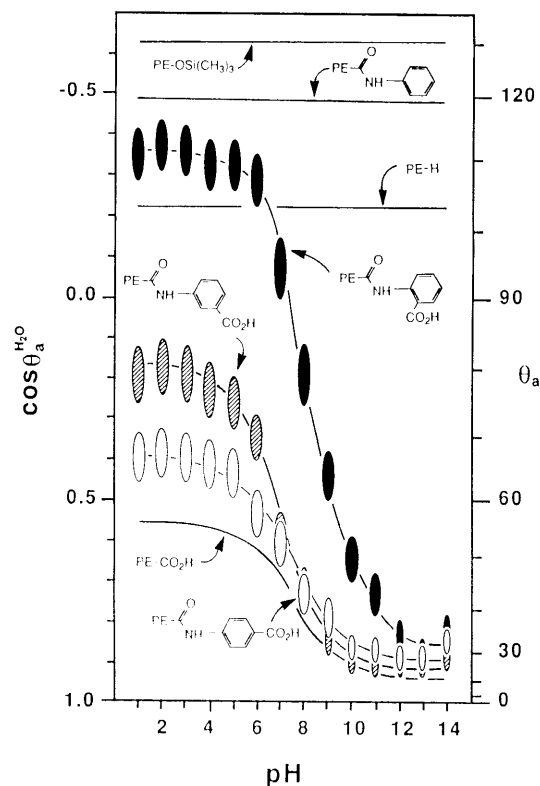


Figure 1. Variation in the advancing contact angle θ_a of water as a function of pH on several anilide derivatives of "polyethylene carboxylic acid", PE-CO₂H. Data for PE-CO₂H, PE-H, PE-CONHC₆H₅, and PE-OSi(CH₃)₃ are given for reference.

of hydrophobicity, since the surface of **2** is rougher than that of PE-H. Very hydrophobic derivatives of PE-CO₂H show values of $\theta_a \geq 130^\circ$ (for example, PE-OSi(CH₃)₃, $\theta_a \approx 130^\circ$; PE-CONHC₁₈H₃₇, $\theta_a \approx 132^\circ$). Nonetheless, **1** is unexpectedly hydrophobic. We interpret the hydrophobicity of this material as indicating that its phenyl groups are sufficiently large to shield the polar amide moieties from contact with water.

Introduction of a carboxylic acid moiety into the position ortho to the amide group of **1** produces only a modest decrease in the value of θ_a at low values of pH. At high pH, however, θ_a is much lower for **2** than for **1**. The amides of *m*- and *p*-aminobenzoic acids (**3** and **4**) have hydrophilicities similar to that of **2** at high pH but are more hydrophilic at low pH and thus show less striking changes in θ_a with pH.

We have not rigorously identified the origin of the large change in θ_a with pH for **2**, but we offer the hypothesis that it lies in a change in conformation of the acyl anthranilate moiety with respect to the surface (represented schematically by **6** \rightleftharpoons **7**). We suggest that at low pH, **2** adopts a conformation that buries both the -CONH- and -CO₂H moieties; in this conformation, **2** resembles **1** from the vantage of the contacting water. At high pH, the carboxylic acid group ionizes, and the free energy of solvation of the resulting carboxylate ion induces a change in conformation that exposes the CO₂⁻ group to water; in this conformation, the surface of **2** resembles that of PE-CO₂⁻. This hypothesized conformational change rationalizes the large change in θ_a with pH but also leaves a question unanswered: Why should **2** adopt the orientation suggested by **6**? By burying the carboxylic acid, conformation **6** sacrifices the polar interaction between the carboxylic acid and the contacting water. The similarity between the wettability of **1** and **2** at low pH does, however, argue for **6** or a similar conformation for **2**. Intramolecular hydrogen bonding between the NH group of the amide and the carboxylic acid (carboxylate anion) may be important, since the behavior of **5** (θ_a (pH 1) = 84° , θ_a (pH 12) = 30°) resembles that of **3** more closely than that of **2**.

The large change in θ_a with pH for **2** suggests that the functional groups at the polyethylene-water interface are conformationally

mobile with respect to that interface and that this mobility, by burying or exposing polar functional groups, can strongly influence macroscopic properties of the interface such as wettability. The high hydrophobicity of **2** at low pH reemphasizes the effectiveness with which small, nonpolar organic groups at an interface can shield underlying polar functionality from contact with water.¹⁰

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