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THE ANTHRANILATE AMIDE OF "POLYETHYLENE CARBOXYLIC ACID" SHOWS AN EXCEPTIONALLY LARGE CHANGE WITH pH IN ITS WETTABILITY BY WATER

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<p>The amide formed from polyethylene carboxylic acid (PE-CO<sub>2</sub>H) and anthranilic acid shows an exceptionally large change in wettability by water with pH. The values of advancing contact angles <math>\theta_a</math> are <math>\theta_a(\text{pH } 1) = 110^\circ</math> and <math>\theta_a(\text{pH } 12) = 33^\circ</math>. Comparison of these values with those for corresponding amides of <u>meta</u>- and <u>para</u>-aminobenzoic acid and aniline suggest that both conformational mobility of the polar functional group at the solid-water interface and surface roughness contribute to this large value.</p>			
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The Anthranilate Amide of "Polyethylene Carboxylic Acid" Shows an Exceptionally Large Change with pH in Its Wettability by Water<sup>1</sup>

Mark D. Wilson and George M. Whitesides\*

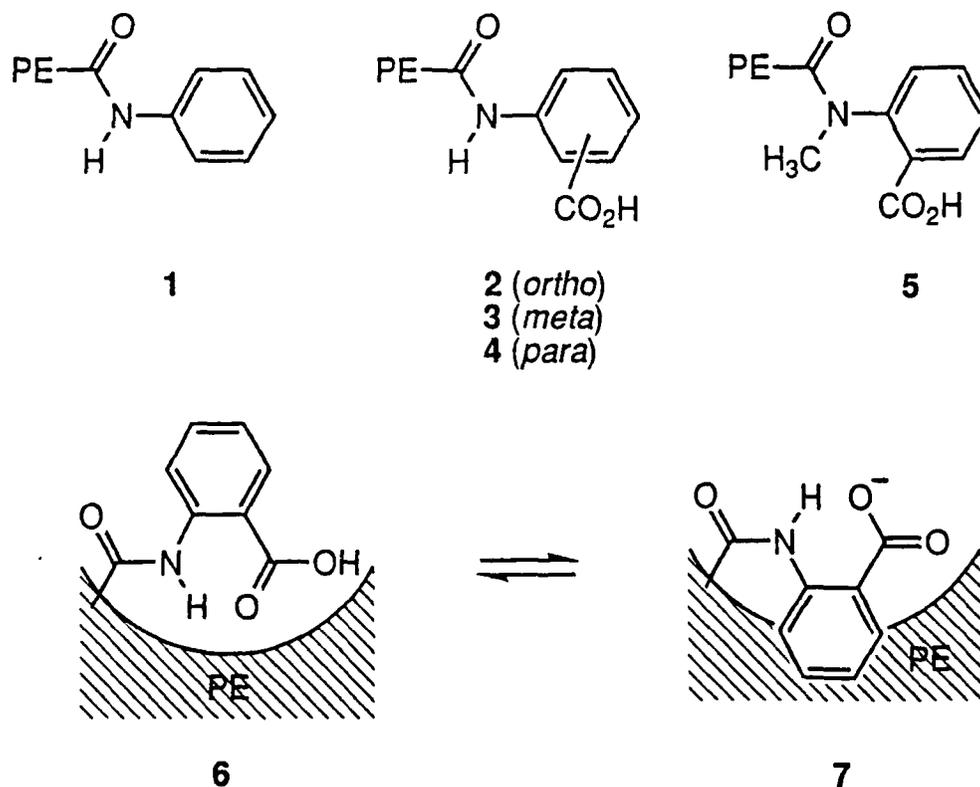
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"Polyethylene carboxylic acid" (PE-CO<sub>2</sub>H) is a material prepared from low-density polyethylene film (PE-H) by generating carboxylic acid groups in a thin ( $\leq 2$  nm) interfacial region using chromic acid solution as oxidant.<sup>2-6</sup> 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-CO<sub>2</sub>H is that its wettability by water depends on pH: for  $\text{pH} \leq 4$ , the carboxylic acid groups are protonated and the surface relatively hydrophobic (the advancing contact angle,  $\theta_a$ , is  $\sim 55^\circ$ ); for  $\text{pH} \geq 10$ , 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-CO<sub>2</sub>H 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 facts that derivatives of PE-CO<sub>2</sub>H seldom show a value of  $\theta_a$  less than  $\sim 20^\circ$  (independent of the relative hydrophilicity of the functional groups present at the polymer-water interface)<sup>6</sup> and that most potentially ionizable derivatives are relatively hydrophilic at low values of pH.<sup>7</sup>

Here we report that the material 2 formed by reaction of PE-COCl with anthranilic acid<sup>8</sup> 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).<sup>9</sup>



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  $\theta_a$  for 1 and PE-H cannot be interpreted directly in terms of hydrophobicity, since the surface of 2 is rougher than that of PE-H. Very hydrophobic derivatives of PE-CO<sub>2</sub>H show values of  $\theta_a \geq 130^\circ$  (for example, PE-OSi(CH<sub>3</sub>)<sub>3</sub>,  $\theta_a \approx 130^\circ$ ; PE-CONHC<sub>18</sub>H<sub>37</sub>,  $\theta_a \approx 132^\circ$ ). Nonetheless, 1 is unexpectedly hydrophobic. We interpret the

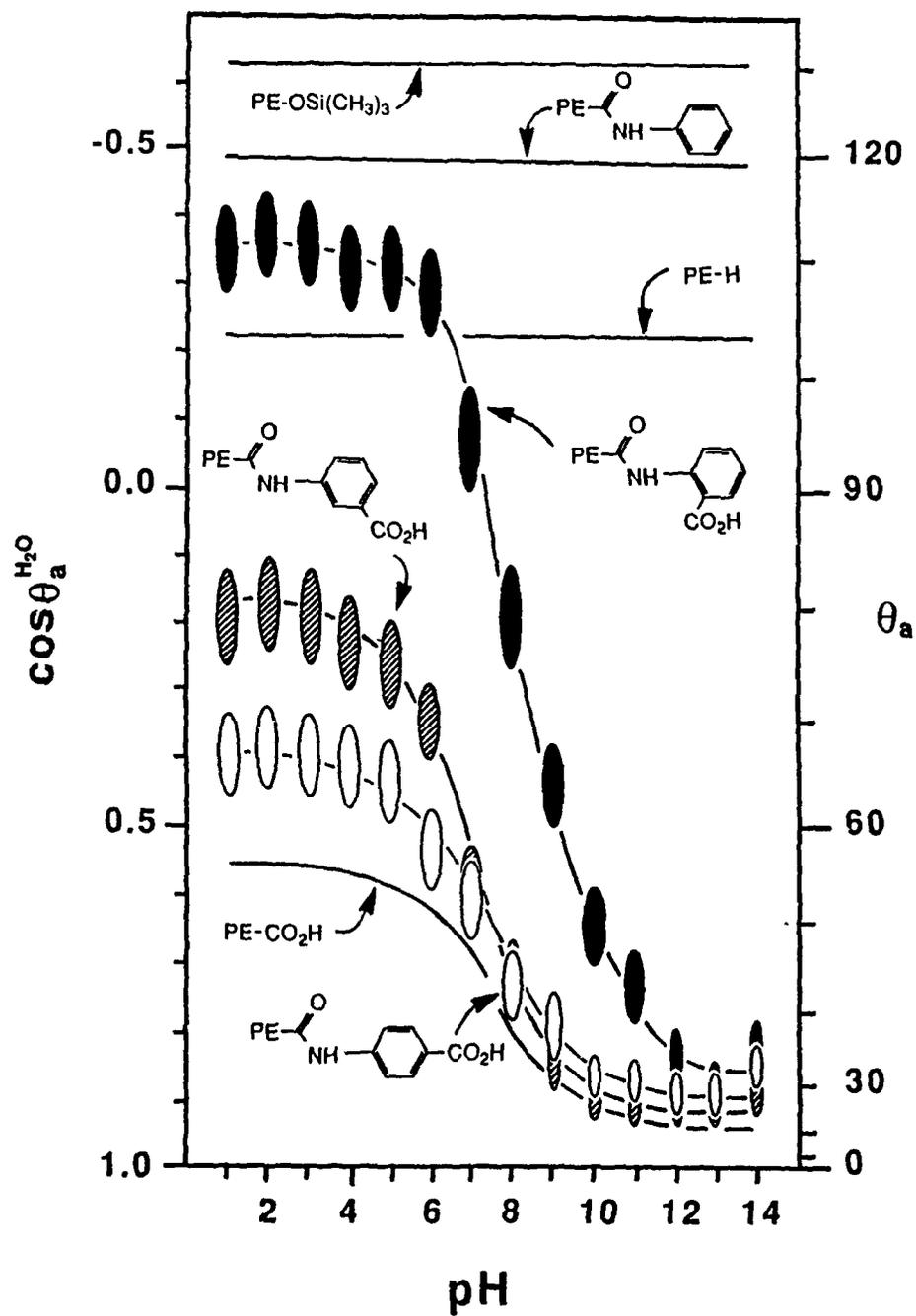


Figure 1. Variation in the advancing contact angle  $\theta_a$  of water as a function of pH on several anilide derivatives of "polyethylene carboxylic acid", PE-CO<sub>2</sub>H. Data for PE-CO<sub>2</sub>H, PE-H, PE-CONHC<sub>6</sub>H<sub>5</sub>, and PE-OSi(CH<sub>3</sub>)<sub>3</sub> are given for reference.

$\theta_a \approx 132^\circ$ ). 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  $\theta_a$  at low values of pH. At high pH, however,  $\theta_a$  is much lower for 2 than for 1. The amides of meta- and para-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  $\theta_a$  with pH.

We have not rigorously identified the origin of the large change in  $\theta_a$  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  $-\text{CONH}-$  and  $-\text{CO}_2\text{H}$  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  $\text{CO}_2^-$  group to water; in this conformation, the surface of 2 resembles that of  $\text{PE-CO}_2^-$ . This hypothesized conformational change rationalizes the large change in  $\theta_a$  with pH, but also leaves unanswered a question: 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 ( $\theta_a(\text{pH } 1) = 84^\circ$ ,  $\theta_a(\text{pH } 12) = 30^\circ$ ) resembles that of 3 more closely than that of 2.

The large change in  $\theta_a$  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, non-polar organic groups at an interface can shield underlying polar functionality from contact with water.<sup>10</sup>

#### References

- 1) The work was supported in part by the Office of Naval Research and the Defense Advanced Projects Research Agency. MDW held an IBM Predoctoral Fellowship in Polymer Science (1986-87).
- 2) Holmes-Farley, S.R.; Reamey, R.H.; McCarthy, T.J.; Deutch, J.; Whitesides, G.M. Langmuir 1985, 1, 725-740.
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- 4) Holmes-Farley, S.R.; Whitesides, G.M. Langmuir 1987, 3, 62-76.
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- 6) Holmes-Farley, S.R.; Bain, C.; 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  $\theta_a$ : Adamson, A.W. Physical Chemistry of Surfaces; Wiley Interscience: New York, 1967.

8. PE-COCl was placed in a flask containing a saturated solution ( $\sim 0.2$  M) of 2-aminobenzoic acid in dry diethyl ether under an atmosphere of  $N_2$ . After  $\sim 12$  h the film was removed and soaked for 10 min alternately in acetone and water (four alternations). The material was dried in air ( $\geq 30$  min) before measuring  $\theta_a$ .
9. All of the surfaces studied here show pronounced hysteresis. Values for receding contact angles  $\theta_r$  are (at pH 1) PE-H  $85^\circ$ ; 1,  $15^\circ$ ; 2,  $0^\circ$ ; 3,  $0^\circ$ ; 4,  $0^\circ$ ; 5,  $0^\circ$ . Although the origin of this hysteresis remains uncertain,<sup>3,5,6</sup> it is clear that the values of  $\theta_a$  do not reflect interfaces at thermodynamic equilibrium.
10. Bain, C.; Whitesides, G.M. J. Am. Chem. Soc. **1988**, 110, 5897-5898.

### Captions

Figure 1. Variation in the advancing contact angle  $\theta_a$  of water as a function of pH on several anilide derivatives of "polyethylene carboxylic acid", PE-CO<sub>2</sub>H. Data for PE-CO<sub>2</sub>H, PE-H, PE-CONHC<sub>6</sub>H<sub>5</sub>, and PE-OSi(CH<sub>3</sub>)<sub>3</sub> are given for reference.

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