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

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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. 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, θA, is ~55°); for pH ≥ 10, the carboxylic acid groups are present as the more hydrophilic carboxylate anions, and the contact angle drops to θA ≈ 20°. 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 θA with pH are limited by the fact that derivatives of PE-CO2H seldom show a value of θA less than ~20° (independent of the relative hydrophilicity of the functional groups present at the polymer-water interface) and that most potentially ionizable derivatives are relatively hydrophilic at low values of pH.

Here we report that the material 2 formed by reaction of PE-COCI with anthranilic acid shows a very large change in contact angle with pH: from θA ≈ 110° (more hydrophobic than unfunctionalized PE-H) at low pH to θA ≈ 33° at high pH (Figure 1). The value of θA ≈ 119° for the reference material 1 is independent of pH and is also higher than that of PE-H. The difference in θA 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 hydrophilic derivatives of PE-CO2H show values of θA ≥ 130° (for example, PE-OSi(CH3)3, θA ≈ 130°; PE-COOH, θA ≈ 132°). Nonetheless, 1 is unexpectedly hydrophilic. We interpret the hydrophilicity 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 θA at low values of pH. At high pH, however, θA 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 θA with pH.

We have not rigorously identified the origin of the large change in θA 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 = 7). We suggest that at low pH, 2 adopts a conformation that buries both the -CONH- and -CO2H moieties; in this conformation, the surface of 2 resembles that of PE-CO2-. This hypothesis provides a possible explanation for the large change in θA with pH for 2, but it also leaves a question unanswered: Why should 2 adopt an orientation suggested by 6? By burying the carboxylic acid, the amine group of 2 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 θA 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, suggest an alternative 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 (θA(pH 1) = 84°, θA(pH 12) = 90°) resembles that of 3 more closely than that of 2.

The large change in θA 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.\(^\text{10}\)