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The Anthranilate Amide of "Polyethylene Carboxylic Acid" Shows an Exceptionally Large Change with pH in Its Wettability by Water[1]

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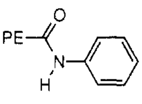
"Polyethylene carboxylic acid" (PE-CO$_2$H) is a material prepared from low-density polyethylene film (PE-H) by generating carboxylic acid groups in a thin ($\leq$2 nm) interfacial region by using chromic acid solution as oxidant.[2-6] This material is a convenient substrate with which to explore the physical-organic chemistry of organic surfaces. One interesting and analytically useful characteristic of PE-CO$_2$H is that its wettability by water depends on pH: for pH $\leq$ 4, the carboxylic acid groups are protonated and the surface relatively hydrophobic (the advancing contact angle, θ_a, is $\sim$55°); for pH $\geq$ 10, the carboxylic acid groups are present as the more hydrophilic carboxylate anions, and the contact angle drops to $\theta_a \simeq 20°$. Other acidic, surface-functionalized derivatives of PE-CO$_2$H also show a pH-dependent contact angle. In most cases the magnitude of the changes in cos θ_a with pH are limited by the fact that derivatives of PE-CO$_2$H seldom show a value of θ_a less than $\sim$20° (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 acid[8] shows a very large change in contact angle with pH: from $\theta_a \simeq 110°$ (more hydrophobic than unfunctionalized PE-H) at low pH to $\theta_a \simeq 33°$ at high pH (Figure 1).[9]

The value of $\theta_a \simeq 119°$ 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 of hydrophobicity, since the surface of **2** is rougher than that of PE-H. Very hydrophobic derivatives of PE-CO$_2$H show values of $\theta_a \geq 130°$ (for example, PE-OSi(CH$_3$)$_3$, $\theta_a \simeq 130°$; PE-CONHC$_{18}$H$_{37}$, $\theta_a \simeq 132°$). 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.



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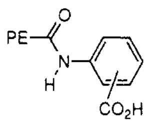
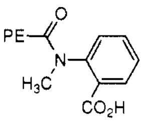


2 (*ortho*)
3 (*meta*)
4 (*para*)



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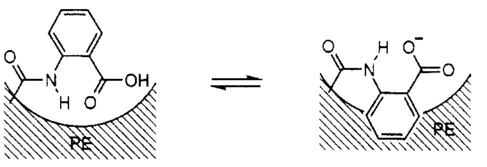

6 **7**

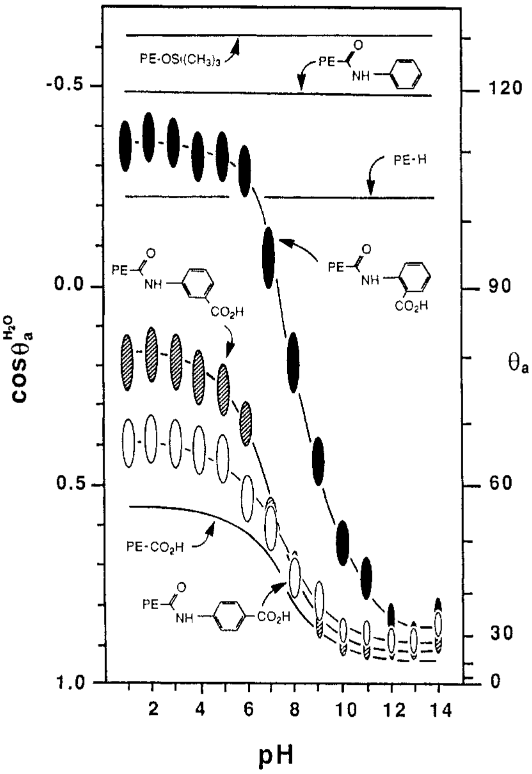

Figure 1. Variation in the advancing contact angle θ_a of water as a function of pH on several anilide derivatives of "polyethylene carboxylic acid", PE-CO$_2$H. Data for PE-CO$_2$H, PE-H, PE-CONHC$_6$H$_5$, and PE-OSi(CH$_3$)$_3$ are given for reference.

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 -CO$_2$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 CO$_2^-$ group to water; in this conformation, the surface of **2** resembles that of PE-CO$_2^-$. 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

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(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.

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

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(7) Cos θ_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 ($\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 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.

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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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Comparison of Migratory Aptitudes of Hydride and Alkyl Groups in β-Migratory Insertion Reactions of $Cp^*(P(OMe)_3)Rh(C_2H_4)R^+$ (R = H, CH_2CH_3)

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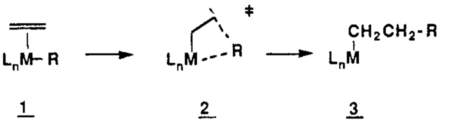
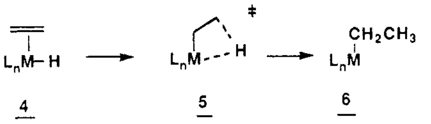
The β-migratory insertion reaction (eq 1) of metal alkyl olefin complexes is thought to be the key step in Ziegler–Natta olefin polymerization reactions and related oligomerizations and dimerizations.[1,2] However, such migratory insertion reactions have rarely been observed for stable complexes of type **1**.[3]

The structure and dynamics of the often more accessible hydride systems (eq 2) should prove useful in predicting the rates of alkyl migrations in ethylene alkyl complexes (eq 1). Earlier[4] we suggested that when the stable form of the hydride complex is the agostic structure **5** (as compared to the terminal structure **4**) the barrier to alkyl migration in the alkyl analogues of these systems should be lower relative to alkyl analogues of terminal hydride systems, **4**. That is, the same factors which favor a bridging over a terminal hydride structure should dictate a smaller energy difference between **1** and **2**. This proposal has been verified in the case of agostic Co(III) systems of the type $Cp^*(L)Co\text{-}CH_2\text{-}CH_2\text{-}\mu\text{-}H^+$.[4]



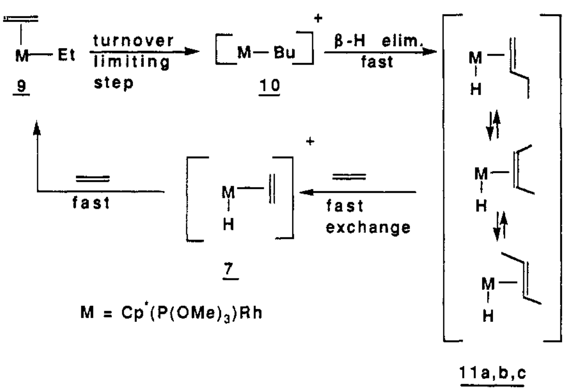
(1)



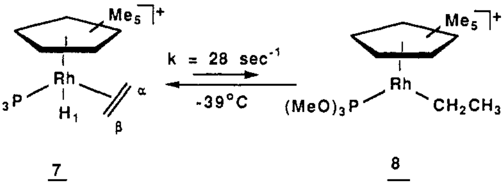
(2)

No quantitative data are currently available regarding relative rates of hydride and alkyl migrations in terminal hydride systems **4** and their alkyl analogues.[5,6] We report here a study of $Cp^*(P(OMe)_3)Rh(H)(C_2H_4)^+$ and the ethyl analogue $Cp^*(P(OMe)_3)Rh(C_2H_5)(C_2H_4)^+$ which establishes migratory aptitudes for -H versus $\text{-}CH_2CH_3$ groups in these systems.

Scheme I



Protonation of $Cp^*(P(OMe)_3)Rh(C_2H_4)$[7] with $HBF_4{\cdot}Me_2O$ in CD_2Cl_2 at −30 °C yields the stable orange-yellow salt $Cp^*(P(OMe)_3)Rh(H)(C_2H_4)^+$, **7**.[7-9] The hydride is terminal and not agostic as indicated by lack of coupling between the rhodium hydride and $^{13}C_\alpha$ or $^{13}C_\beta$ (<4 Hz) and the large values of J_{Rh-H} (18 Hz) and J_{P-H} (18 Hz). Complex **7** exhibits two dynamic processes. Ethylene rotation is rapid, and from line shape analysis a rotational barrier of ca. 9.6 ± 0.4 kcal/mol at −60 °C can be estimated. At higher temperatures the hydride signal at −9.95 ppm broadens and averages with the ^1H signals of the ethylene ligand due to a reversible migratory insertion reaction shown in



(3)

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(1) See, for example: (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; Chapters 3–5. (b) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapters 6 and 11. (c) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594.

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(6) Activation barriers may be crudely estimated for the migratory insertion reactions of $CpNi(C_2H_4)R$,[3a] $CpCo(C_2H_4)(CH_3)_2$,[3b] and $Cp^*Co(C_2H_4)(CH_3)_2$;[3c] but in each case the hydride analogue is unknown, and thus a comparison of hydride and alkyl migration barriers is not possible.

(7) (a) Prepared by the reaction of $Cp^*Rh(C_2H_4)_2$ with $P(OMe)_3$ in analogy with the preparation of $Cp^*Rh(C_2H_4)(PMe_3)$: Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376. (b) ^1H NMR (25 °C, C_6D_6) δ 3.29 (d, J_{P-H} = 12.8 Hz, $P(OMe)_3$), δ 1.87 (d, J_{P-H} = 3 Hz, C_5Me_5), δ 2.21, 1.7 (multiplets, C_2H_4). Anal. Found: (Calcd): C, 45.94 (46.16); H, 6.99 (7.23).

(8) ^1H NMR parameters for **7** are similar to those for $Cp(PMe_3)Rh(C_2H_4)(H)^+BF_4^-$ reported by Werner.[5b,c]

(9) **7**: ^1H NMR (−94 °C, CD_2Cl_2), δ −9.95 (t, $J_{P-H} = J_{Rh-H}$ = 18 Hz, H_1), δ 2.5, 2.6, 2.9, 3.0 (multiplets, four inequivalent protons of C_2H_4), δ 1.85 (d, J_{P-H} = 4 Hz, C_5Me_5), δ 3.5 (d, J_{P-H} = 13 Hz, $P(OMe)_3$); ^{13}C NMR (−94 °C, CD_2Cl_2), δ 104 (s, C_5Me_5), δ 52.7 (dq, J_{P-C} = 3.3 Hz, J_{C-H} = 149 Hz, $P(OMe)_3$), δ 9.98 (q, J_{C-H} = 129 Hz, C_5Me_5). Ethylene signals are obscured by CD_2Cl_2 but are visible in acetone-d_6 at −94 °C: δ 53.4 (t, J_{C-H} = 161 Hz, C_α or C_β), δ 54.6 (t, J_{C-H} = 161 Hz, C_α or C_β).

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