pH and Solvent Responsive Reactivity of Surface-Grafted Polyethylene Films

David E. Bergbreiter* and Ashok Bandella

Department of Chemistry, Texas A&M University
College Station, Texas 77843

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The surface reactivity of macromolecules is a consideration in many applications of functional polymers in biochemistry and in materials science.[1,2] However, in spite of considerable strides in the understanding of acid−base chemistry at interfaces and surfaces,[3,4] there is still a limited amount of information about the behavior of weak acids or weak polyacids at interfaces. Such chemistry is, however, of both practical and theoretical interest in chemistry, biochemistry, and materials science.[5,6] In connection with a broad program of work directed at the design, synthesis, and characterization of surface-functionalized polyethylene,[7] we have prepared a surface-grafted polyethylene that contains a poly(acrylic acid) graft that exhibits a significant change in its reactivity with changes in either solvent or pH.

The surface-grafted polyethylene we prepared was derived from an entrapment-functionalized polymer containing a phenyl−pyrenyl-terminated polyethylene oligomer (**1**) as both a spectroscopic probe and a macroinitiator for surface grafting. The necessary oligomer was derived from anionic oligomerization of ethylene as reported previously.[8] The oligomers so prepared were then mixed with a 100-fold excess by weight of additive-free linear low-density polyethylene in a blending process to prepare a surface-functionalized polyethylene that contained a weakly acidic phenylpyrenylmethyl group. This blending process used a previously described procedure[7] in which the mixture of oligomer and host polymer was initially dissolved in *o*-dichlorobenzene followed by film formation by solvent casting. The resulting films were ca. 50 μm thick and were extracted for 24 h with CH_2Cl_2 prior to use in the grafting and fluorescence experiments described below.

Lithiation of the $PE/PE_{Olig}-CH(Ph)pyrenyl$ film (PE/**1**) with BuLi in THF followed by addition of *tert*-butyl acrylate yielded a $PE/\mathbf{1}\text{-}g\text{-}(CH_2CH(CO_2C(CH_3)_3))_n$ surface-grafted polymer. Hydrolysis of the acid-labile *tert*-butyl ester (HBr, methanol) yielded an acrylic acid grafted surface, $PE/\mathbf{1}\text{-}g\text{-}(CH_2CH(CO_2C(CH_3)_3))_n$. These surface-grafted polymers were characterized by XPS, contact angle analysis, and ATR-IR spectroscopy (product, O_{1s}/C_{1s}, Θ_a (water), $\nu_{C=O}$) (PE/**1**, 0.008, 106 ± 3°, no $\nu_{C=O}$ peak; $PE/\mathbf{1}\text{-}g\text{-}(CH_2CH(CO_2C(CH_3)_3))_n$, 0.021, 94 ± 3°, $\nu_{C=O}$ peak at 1735 cm^{-1}; $PE/\mathbf{1}\text{-}g\text{-}(CH_2CH(CO_2H))_n$, 0.053, 81 ± 3°, $\nu_{C=O}$ peak at 1710 cm^{-1}). The average degree of polymerization of the acrylate graft of the $PE/\mathbf{1}\text{-}g\text{-}CH_2CH(CO_2C(CH_3)_3))_n$ was estimated to be 20−30 based on our prior work with polymethacrylonitrile grafts.[8]

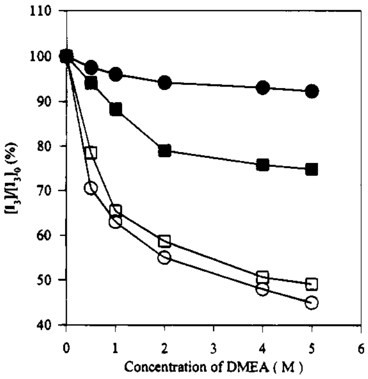

Figure 1. Quenching of pyrene groups by *N*,*N*-dimethylethanolamine solutions at ambient temperature as measured by the change in intensity for the I_3 peak of pyrene fluorescence in water (circles) and methanol (squares) for $PE/PE_{Olig}-C(Ph)(pyrene)\text{-}g\text{-}(CH_2CH(CO_2C(CH_3)_3))_n$ (filled symbols) and $PE/PE_{Olig}-C(Ph)(pyrene)\text{-}g\text{-}(CH_2CH(CO_2H))_n$ (open symbols).

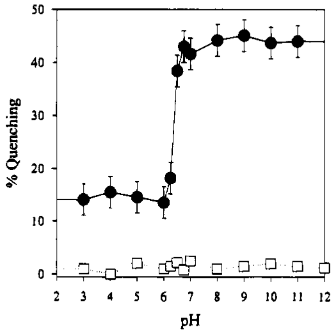

Figure 2. Effect of pH on quenching of $PE/PE_{Olig}-C(Ph)(pyrene)\text{-}g\text{-}(CH_2CH(CO_2H))_n$ based on changes in the intensity of the I_3 peak in fluorescence spectra of (●) 1 M NaI in buffered aqueous solutions and (□) buffer solutions without added quencher.

While the XPS, contact angle analyses, and IR data were all consistent with the assigned structures, fluorescence-quenching studies were most useful in verifying that most of the pyrene groups of $PE/\mathbf{1}\text{-}g\text{-}(CH_2CH(CO_2C(CH_3)_3))_n$ and $PE/\mathbf{1}\text{-}g\text{-}(CH_2CH(CO_2H))_n$ were at the polyethylene solvent interface or surface on the basis of their accessibility to reagents that do not readily permeate polyethylene. These experiments studied quenching of the polymer-bound pyrene groups by *N*,*N*-dimethylethanolamine (DMEA) in either methanol or water suspensions. Figure 1 shows the changes in the I_3 (389 nm) peak intensity for each of these grafted polymers with DMEA solutions in these solvents.[9] The observed solvent effects wherein the same quenching agent goes from <5% efficiency in water to over 50% efficiency are very consistent with a modified polymer in which a majority of the pyrene groups and the grafts are at a solution accessible polymer/solution interface and where the graft determines the surface reactivity and accessibility.[1,7,8] Not shown on these plots are the effects of 4 M DMEA methanol and water solutions on quenching of the fluorescence of the ungrafted PE/**1** film (10% and 6% quenching, respectively).

The data in Figure 1 show significant differences in solvation depending on the hydrolysis of the esters. The changes seen are expected for these grafted interfaces or surfaces because of the expected greater solubility of a poly(acrylic acid) graft over a polyester graft in a basic protic solvent. The effects of pH changes on the accessibility and reactivity of the pyrene groups of $PE/\mathbf{1}\text{-}g\text{-}(CH_2CH(CO_2H))_n$ shown in Figure 2 are more notable. This figure includes two experiments. First, the lack of quenching by a series of buffers ranging from pH 3 to pH

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[1] Ferguson, G. S., Whitesides, G. M. In *Modern Approaches to Wettability: Theory and Applications*; Schrader, M. E., Loeb, G. I., Eds.; Plenum: New York, 1991.

[2] MacRitchie, F. *Chemistry at Interfaces*; Academic Press: San Diego, 1990.

[3] Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87−96.

[4] Thomas, J. L.; Tirrell, D. A. *Acc. Chem. Res.* **1992**, *25*, 336−342.

[5] Israels, R.; Gersappe, D.; Fasolka, M.; Roberts, V. A.; Balzacs, A. C. *Macromolecules* **1994**, *27*, 6679−6682. Lyatskaya, Y. V.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1995**, *28*, 3562−3569.

[6] Thomas, J. L.; You, H.; Tirrell, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 2945−2946.

[7] Bergbreiter, D. E. *Prog. Polym. Sci.* **1994**, *19*, 529−60.

[8] Bergbreiter, D. E.; Gray, H. N.; Srinivas, B. *Macromolecules* **1994**, *27*, 7294−7301.

[9] Fluorescence intensities were all measured without degassing the solvents since separate experiments showed only a 3−5% change in the measured I_3 peak intensity on oxygen removal.

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12 is shown. A second set of experiments in Figure 2 shows the effects of pH on NaI quenching. In these experiments, the quenching agent NaI is minimally effective at acidic pH values because the pyrene groups are apparently covered by the poly(acrylic acid) graft. At basic pHs where the poly(acrylic acid) was a sodium salt (IR, $\nu_{C=O}$ 1560 cm^{-1}), NaI was an effective quenching agent. Most notable is that the change in the extent of quenching with pH is surprisingly sharp, occurring over a pH range that is sharper than that seen for poly(acrylic acid) in solution. These changes were also fully reversible. The quenching of the pyrene groups by DMEA was also followed as a function of pH.[8] As could be expected, the amount of quenching was minimal at low pH values where the amine was protonated and was high at basic pH values where the free amine was present. The transition near the amine's expected pK_a (ca. 9.5) was that expected for a weak acid.

The solvent-dependent changes in reactivity of these grafted polyethylene surfaces or interfaces are consistent with the solubility characteristics of the grafted polymer chains. They show that even small grafts can significantly alter chemistry and solvation at a polymer/solvent interface. However, the strong acid-like pseudotitration curve seen for PE/**1**-*g*-$(CH_2CH(CO_2H))_n$ was not expected. Indeed, the titration curve for the acrylic acid graft is sharper than that for acrylic acid in solution. Solution studies of polyelectrolytes show similar but broader transitions occurring over a pH range of 4–6.[11] Devices have also been fabricated that use the pH-dependent behavior of polyelectrolytes to control processes like permeability and drug release, but these changes too have been studied over broader pH ranges.[5,6,10] One explanation advanced[12] for the known changes in pyrene fluorescence and quenching in solutions of polyelectrolytes included a highly cooperative conformational change. We speculate that the even sharper change seen here for surface-grafted poly(acrylic acid) may also be explained by such a cooperative pH-induced conformational change. Specifically, the significant difference between the low-dielectric medium of a functionalized polyethylene surface and the polar aqueous buffer solution would exaggerate the solubility difference for a partially deprotonated polyelectrolyte. Thus, a small pH change may induce a conformational change. Regardless of the explanation, our work shows that the incorporation by design of small grafts at polymer surfaces usefully and interestingly alters surface chemistry.

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(10) Olea, A. F.; Thomas, J. K. *Macromolecules* **1989**, *22*, 1165–1169.

(11) Niwa, M.; Mukai, A.; Higashi, N. *Langmuir* **1990**, *6*, 1432–1434.

(12) Anufrieva, E. V.; Birshtein, T. M.; Nekrasova, T. N.; Ptitsyn, C. B.; Sheveleva, T. V. *J. Polym. Sci., Part C* **1968**, *16*, 3519–3531.