Temperature-Responsive Surface-Functionalized Polyethylene Films

David E. Bergbreiter,* Bill C. Ponder, Gaston Aguilar, and B. Srinivas

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

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Polyethylene−poly(ethylene glycol) co-oligomers were used to surface functionalize polyethylene films via an entrapment process. When immersed in water, the poly(ethylene glycol) groups at these surfaces had solvation behavior that resembled the known inverse temperature-dependent solubility properties of poly(ethylene glycol) in water. The responsiveness of these films' surfaces was characterized by fluorescence spectroscopy and kinetic studies using pyrene ester labels. Changes in the ratio of the I_1/I_3 peaks in the emission spectrum of the pyrene probe showed that the interface micropolarity was higher at low temperature and lower at high temperature. Repeated heating and cooling (5 °C → 65 °C → 5 °C → 65 °C) with the same sample showed that these interface changes were substantially reversible. Interface solvation was measured by comparing I_1/I_3 ratios for pyrene-labeled oligomers in water, ethanol, and toluene solutions with similar labels on films suspended in these same solvents. The results show that interface solvation was independent of temperature in toluene, directly dependent on temperature in ethanol, and inversely dependent on temperature in water. These changes in surface solvation lead to changes in surface reactivity. In water suspensions, these pyrene-labeled poly(ethylene glycol)-functionalized polyethylene films had hydrolysis kinetics that did not follow an Arrhenius relationship.

Introduction

Responsive or "smart" materials are an attractive area of research in polymer chemistry and materials science. Such materials respond in useful ways to environmental stimuli and can be used in mechanical devices, in sensors, in catalysis, and in separation processes.[1−4] Several recent reports have also described surfaces and interfaces that respond in a predictable and useful manner to changes in their environment's pH or temperature.[5−8] These changes in surface solvation impact adhesion, permeability, wettability, and other surface phenomena. Because of our long-standing interest in polyolefin surface chemistry, we were interested in determining how functionalized polyethylene surface chemistry was affected by temperature changes.

Here we report temperature-responsive surface chemistry for functionalized polyethylene surfaces. The specific surfaces we describe below are polyethylene surfaces functionalized with PEG oligomers that are tagged with a pyrene fluorophore. This pyrene fluorophore has an emission spectrum with peak intensities that are dependent on the microenvironment of the pyrene. Thus, these probes can be used to monitor changes of the resulting polymer/water interface environment in response to changes in temperature. We specifically examined changes in the ratio of the first and third emission peaks in the pyrene probe's fluorescence spectrum. It is known that the I_1/I_3 ratio in pyrene's fluorescence spectrum is a measure of a pyrene probe's environment.[9] The results of our studies described below show that normal and inverse solvation of these interfaces occurs with increasing temperature. Similar conclusions about surface solvation based on wettability studies have recently been reported.[8]

The basis for our design of responsive surfaces is the known inverse temperature-dependent solubility of poly(alkene oxide)s in water. Similar effects are also known for other polymers in both non-hydrogen-bonding and hydrogen-bonding solvents.[10] In water, these effects often occur in the temperature range 0−100 °C. The temperature at which insolubility or phase separation occurs is normally called the lower critical solution temperature (LCST) and depends on the structure and hydrophobicity of the polymer being studied.[10,11]

The results below show that this well-known LCST behavior of polymers can be used to produce surface-

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* E-mail: Bergbreiter@chemvx.tamu.edu.

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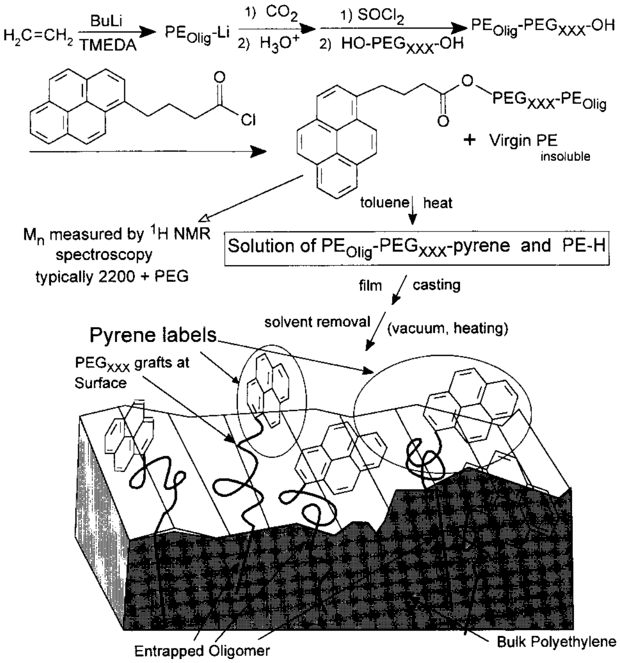
Scheme 1. Synthetic Route to Pyrene-Labeled Co-oligomers of Polyethylene and Poly(ethylene glycol) and Their Blending To Form a Polyethylene Film Surface Functionalized with Pyrene-Labeled Poly(ethylene glycol) Grafts by Entrapment Functionalization



modified polymers that reversibly change their hydrophilicity and solvation with changes in temperature. As shown by the fluorescence studies below, the surfaces we have prepared are more polar (hydrophilic) at low temperature and less polar (hydrophobic) at high temperature when suspended in a polar protic solvent such as water.

Results and Discussion

Our initial goal in this work was to prepare surface-functionalized polyethylene films that contained polymer grafts that might be expected to exhibit inverse temperature-dependent solubility. Our prior work in synthesis of PEG-grafted polyethylene surfaces by entrapment functionalization suggested the approach shown in Scheme 1.[12] We first prepared a $\text{PE}_{\text{Olig}}-\text{CO}_2-\text{PEG}_{\text{Olig}}-\text{OH}$ block cooligomer. Addition of pyrene butyric acid chloride then added a pyrene fluorophore to the hydrophilic end of this diblock cooligomer. This synthesis was carried out with different sized PEG oligomers. Once prepared, the pyrene-tagged PE−PEG diblock cooligomers were used in an entrapment functionalization.[12,13] In a typical procedure, a 1% by weight functionalized film was prepared by mixing a 100-fold excess of virgin linear high-density polyethylene with the block co-oligomer. Complete mixing was ensured by completely dissolving both the host virgin polyethylene along with the co-oligomer in *o*-dichlorobenzene at reflux. Cooling of the solution precipitated the entrapped powder. Films were then produced as needed by solvent casting from *o*-dichlorobenzene solutions. The films so formed were typically 50 μm ± 10 μm thick. The resulting $\text{PE}_{\text{Olig}}-\text{PEG}_{\text{xxx}}-\text{O}_2\text{C(CH}_2)_3$pyrene groups are at the surface of the product film in part because of the PE−PEG incompatibility as discussed previously.[12]

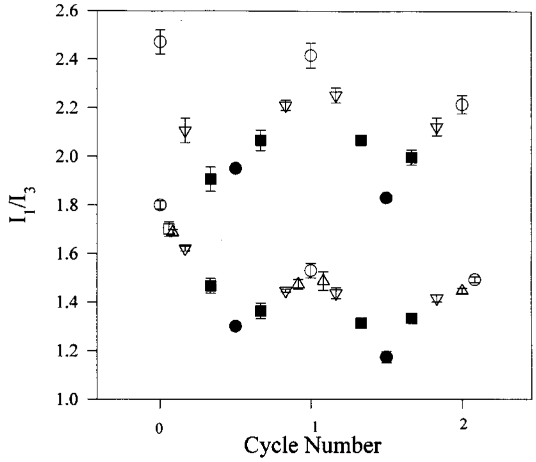


Figure 1. Plots of I_1/I_3 vs temperature measured through two heating/cooling cycles for two different sized $\text{PE}_{\text{Olig}}-\text{PEG}_{\text{Olig}}-\text{O}_2\text{C(CH}_2)_3$pyrene functionalized polyethylene films: $\text{PE}_{\text{Olig}}-\text{PEG}_{600}-\text{O}_2\text{C(CH}_2)_3$pyrene (plot is offset by −0.5 on the *y*-axis for clarity); 5 °C (○), 10 °C (□), 15 °C (△), 25 °C (▽), 45 °C (■), 65 °C (●); $\text{PE}_{\text{Olig}}-\text{PEG}_{2000}-\text{O}_2\text{C(CH}_2)_3$pyrene 5 °C (○), 25 °C (▽), 45 °C (■), 65 °C (●).

Because the I_1/I_3 ratio is a measure of pyrene's microenvironment,[9] we expected to be able to monitor the effects of changing temperature upon the microenvironment of the interface by following the changes in the peak intensity ratio. Films under study were exposed to an excitation wavelength of 343 nm, with steady-state emission analysis from 350 to 600 nm (I_1, 377.5 nm; I_3, 389.5 nm). Five readings were taken at approximately 5 min intervals for each temperature. An equilibration time of 30 min at each temperature preceded each measurement of peak intensity. At least two temperature cycles (5 °C → 65 °C → 5 °C) were followed for each film. While temperatures below 5 °C or above 65 °C might have been used, the freezing point of water, the boiling point of ethanol, and the likely problem of irreversible dissolution of polyethylene in toluene at higher temperatures limit the temperature range at which functionalized polyethylene surfaces can be studied in these solvents.

Data for the changes in the I_1/I_3 ratio with temperature are shown in Figure 1 for $\text{PE/PE}_{\text{Olig}}-\text{PEG}_{600}-\text{O}_2\text{C(CH}_2)_3$pyrene and $\text{PE/PE}_{\text{Olig}}-\text{PEG}_{2000}-\text{O}_2\text{C(CH}_2)_3$-pyrene films suspended in water through two cycles of heating and cooling. In each case, the I_1/I_3 values decreased as temperature increased. This graph also shows some hysteresis of the I_1/I_3 response to temperature in the PEG_{600} system. We attribute the observed hysteresis to surface reconstruction. Reorganization of grafted chains and functional groups on polymer surfaces has been well documented.[14−16] The difference in the extent of hysteresis for the PEG_{2000} and PEG_{600} systems seen in Figure 1 may reflect the greater PE

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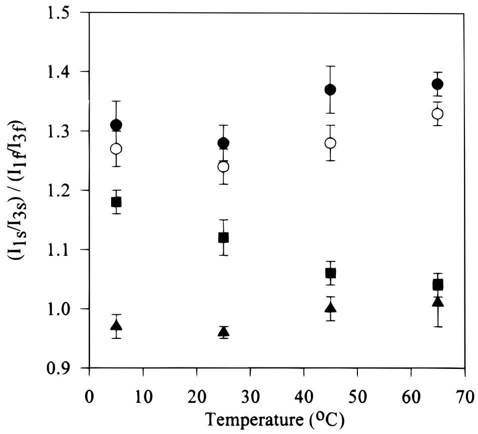
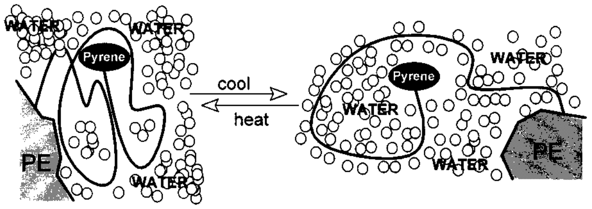


Figure 2. Plots of I_1/I_3 values of HO−PEG$_{600}$−O$_2$C(CH$_2$)$_3$-pyrene oligomers in various solutions divided by the I_1/I_3 values of a film of PE/PE$_{\text{Olig}}$−PEG$_{600}$−O$_2$C(CH$_2$)$_3$pyrene (filled circles, water; filled triangles, toluene; filled squares, ethanol) or PE/PE$_{\text{Olig}}$−PEG$_{2000}$−O$_2$C(CH$_2$)$_3$pyrene (open circles, water) suspended in the same solvent. The numerical data for the I_1/I_3 values are listed in the table in the Supporting Information.

incompatibility of the former oligomers with bulk polyethylene.[12]

The data in Figure 1 are in accord with the process illustrated schematically in eq 1. However, separate experiments also showed that changes in the I_1/I_3 ratio with temperature occurred even in homogeneous water, ethanol, and toluene solutions with temperature for pyrene-labeled oligomers such as CH$_3$O−PEG$_{600}$−O$_2$C(CH$_2$)$_3$pyrene, **1**. We believe that these changes in solution and, in part, the changes in Figure 1 are due to changes in the fluorescence lifetimes of the fluorophores with temperature. This sort of temperature effect on I_1/I_3 values has not been reported previously. It is, however, reasonable given that fluorescence lifetimes are affected by temperature and that the intensity of the I_1 and I_3 peaks could change to different extents with changes in the fluorescence lifetime. Indeed, we observed a decrease in emission intensity for both films and solutions of the pyrene-labeled PEG oligomer that was consistent with a decreased fluorescence lifetime with increasing temperature.



(1)

The temperature effects on I_1/I_3 values complicate the interpretation of Figure 1. However, a plot (Figure 2) of the I_1/I_3 values of free HO−PEG$_{600}$−O$_2$C(CH$_2$)$_3$pyrene in water, ethanol and toluene divided by the I_1/I_3 values of the corresponding films suspended in water, ethanol, or toluene shows that the response of the surface graft structure to temperature is consistent with the changes shown in eq 1. These data (Figure 2) indicate that there is no difference in the I_1/I_3 ratios associated with the free pyrene-tagged PEG$_{600}$ oligomer and the corresponding film in toluene. This is manifested by the lower graph which $(I_{1s}/I_{3s})/(I_{1f}/I_{3f})$ (I_{ns} = corresponding intensity value in solvent and I_{nf} = the same with suspended film) is unity throughout the temperature range shown. This makes sense intuitively since toluene is a "good" solvent for both PEG and PE. Therefore, the pyrene-labeled oligomers at a solvent-swollen PE-grafted surface should exhibit solution-state behavior.

On the other hand, ethanol is a "poor" solvent for both PE and PEG. PEG solubility, however, increases in ethanol on heating. Therefore, temperature-dependent solvation in ethanol of these pyrene-labeled PEG grafts was different than that seen for toluene or water. As shown in Figure 2 heating the suspension of the film in ethanol resulted in I_1/I_3 values that gradually approached those observed with HO−PEG$_{600}$−O$_2$C(CH$_2$)$_3$-pyrene in solution. This is what would be expected if ethanol solvation of the PEG groups at the PE/solvent interface increased with increasing temperature.

Finally, the data in Figure 2 show that films containing either pyrene-labeled PEG$_{600}$ or PEG$_{2000}$ oligomers suspended in water show the greatest I_1/I_3 divergence from those found in aqueous solution. Though water is a "good" solvent for PEG, the nonpolar nature of the PE part of the interface likely leads to a lower I_1/I_3 ratio for the film. More importantly, in water the film's I_1/I_3 ratio diverged even more from the solution's I_1/I_3 ratio at higher temperature. This is in accordance with the LCST phenomenon characteristic of PEG (illustrated in eq 1). Overall, these data are consistent with a reversible conformational change of the PEG oligomers grafted to the polyethylene surface from an extended conformation at low temperature to a more hydrophobic and collapsed interface at high temperature.

The absolute values for the I_1/I_3 ratios for pyrene groups bound to oligomers in toluene, ethanol, and water become successively larger as the solvent becomes less polar. However, while the value of this ratio increases as solvent polarity decreases (2.18, 2.51, and 2.78 in toluene, ethanol, and water, respectively), we prefer to use these changes as a qualitative rather than as a quantitative guide to solvation. The I_1/I_3 values for pyrene groups bound to a polyethylene surface via a PEG tether at room temperature also were found to be slightly dependent on the PEG size with the PEG$_{2000}$-bound pyrene having a more solution-like environment though this effect was not very pronounced (see table in the Supporting Information).

The implication of the fluorescence studies above is that polymers grafted with poly(ethylene glycol) should generally have temperature-dependent solvation or swellability. A study with PEG-grafted polystyrene substantiated this premise.

Poly(ethylene glycol)-grafted 1% divinylbenzene cross-linked polystyrene is a widely used support in peptide and nucleotide synthesis.[16] This support containing varying sorts of terminal functional groups on the solution end of the graft PEG chain facilitates peptide chemistry because of the PEG spacer group. Unlike the chloromethylated polystyrene base polymer, the PEG-grafted material is swellable in water. This polymer swells by about 106% when placed in water at 25 °C, an extent of swelling that is comparable to that seen on suspending these cross-linked polymer beads in solvents like toluene (54%) or ethanol (30%). The PEG-grafted polystyrene beads have temperature invariant swelling in toluene. However, the swelling of these PEG-grafted polystyrene beads changes with tempera-

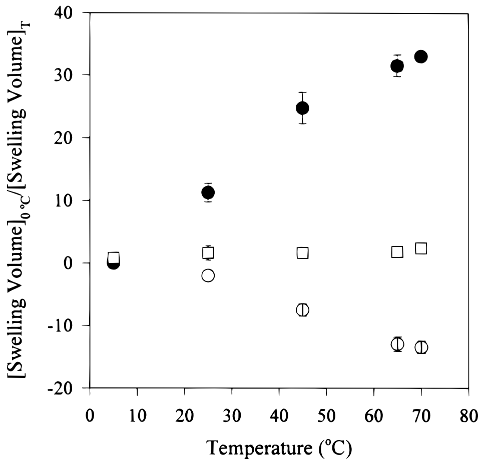


Figure 3. Volume changes for a PEG-grafted DVB-cross-linked polystyrene in water, ethanol, and toluene as a function of temperature. The volume of the dry resin was measured at 25 °C and was invariant with temperature (data not shown). The change in swelling volume was measured based on the volume increase of the swollen resin in ethanol (●), toluene (□), or water (○) relative to the volume of the dry resin was measured in a thermostated test tube. The indicated error bars represent the standard deviation of five separate measurements of swelling volume.

ture in either ethanol or water. In ethanol, the swelling increases with temperature, paralleling the effects seen in a PEG-modified polyethylene surface. In water, swelling decreases with temperature again in a manner that is consistent with the suggested inverse temperature-dependent solvation of grafts seen for pyrene-labeled PEG grafts on polyethylene films (Figure 3).

Changes in reactivity of polymer-bound groups due to the placement of "spacer" groups is a well-established phenomenon in chemical studies using insoluble polymer-supported reagents and catalysts.[18] The increase in reactivity often seen when spacer groups are used has been used to advantage in many aspects of classical solid-state synthesis chemistry. These examples suggest that a PE surface with pyrene-ester-labeled PEG groups should both react to a greater extent and should be kinetically more reactive than a simple PE surface with pyrene esters. Our studies below agree with this assumption. More interestingly, our fluorescence studies suggest that functional groups at thermally responsive interfaces could have reactivity that has an unusual temperature dependence. If, as we suggest qualitatively in eq 1, the pyrene ester groups and PEG chains collapse at higher temperature in water suspension, the reactivity of the end groups should be affected. This premise too is supported by the kinetic studies described below.

Normally reaction rates increase with increasing temperature according to the Arrhenius relationship. We have found in other work using LCST-containing material that reactivity of other polymer-bound groups can exhibit non-Arrhenius behavior with reactivity actually decreasing or ceasing at higher temperature.[3] We have examined the reactivity of these surfaces, and we find that they too exhibit non-Arrhenius behavior in solvents where fluorescence suggests LCST-like solvation changes occur. This is illustrated by the kinetic data shown in Figure 4. As shown, the hydrolysis rate of the surface-bound pyrene esters decreases slightly at higher temperatures. However, the reaction does not stop. We speculate that the polyethylene film/solvent interface in this instance changes enough to suppress the hydrolysis reaction rate but that the less hydrophilic interface is still reactive at higher temperature. It is possible that other thicker functional surfaces could exhibit a more pronounced change in solvation and reactivity. Regardless, the changes in reactivity are notable in that they imply that there could be "surface" reactions that would best be run at low temperature because they could be kinetically slow at high temperature.

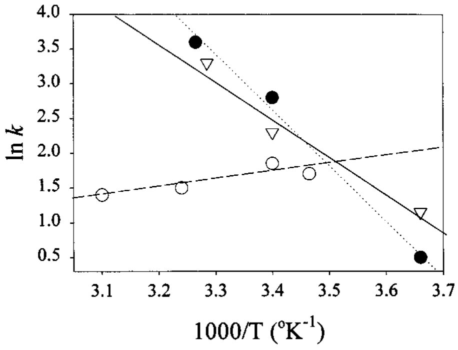


Figure 4. Temperature effects on hydrolysis or transesterification rates for films $PE-g\text{-}PE_{Olig}-CO_2-PEG_{Olig}-O_2C(CH_2)_3$-pyrene treated with aqueous NaOH or with EtONa in 1/1 (v/v) ethanol/toluene: PEG_{2000}, water (○); PEG_{400}, ethanol/toluene (●); PEG_{2000}, ethanol/toluene (▼).

While our fluorescence studies suggest that pyrene-PEG-labeled functionalized polyethylene surfaces change on heating in water to make the pyrene groups kinetically less reactive, our studies in other solvents suggest that these effects are absent in other solvents. We probed this issue by examining the rate of transesterification of pyrene groups at pyrene-PEG-labeled functionalized polyethylene as a function of temperatures. The resulting kinetic data in Figure 4 show that normal Arrhenius behavior is seen in ethanol/toluene suspensions. These results are in accord with the studies of I_1/I_3 ratios in ethanol and toluene in Figure 3 that indicated a normal temperature-dependent change in solvation (increasing solvation of the pyrene chromophore in EtOH) or no change in solvation with temperature (toluene). Specifically, the rate data in Figure 4 show that increasing temperature in a water suspension does not increase the rate of hydrolysis of the pyrene groups and Figure 3 shows that pyrene-labeled PEG oligomers at these polyethylene surfaces are less solvated by water at higher temperature. In contrast, ethanol suspensions of a PEG-pyrene labeled film show increasing solvation with temperature and the kinetic studies of transesterification show increased rates (Arrhenius kinetics).

We also compared the extent of reaction in ester hydrolysis and transesterification with a simple pyrene-functionalized polyethylene film. In earlier work, we had shown that polyethylene films containing a 4-

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Table 1. Kinetic Data for Ethanolysis of Polyethylene Films Functionalized with Pyrene Esters by Sodium Ethoxide in Ethanol/Toluene Suspension at 21 °C[a]

	k (M^{-1} h^{-1})[b]	
PEG M_n	fluorescence	UV−vis
0[c]	0.95 ± 0.5[c]	1.33 ± 0.5[c]
200	7.22 ± 0.14	7.07 ± 0.14
400	9.96 ± 0.43	10.51 ± 0.34
2000	17.42 ± 0.53	17.24 ± 0.53

[a] Reactions were carried out in 1/1 (v/v) ethanol/toluene mixtures at 21 °C. [b] Errors are based on the average of four determinations of a pseudo-first-order rate constants. [c] The rate constants for the PE/PE_{Olig}−$O_2C(CH_2)_3$pyrene transesterifications are for a pyrene ester directly attached to polyethylene with no PEG group. These rate constants have a greater error because the ethoxide concentrations were not accurately measured.

pyrenebutyl ester undergo partial transesterification in alcohols and that the extent of transesterification varied with the nature of the alcohol reactant and solvent.[18] In water, such films were essentially unreactive (<5% hydrolysis). As noted above, we expected a greater extent of reactivity for pyrene esters attached to the polyethylene film by a PEG tether. This was the result. In water, the PEG_{2000}-tethered pyrene ester reacted to a maximum of 60%. In ethanol/toluene suspensions, the PEG-tethered substrates generally reacted to extents of >90% as compared with an extent of reactivity of <50% in cases where no PEG tether was present. The rate for these transesterifications was also affected by the presence of tethering groups as shown by the data in Table 1. Measured rate constants that reflect the large excess of sodium ethoxide show that the PEG tether does indeed increase the reactivity of pyrene-bound esters with the reactions proceeding faster with PEG-tethered substrates whose PEG tethers are largest.

Conclusion

The idea that grafting can change surface character and make surfaces more reactive is well established. This generalization is also illustrated by our examples above. However, the idea that grafted surfaces can be prepared so that they change their character in response to external stimuli is less recognized. The thermally responsive surfaces described here are examples of this latter effect. Although the resulting reactivity changes seen here are modest, they suggest it should be possible to prepare other interfaces either with different functional groups or with higher densities of functional groups that exhibit more dramatic and/or more useful changes in reactivity in response to temperature or other stimuli.

Experimental Section

Preparation of Monosubstituted 1-Pyrenebutyric Acid Ester Derivatives of Poly(ethylene glycol) Oligomers of M_n 200 and 400.[11] 1-Pyrenebutyric acid (0.25 g, 0.87 mmol) was placed in 250-mL round-bottomed flask and dissolved in 150 mL of benzene. An excess of thionyl chloride (1 mL, 13.7 mmol) and a catalytic amount of dimethyl formamide was then added. The solution was stirred at room temperature for 1.5 h, after which the benzene and thionyl chloride were removed by distillation. The residue oil was then dissolved in 150 mL of methylene chloride and added dropwise to a second 250-mL round-bottomed flask containing a 10-fold excess of the poly(ethylene glycol) in 50 mL of methylene chloride. The mixture was stirred for about 2 h and was then extracted three times with 50 mL portions of saturated sodium bicarbonate aqueous solution followed by three extractions with 50 mL aliquots of pure water. The organic layer was then dried over anhydrous magnesium sulfate and filtered to remove the drying agent. The solvent was distilled to yield the product which was a viscous oil: IR (thin film between salts plates) 3500, 3027, 2920, 2874, 1735, 1604, 1495, 1461, 1380, 1105, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8−8.3 (m), 4.15 (t), 3.38 (t), 2.5 (t), 2.2 (t), 3.65 (br).

Preparation of Monosubstituted 1-Pyrenebutyric Acid Ester Derivative of Poly(ethylene glycol) Oligomer of M_n 2000. The preparation of this monopyrene derivative of poly(ethylene glycol) was identical with that for smaller PEG oligomers except that a slight excess of the 1-pyrenebutyric acid chloride was used instead of 10 mol excess of the poly(ethylene glycol). This was done to ensure that no unreacted poly(ethylene glycol) remained since this larger poly(ethylene glycol) oligomer cannot be removed from the desired product by aqueous extraction. The difunctionalized poly(ethylene glycol) byproduct formed in the reaction unlike the poly(ethylene glycol) starting material is protected from any further esterfication and did not interfere following synthesis of polyethylene−poly(ethylene glycol) co-oligomer ester of 1-pyrenebutyric acid.

Preparation of Polyethylene−Poly(ethylene glycol) Co-oligomer Ester of 1-Pyrenebutyric Acid. Purified carboxyl-terminated ethylene oligomer (0.5 g, 0.28 mmol) was placed in 250 mL dry round-bottomed flask with about 100 mL of toluene and about 1 mL of thionyl chloride (13.7 mmol). The solution was refluxed for about 3 h. After this time, the solution was cooled and the precipitate filtered. A small sample of the precipitate was analyzed by IR spectroscopy to assure complete conversion from carboxylic acid ($\nu_{C=O}$ 1710 cm^{-1}) to the acid chloride ($\nu_{C=O}$ 1799 cm^{-1}). The precipitate was then transferred to a clean 250 mL round-bottomed flask containing fresh toluene and the mono pyrenebutyric acid ester of poly(ethylene glycol) (~0.87 mmol). The solution was refluxed for 3 h and then cooled to precipitate out the product. The product was filtered, washed with methanol and ether, and dried under vacuum (0.05 Torr) for 24 h. The polyethylene−poly(ethylene glycol) cooligomer ester of 1-pyrenebutyric acid was characterized by IR and ^1H NMR spectroscopy: IR (KBr pellet) 3027, 2920, 2874, 1735, 1604, 1495, 1472, 1462, 1380, 1369, 1105, 730, 720 cm^{-1}; ^1H NMR (105 °C, toluene-d_8) 0.9 (t), 1.4 (br, s), 3.65 (br), 4.15 (t), 7.8−8.3 (m), 3.38 (t), 2.5 (t), 2.3 (t).

Preparation of Entrapment Functionalized Polyethylene Powders. Polyethylene powders containing the oligomers with 1-pyrenebutyric acid esters were prepared by cooling a 110 °C toluene solution of 1 part functionalized ethylene oligomer to 100 parts of the virgin high molecular weight polyethylene. Any fluorophore that was not covalent attached was removed by extraction of the entrapment functionalized powder with CH_2Cl_2 in a Soxhlet apparatus for 24 h.

Preparation of Entrapment Functionalized Polyethylene Films. A homogeneous solution of 0.22 g of entrapped oligomers in polyethylene was prepared by using 25 mL of hot 1,2-dichlorobenzene. The solution was then poured into a Petri dish maintained at 135 °C in an explosion-proof Friction-Aire oven for exactly 1 h. The dish was covered with a pane of glass, and solvent was allowed to evaporate through a small opening between the dish and the pane. The Petri dish was removed from the oven and allowed to cool to room temperature. The film was then removed from the dish in rectangular pieces with forceps and stored between clean glass plates. The absence of the casting solvent in the product film was verified by IR spectroscopy by the absence of strong aromatic and C−Cl stretches observed in dichlorobenzene.

General Fluorescence Measurements. All solution samples to be measured for fluorescence were subjected to oxygen removal prior to analysis. This was accomplished directly in the sample cuvettes by combination of N_2 purge and sonication. More specifically, the cuvettes were stoppered with rubber septa and hypodermic needles were used for the purging and ventilation. The sonication was done at room temperature with a Bransonic 52 ultrasonic cleaner. The fluorescence spectra of functionalized films were taken by placing films between two metal plates with large openings which exposed the films. The metal plates with the films were then placed diagonally into cuvettes so that the films were in a reproducible location in the spectrometer. The polymer films or solutions containing pyrene derivatives were analyzed using an $\lambda_{\text{excitation}}$ of 341 nm.

Preparation of Alkoxide Reaction Solutions for Solvolysis of Pyrene Labeled Esters at Polyethylene−Solution Interfaces. Reaction solutions used ethanol mixed with toluene 1:1 (volume:volume) to which pure sodium was added and dissolved to form the sodium ethoxide.

General Procedure for Solvolysis Reactions of Pyrene Labeled Esters at Polyethylene−Solvent Interfaces. For reactions conducted at room temperature, a preweighed piece of 2−5 mg of entrapment functionalized polyethylene film was placed in capped scintillation vials along with 10 mL of the toluene/ethanol sodium ethoxide reaction solutions. Shaking on a wrist action shaker served to agitate the reaction. Reactions conducted at different temperatures used films that had been placed in 25-mL round-bottomed flasks along with the appropriate reaction solutions. In these cases, agitation was effected using a magnetic stirrer. Temperatures were maintained by placing the reaction flasks in a water bath which was connected to a constant temperature bath and circulator. All reaction solutions were periodically sampled and quantitatively analyzed for pyrene by fluorescence spectroscopy.

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Supporting Information Available: Table of I_1/I_3 ratios and experimental procedures (3 pages). Ordering information is given on any current masthead page.

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