Studies of Two-Dimensional Morphology at Surface-Functionalized Polyethylene Films

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ABSTRACT: Polyethylene simultaneously functionalized with both pyrene labels and amine quencher groups has been studied to determine the extent to which self-organization and segregation of functional groups occurred during formation of a surface-bifunctionalized polymer. By measuring pyrene fluorescence in the presence of a surface-bound amine quencher, pyrene fluorescence after the surface bound quenchers had been protonated, and the total amount of polymer-bound pyrene based on the amount of quenching seen with a large excess of an external quencher, we have been able to show that the mixture of functional groups at the surface is not highly segregated. The suggested integrated morphology was further supported by studies where the ratio of pyrene to internal quencher was varied over approximately 2 orders of magnitude. These studies of a bifunctional surface-modified polymer also showed that the percentage of bound pyrene that was internally quenched varied in a roughly linear way with the molar ratio of pyrene to internal quencher and that mild annealing did not change the observed two-dimensional morphology.

Introduction

Molecular recognition, supramolecular chemistry, and molecular engineering are developing areas of chemistry and technology that critically depend on understanding the organization of assemblies of molecules either in solution or in the solid state.[1–4] Such issues have been exemplified in recent studies of organization and morphology in mixtures of molecules in self-assembled monolayers and in membranes.[5,6] Indeed, the ability to induce organization in the former case is developing into an important area that could have practical applications.[7,8] However, less is known about the two-dimensional organization of surface-functionalized polymers that typically have an interface of functionality.

We have been interested in questions of synthesis, organization, and reconstruction of surface-modified polymers. Such materials are by their very nature chemically and dimensionally inhomogeneous. While problems of the three-dimensional inhomogeneities of such interfaces have been discussed and studied,[9–11] the two-dimensional organization of functionalized polymer surfaces is less understood. Newer microscopic techniques like atomic force microscopy (AFM) can help address the issue of two-dimensional morphology when well-defined functionalized polymer surfaces are being studied.[12] However, many surface-functionalized polymers in contact with a solvent have a surface that is better described as an interface of functionality the morphology of which can vary in both a two- and three-dimensional way. Such complicated interfaces require a different approach for analysis of their "two-dimensional" or lateral morphology since only the exterior of these interfaces can be interrogated by microscopy.

This paper describes our initial studies using a combined fluorescence spectroscopy and chemical approach that address this issue. Specifically, we used a mixture of fluorophores and quenchers to prepare a bifunctional surface-functionalized polymer. A blending process was used to simultaneously introduce both groups into a surface-functionalized polyethylene film. A combination of fluorescence and chemistry then used steady state fluorescence measurements of this mixture of quenchers and pyrene fluorophores at a functionalized polyethylene surface to provide information about the two-dimensional morphology of these interfaces. In the particular instance of these bifunctionalized polyethylenes, a random or amorphous distribution of functional groups is indicated.

Results and Discussion

Our approach to examine the two-dimensional morphology of polyfunctional polyethylene surfaces relied on intrasurface or internal fluorescence quenching of a macrofluorophore by a macromolecular amine quencher. Polyethylene-bound pyrene fluorophores and amine quenchers PE_{Olig}-**1** and PE_{Olig}-**2** were first prepared via an intermediate lithiated polyethylene oligomer (eqs 1 and 2 of Scheme 1).[13] The macroquencher PE_{Olig}-**1** was prepared from a living anionic polyethylene oligomer via termination of the lithiated polyethylene by $CO_2(g)$. The carboxyl-terminated polyethylene oligomer was then converted to the acid chloride by reaction with thionyl chloride. The complete conversion of the acid to the acid chloride was confirmed by FTIR spectroscopy ($\nu_{C=O}$, 1710–1800 cm^{-1}). The acid chloride was then converted to the amide via nucleophilic addition of 4-(*N,N*-dimethylamino)benzylamine with loss of HCl. The presence of the amide was confirmed via FTIR spectroscopy ($\nu_{C=O}$, 1637 cm^{-1}) and by end group analysis using high-temperature ^1H NMR spectroscopy. The purity of the amide-terminated oligomer was determined to be 88% by analysis of the aryl and methyl regions of the ^1H NMR spectrum. The synthesis and characterization of the pyrene-terminated polyethylene oligomer **2** (PE_{Olig}-**2**) used procedures reported elsewhere.[14]

Codissolution of these oligomers with a large excess of host high molecular weight polyethylene in 1,2-dichlorobenzene followed by solution casting yielded a surface-modified polymer via the process we call entrapment functionalization (Scheme 2).[10] Using this process, we could prepare a number of films with varying molar ratios of surface-bound PE_{Olig}-**1** to PE_{Olig}-**2**. Films containing a single functional group have been prepared in a similar manner and have been studied earlier by our group. These studies have consistently shown that the terminal groups of oligomers like PE_{Olig}-**1** or -**2** end

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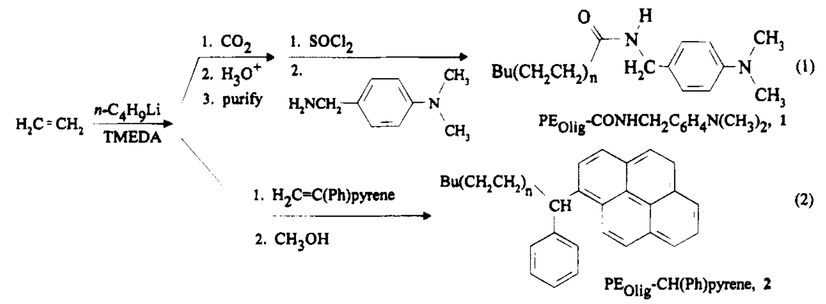
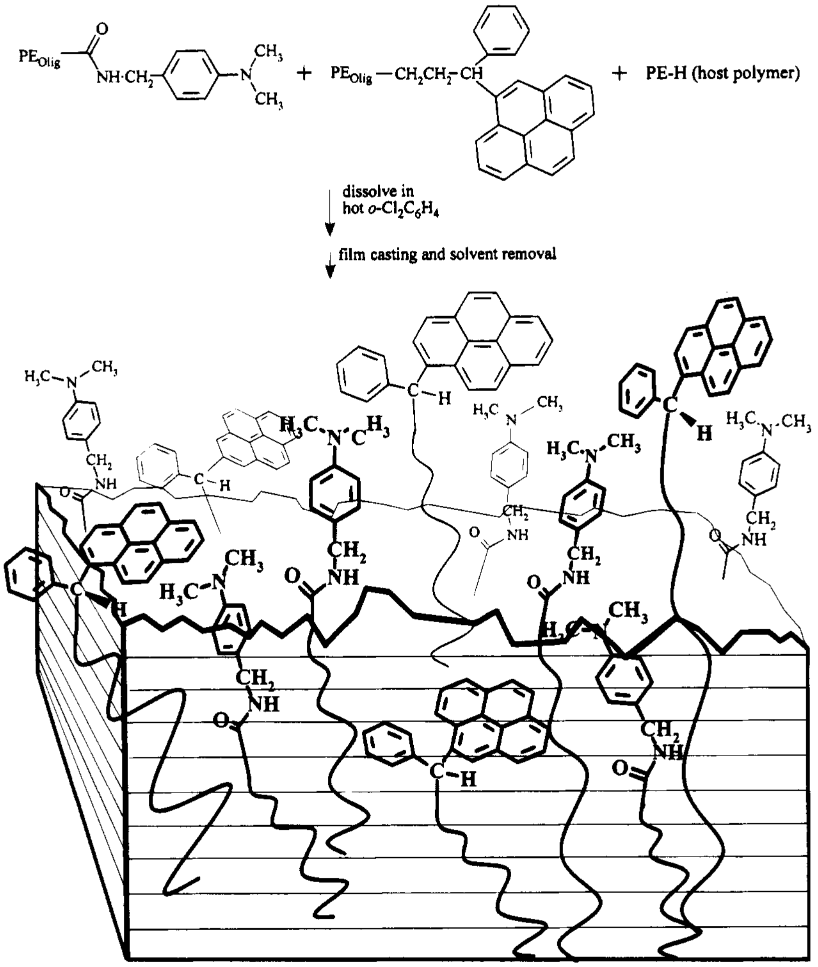
Scheme 1



Scheme 2. Entrapment Functionalization To Prepare Surface Bifunctionalized Polyethylene Films with Both a Fluorophore and Fluorescence Quencher at the Polymer Surface



up predominately at the "surface" of the solvent-cast polyethylene films.[10,14] As is crudely shown in the Scheme 2, the product film contains an interfacial region or "surface" with functional groups which are accessible to solvent or to polyethylene-incompatible reagents.

The resulting films of PE_{Olig}-**1**, PE_{Olig}-**2**, or PE_{Olig}-**1**,**2** were then analyzed by fluorescence spectroscopy. As expected, PE_{Olig}-**1** showed no fluorescence. A steady state fluorescence spectrum of PE_{Olig}-**2** was essentially the same as that shown in Figure 1 for a bifunctionalized film containing a 1:1 (mmol/mmol) mixture of PE_{Olig}-**1** and PE_{Olig}-**2**. The measurements of fluorescence intensity described below always used a single film. Nonetheless, it was possible to qualitatively compare the fluorescence intensity for a film containing only PE_{Olig}-**2** with that of a film containing a similar amount of PE_{Olig}-**2** along with an equimolar amount of PE_{Olig}-**1**. The film without quencher exhibited greater fluorescence intensity, in accord with the implication of the studies below that show internal quenching can occur. It should also be noted that, at the concentrations of pyrene used, no excimer formed. Other reported studies of similar films have shown that higher concentrations of PE_{Olig}-**2** are necessary before excimer formation is seen in these solids. At these higher concentrations of PE_{Olig}-**2**, the excimer peak maximum of excimer emission intensity appears at 477 nm.[14]

As noted above, the fluorescence spectrum of a bifunctional film containing both PE_{Olig}-**1** and -**2** indicated some quenching of PE_{Olig}-**2** by PE_{Olig}-**1**. This result shows that the functionalized surfaces contain a mixture of PE_{Olig}-**1** and -**2** in which some of the pyrene groups of PE_{Olig}-**2** are accessible to the amine groups of some PE_{Olig}-**1**. It however, does not discriminate between the two extreme morphologies shown below (**I** and **II**). One of these two morphologies (**I**) has an intimate, integrated mixture of polymer-bound fluorophores and quenchers. The other morphology (**II**) has separate

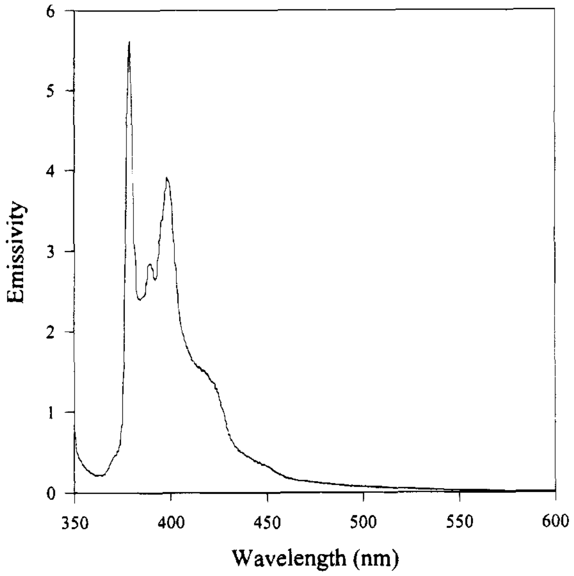
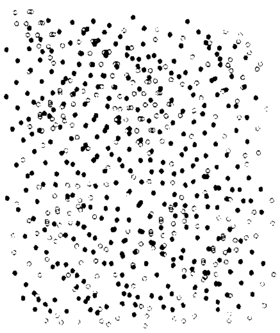
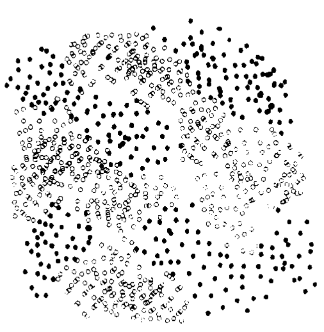


Figure 1. The steady state fluorescence spectrum of a bifunctionalized polyethylene film containing **2** (PE-2).



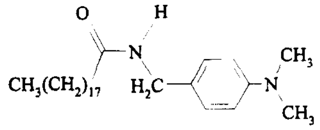
I



II

segregated domains of fluorophores and quenchers. Our goal was to see if a combination of fluorescence quenching and chemistry could differentiate between these two extreme organizational motifs.

A combination of steady state fluorescence spectroscopy and chemistry using films containing varying amounts of PE_{Olig}-**1** and -**2** did successfully distinguish between these two morphologies. First, we measured the fluorescence of a given pyrene/quencher-labeled film in a THF suspension. Then we added a 10% trifluoroacetic acid/THF solution to this film. This led to an enhancement of the fluorescence of the polyethylene-bound pyrene groups due to protonation of the polymer-bound amine quencher groups (Figure 2). Finally, the trifluoroacetic acid solution was removed and replaced with a THF solution of a soluble amine quencher, *N*-[[4-(dimethylamino)phenyl]methyl] octadecanamide (**3**). This solution quenched the fluorescence of all the pyrene groups.



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The difference in fluorescence emission intensity in the first and second experiments was due to polymer-bound pyrenes that had been quenched by polymer-bound quenchers. This premise is based on the assumption that quenching of the pyrene by protonated amine would be much less important. The third experiment determined the total number of pyrene groups. Thus, we could calculate the percentage of pyrene groups that were accessible to a coentrapped quencher for any given film. The fluorescence changes seen in these experiments and the time frame for these changes are illustrated by the data in Figure 3. In these experiments, films of PE_{Olig}-**1** or PE_{Olig}-**1**,**2** were analyzed without complete exclusion of oxygen since background oxygen quenching changed the observed fluorescence emissivity by only 5%. These experiments and the calculations below also assume that all of the amine groups of PE_{Olig}-**1** are protonated by trifluoroacetic acid. It was not possible to rigorously verify this. However, the gradual change in fluorescence quenching and the lack of further change in fluorescence intensity over an extended period of time indicate that all the accessible polymer-bound amines were protonated. The fact that the time frame for these experiments exceeded that of protonations of functionalized amine-containing polyethylenes we had earlier studied[15] also suggests that protonation was complete.

We then used this sequence of experiments to study bifunctional surfaces containing varying ratios of pyrene and quencher. The results of these series of experiments produced values for the amount of pyrene internally quenched versus the mole percent of entrapped pyrene at the polymer surface. These experiments were carried out for varying mole ratios of entrapped quencher to entrapped fluorophore (Figure 4) for a given weight percent functionalized film. We reasoned that if a morphology like **II** was present, gradually changing the molar ratio of PE_{Olig}-quencher/PE_{Olig}-pyrene from a ca. 9:1 to a ca. 1:9 ratio would not lead to much change in the amount of internal quenching since the interfacial surface area between domains of the quenching agent and pyrene-containing domains in a highly segregated system would not change appreciably with this change in the ratio of PE_{Olig}-**1**:PE_{Olig}-**2**. On the other hand, if polymer-bound quenchers and polymer-bound pyrenes were evenly distributed, the effects of this change in quencher:pyrene ratio should manifest itself in a more significant change in the mole percent of polymer-bound pyrene that was internally quenched. This latter expectation most closely corresponded to reality as shown by the plot of mole % pyrene quenched versus mole % quencher for a 0.5 wt % functionalized polymer in Figure 4. In this figure, a 9:1 quencher to pyrene ratio led to over 80% internal quenching while a 1:5 ratio of quencher to pyrene produced a films with only ca. 10% internal quenching of the pyrene.

Figure 5 shows the effect of increasing total oligomer loading on the amount of PE_{Olig}-**2** quenched by PE_{Olig}-**1**. While the general trend is much like that of Figure 4, the percentage of pyrene internally quenched changed as the film loading was increased. As the total weight percent oligomer loading increased, internal quenching of PE_{Olig}-**2** by PE_{Olig}-**1** became progressively less efficient. On the basis of our previous work,[16] we believe that this reflects a broader three-dimensional distribution of added oligomers throughout the polymer at increasing total weight percent loadings of entrapped oligomer. Even if this were the case, the total amount of pyrene quenched should not decrease. When the absolute amount of pyrene quenched was calculated, we found that it gradually approached a constant value as the total weight percent loading of oligomer increased. Specifically, at 0.5, 1.0, 2.0 and 3.1% weight loading,

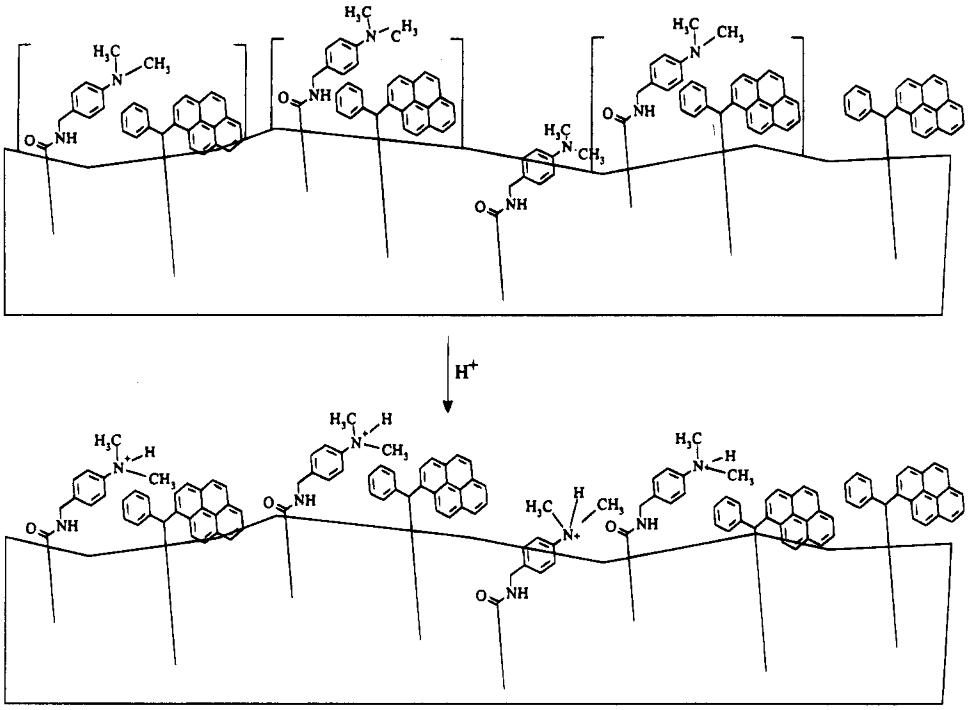

Figure 2. Internal quenching of coentrapped films and recovery via addition of acid. Pairs of polymer-bound amines quenching a pyrene are shown in brackets before addition of the acid that protonates the dimethylamino groups.

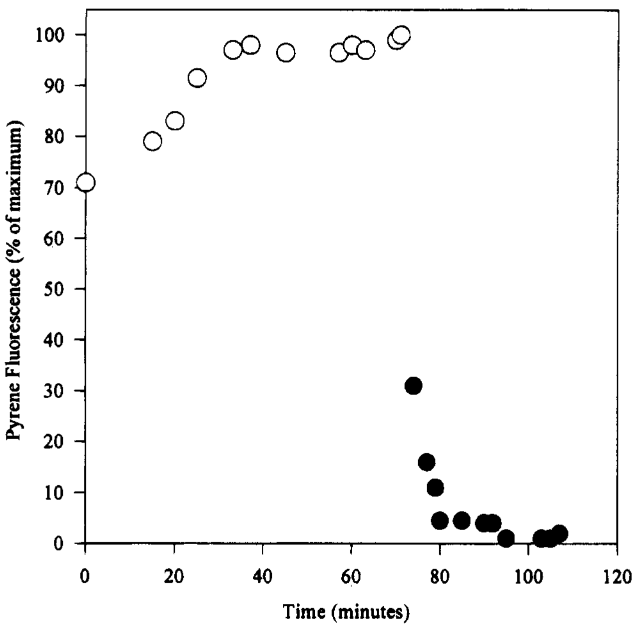

Figure 3. Time course for recovery of the pyrene fluorescence quenched internally by amines in coentrapped PE_{Olig}–CH(Ph)-pyrene and PE_{Olig}–$CONHCH_2C_6H_4N(CH_3)_2$ at a 1:1 pyrene: quencher mole ratio with 1 wt % total oligomer on addition of 10% trifluoroacetic acid in THF (○) followed by external quenching with **3** (●).

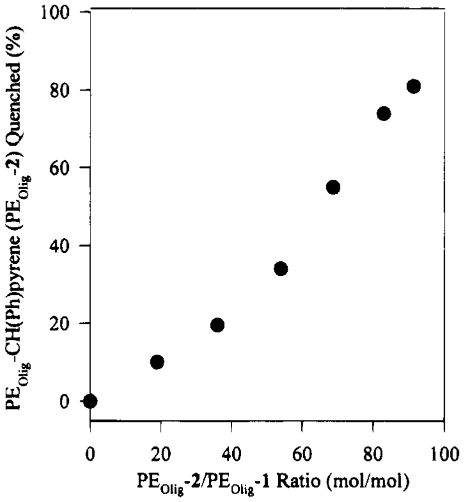

Figure 4. Plot of the mole percent of the entrapped pyrene (PE_{Olig}-**2**) quenched by added PE_{Olig}–$COCH_2C_6H_4N(CH_3)_2$ as a function of the molar ratio of PE_{Olig}-**1**/PE_{Olig}-**2** in a film containing 0.5 wt % total loading of oligomer.

the amount of pyrene that was quenched at a ca. 9:1 quencher:pyrene ratio was 0.5×10^{15}, 1.11×10^{15}, 1.24×10^{15}, and 1.38×10^{15} molecules/cm^2,[17] respectively.

Preliminary annealing experiments have also addressed the thermal stability of these bifunctional surfaces. Heating films containing PE_{Olig}-**1,2** in vacuum at 60 °C for 48 h produced a second annealed sample. This sample showed no change in the amount of internal quenching of pyrene by the coentrapped quencher, indicating that the surface morphology and distribution of functional groups was unchanged under these conditions. Although no reconstruction was seen in a simple functional film of PE_{Olig}-**1,2**, reconstruction is seen in simple surface functionalized polyethylene films under similar conditions.[18,19] Evidently the surface-functionalized polymers prepared here are more stable.

Conclusions

In summary, the blending of pairs of functionalized oligomers into a host polymer produces a bifunctionalized surface. The results described here show that it is possible to use internal quenching of fluorescence of spectroscopic reporter groups to evaluate the two-dimensional morphology of a surface-functionalized polymer. The results of these studies show that significant segregation of chemically disparate functional groups does not occur in preparation of a surface-modified polyethylene, at least for the systems studied here. The roughly linear changes in the extent of pyrene quenching with the ratio of pyrene/quencher are

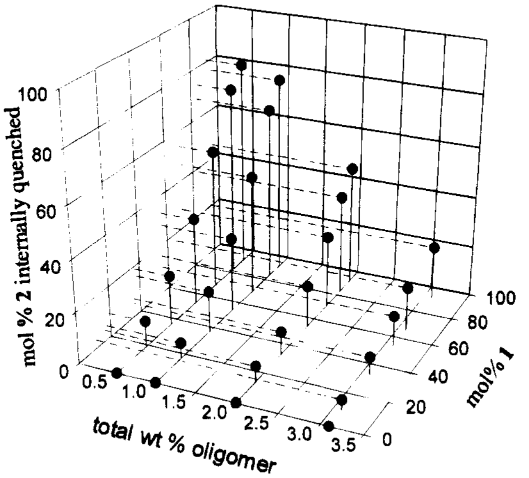

Figure 5. Three-dimensional plot showing internal quenching as a function of both weight percent of total oligomer and mole % of quenching agent.

most consistent with a more or less uniform distribution of groups. These polyfunctional interfaces also do not measurably reconstruct on mild heating. Such polyfunctional polymer surfaces should be amenable to further studies of two- and three-dimensional organization and to further synthetic manipulations, possibly leading to surfaces cografted with structurally different grafts.

Experimental Section

General Methods. All chemicals used were reagent grade unless otherwise specified. Ethylene and carbon dioxide were purchased from Matheson Co. and used as received. Heptane, tetrahydrofuran (THF), and diethyl ether were dried via distillation from sodium benzophenone anion under nitrogen. Other solvents were used as received. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled from potassium metal and stored over potassium metal under nitrogen. The *n*-BuLi used was a 1.6 M solution in heptane and was titrated before use.[20] The polyethylene used in the entrapment procedures was obtained from Allied Chemical Co. and had an M_n of 180 000–200 000 g/mol and a density of 0.96 g/mL. All air-sensitive reactions and manipulations were carried out under argon or nitrogen that had been passed through a calcium chloride drying tower.

All variable temperature NMR spectra were recorded on a Varian XL 200E FT NMR spectrometer at 105 °C in deuterated toluene using hexamethyldisiloxane (HMDS) as the internal standard. Infrared spectra were recorded on a Mattson Galaxy 4021 FT IR spectrophotometer. The spectra were recorded using a Hg–Cd–Te detector at 1 cm^{-1} resolution. The FTIR spectra of polymer powders were measured using dispersions of the polymers in thin transparent KBr pellets.

Preparation of $CH_3(CH_2CH_2)_nCH_2CONHCH_2C_6H_4N(CH_3)_2$ (1). Lithiated polyethylene oligomer was prepared as reported previously.[13] The ethylene was allowed to exit the pressure bottle through a bubbler and nitrogen (10 psig) was added. The suspension was cooled to −78 °C, the nitrogen was removed through a bubbler, and CO_2 (30 psig) was added to the bottle. The suspension was allowed to warm to room temperature after stirring 3 h and was stirred an additional 47 h at room temperature. The off-pink oligomer $CH_3(CH_2CH_2)_nCH_2COOLi$ was collected via filtration and washed three times with ethanol and five times with diethyl ether. The lithiated polyethylene carboxylic acid was protonated by adding it to 500 mL of toluene with 1 mL of HCl and heating for 1 h. The polyethylene carboxylic acid produced was purified using basic alumina (10/1, wt/wt, alumina/oligomer) as described previously. The oligomer was determined to be >90% functionalized by ^1H NMR spectroscopic analysis of a methyl ester derivative.[21]

Polyethylene carboxylic acid was converted to the acid chloride via reaction with $SOCl_2$. Polyethylene carboxylic acid (0.21 g) was added to 100 mL of toluene under argon. Thionyl chloride (5 mL) and a catalytic amount of DMF was added via syringe and the suspension was heated until the oligomer dissolved and then refluxed for 11 h. A distillation apparatus was connected to the reaction flask and the solvent was removed by distillation until about 2 mL of solution remained. The last portion of solvent was then removed under vacuum without heating. Complete conversion of the acid to the acid chloride was confirmed by the appearance of the acid chloride carbonyl at 1800 cm^{-1} in the FT IR spectrum.

The amide was then prepared by adding 0.527 g of (*N,N*-dimethylamino)benzylamine (DMABA) and 1 mL of triethylamine to a suspension of the polyethylene carboxylic acid chloride in 100 mL of toluene. The suspension was heated until the oligomer dissolved and then refluxed for 12 h. After cooling, the precipitate of amide-terminated oligomer was collected by filtration and washed first with ethanol and then with ether. The solid was added to 100 mL of toluene containing 5 mL of triethylamine and dissolved by heating. Refluxing this solution for 30 min insured that the tertiary amine end group of the functionalized oligomer was not protonated. The solution was cooled, the oligomer was collected via filtration, washed with ethanol and ether, and dried under vacuum (24 h) ^1H NMR spectrum (105 °C, toluene-d_8): δ 6.9 (d, phenyl, partially covered by toluene-d_8), 6.5 (d, phenyl), 4.15 (d, $-NHCH_2-$), 2.5 (s, $N(CH_3)_2$), 1.8 (t, $-CH_2CONH-$), 1.0–1.6 (PE, CH_2), 0.8 (PE, CH_3). FTIR (KBr pellet): 1637 cm^{-1} ($\nu_{C=O}$).

Preparation of 1-Phenyl-1-(1′-pyrenyl)polyethylene (2). This diarylmethyl-terminated polyethylene oligomer was prepared from a lithiated polyethylene oligomer as described previously.[14] The product was analyzed using variable temperature ^1H NMR spectrum at 105 °C both with and without an internal standard ($Cl_2CHCHCl_2$) for molecular weight determination ^1H NMR spectrum (toluene-d_8): δ 7.1–7.6 (m, phenyl), 7.8–8.3 (m, pyrenyl), 5.2 (t, methine), 1.2–1.9 (m, CH_2), 1.05 (t, CH_3). Using the integrations for the doublet at δ 8.25 (1H) and the methyl signal at δ 0.9, the percentage functionalization was calculated to be 76%. Using the integrations of an internal standard ($Cl_2CHCHCl_2$) and the methylene region of the oligomer, the molecular weight (M_n) of the oligomer was calculated to be ≈2045 g/mol. The oligomer also exhibited a characteristic pyrene fluorescence spectrum.

Preparation of Coentrapped Polyethylene Films Containing Both a Fluorophore and a Fluorescence Quenching Agent. To a dry 500-mL round-bottomed flask were added virgin polyethylene, $CH_3(CH_2CH_2)_nCH_2CHPhPy$, $CH_3(CH_2CH_2)_nCH_2CONHCH_2C_6H_4N(CH_3)_2$, and 600 mL of toluene. The relative amounts of the oligomers and virgin polyethylene were varied, depending on the type of film desired. The flask was fitted with a condenser and the solution was refluxed for 1 h. The solution was allowed to cool, and the coentrapped powder was collected by vacuum filtration. The solid was washed with ethanol and then ether and dried in vacuo for 2 days. Various films were prepared by altering the relative amounts of each oligomer, and the percentage of total oligomer in the film. Functionalized films were cast from solution as described below.

Solution Casting of Surface-Functionalized Polyethylene Films. All films were cast by dissolving approximately 0.22 g of the polymer or entrapped oligomer in hot 1,2-dichlorobenzene and then pouring the hot solution into a recrystallizing dish in a well ventilated oven maintained at 135 °C. It was critical that the bottom of the dish be very flat. After 1 h, the dish was removed from the oven and allowed to cool in a desiccator under vacuum. The films were dried in vacuo for at least 24 h before being cut into strips. Great care was taken not to touch the films with anything but clean instruments. The films that were cast were used in subsequent experiments within 1–2 weeks. Fragmentary evidence from studies of films that had stood in sealed vials for longer periods (1–2 months) showed no apparent change in the fluorescence behavior, a result that might be expected given the lack of change in fluorescence for films annealed for 48 h at 60 °C.

General Procedure for the Analysis of Internal Fluorescence Quenching. (Phenylpyrenyl)methyl and dimethylamino cofunctionalized polyethylene films were held in place in a quartz cuvette by a metal yoke. The cuvette was placed in a fluorometer and made immobile by wedging a piece of folded paper between the cuvette and the sample carousel of the instrument. The fluorescence spectra of the films were measured in THF solutions with an excitation wavelength of 343 nm. No special precautions were taken to avoid oxygen quenching during the experiments since control experiments that completely excluded oxygen did not show significant changes in the fluorescence intensity of the suspended films. Specifically, when we rigorously excluded oxygen, there was only a 5% enhancement of the pyrene fluorophore's emissivity. The THF was removed from the cuvette and 10% trifluoroacetic acid in THF was added. The fluorescence spectra of the films were measured over time until there was no longer any increase in intensity. The percentage increase in intensity of the film was recorded as the percentage internal quenching. The acid solution was then removed, and the films were washed twice with THF. Then a 2 M THF solution of **3** was added. The fluorescence of **1** in PE-**1**,**2** was almost totally quenched (ca. 97%). A separate experiment using films containing only PE-**1** likewise showed that **3** was an excellent quenching agent for pyrene in these films.

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