# Fluorescence Studies of Solvent–Polymer Interactions at Surface Functionalized Polyethylene Films

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*Received July 12, 1994; Revised Manuscript Received September 6, 1994®*

ABSTRACT: The effects of solvent on the accessibility and reactivity of an ester-bound fluorophore at a functionalized polyethylene–solvent interface have been studied. Fluorophore-labeled polyethylene surfaces were prepared by blending together a small amount of either a phenylpyrenylmethyl-terminated ethylene oligomer or a pyrene ester-terminated ethylene–ethylene glycol block cooligomer and a 20–200-fold excess of high molecular weight additive-free high-density polyethylene. Solution casting of 1,2-dichlorobenzene solutions of these mixtures generated films containing the pyrene labels. Studies of the $I_1/I_3$ values for these films in a series of solvents, studies of the extent of excimer formation, and studies of quenching of the amine fluorescence by soluble amines that are incompatible in bulk high-density polyethylene all suggest that the fluorophores are near or in the solvent–polymer interface. In contrast to soluble pyrene-labeled polymers, the extent of excimer formation for surface-bound pyrene labels was greatest with good solvents. Short grafts where the pyrene label was attached either at the graft origin or at the graft terminus produced significantly different behavior for the pyrene fluorophore label.

Surface modification of polymers is important technologically and as a fundamental research problem.[1–3] Such chemistry has received increasing attention in the last few years because of the potential of such chemistry. For example, surface modification of polymers is often carried out to affect properties like permeability or adhesion.[4,5] Polymer surface chemistry also affects a polymer's hydrophilicity and biocompatibility.[6,7] In this paper, we describe ways pyrene labels can be used to study solvation changes that occur at surface-functionalized polyethylenes.

It is well recognized that the chemistry of functional groups located at polymer surfaces can be influenced by the medium the functional groups encounter at the polymer–solvent interface. It is also becoming increasingly apparent that the term "surface" with respect to an organic polymer is ambiguous.[8,9] The definition of what constitutes the "surface" of an insoluble but swellable polymer like polyethylene depends largely on the phenomena one chooses to study and on the experimental conditions of the determination. For example, water contact angles respond to functional groups in the top 5 Å of an otherwise hydrophobic polymer or hydrophobic substrate.[10] X-ray photoelectron spectroscopy (XPS) detects groups in the outermost 50–100 Å of a surface.[11,12] However, both of these assays involve chemistry where relatively well-defined phase boundaries are present. The situation is less clear for an organic polymer suspended in an organic solvent. For a polymer film suspended in a solvent, we would define the polymer surface as consisting of a solvent–polymer interfacial region where bound functional groups can interact with solvent or reagents in solution. The depth of this interface would depend on how the solvent interacts with the polymer and with the functionalized interface. The interface could be different for each solvent. The depth of this interface would also depend on the solvent and the structure of the penetrant or reagent. While quantitative estimates of the thickness of the solvated interfacial region where this chemistry can occur are problematic, spectroscopic techniques like fluorescence spectroscopy can provide detailed information about functional group mobility, reactivity, and solvation at such interfaces as shown below.

The surface-functionalized polymers studied in this work were all prepared by entrapment functionalization. Polymer modification by entrapment functionalization is a technique that has been developed in our group to modify polyethylene surfaces with both simple functional groups and grafts.[9,13–16] Entrapment functionalization involves the blending of a short-chain terminally functionalized polyethylene oligomer with high molecular weight high-density polyethylene. Surface spectroscopic studies and contact angle analyses have shown that the oligomers' terminal groups end up predominantly at the functionalized polyethylene–solvent interface in these product entrapment functionalized polyethylene films.[9,13,15–17] The low molecular weight oligomers used in the blending process were synthesized by established methods. Pyrene was introduced at the termini of a block cooligomer of polyethylene–poly(ethylene glycol) as an ester or at the end of a polyethylene chain by quenching a lithiated ethylene oligomer with 1-phenyl-1-(1′-pyrenyl)ethene.[19]

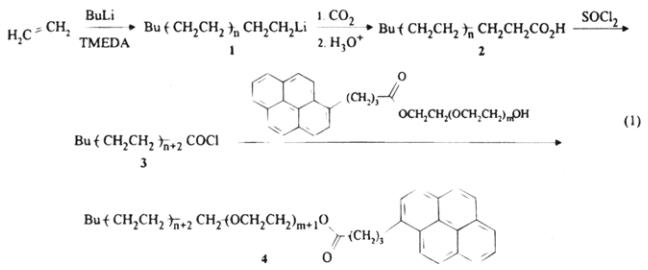
The spectroscopic studies below all use pyrene derivatives. Pyrene derivatives have been widely used to study molecular assemblies like micelles and Langmuir–Blodgett films and functionalized polyethylene surfaces.[20–24] This fluorophore possesses many properties that can be used to study entrapment functionalized polyethylene films. Excimer formation of pyrene labels can be used to measure aggregation of labels, and the extent of excimer formation (the $I_e/I_m$ ratio) has been correlated to the mobility of the pyrene.[20,21,23,24] Pyrene polarization likewise measures the mobility of these labels.[22] The polarity of a pyrene label's microenvironment can be probed by measuring the peak ratios of the first and third peak ($I_1/I_3$) in pyrene's vibronic emission spectrum.[23] Finally, the extent to which a quencher interacts with pyrene can be used to obtain information about diffusion rates and accessibility of a pyrene group at the polymer–solvent interface.[23,24] All these techniques have been used to obtain information about the interface swelled by the solvent in contact with the entrapment functionalized polymer film.

® Abstract published in *Advance ACS Abstracts,* November 1, 1994.

0024-9297/94/2227-7294$04.50/0 

## Results and Discussion

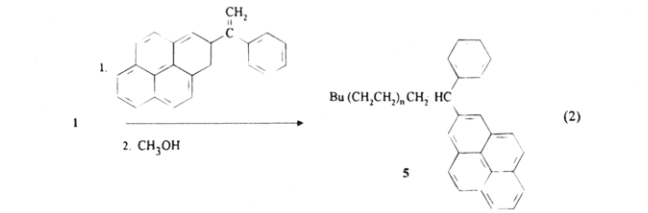
The oligomers used in the present study were synthesized by anionic oligomerization of ethylene initiated by *n*-BuLi–TMEDA.[18] Spectroscopic labels were attached via terminal functional groups. In the case of the block cooligomers of polyethylene and poly(ethylene glycol), the pyrene label was coupled to the block cooligomer via an ester bond. The necessary monopyrene derivative of poly(ethylene glycol) was obtained by reaction of the acid chloride of pyrenebutyric acid with excess poly(ethylene glycol). This monoester was then reacted with the acid chloride **3** to cap the other end of the poly(ethylene glycol) with a polyethylene chain as shown in eq 1. $^1$H NMR spectroscopy at 105




(1)

°C in toluene-$d_8$ was used to calculate the loading and the molecular weight of these dicapped fluorescent labeled oligomers using an internal standard. Typically these oligomers had a molecular weight of ca. 2100.

Pyrene-terminated oligomers were also obtained by quenching the living oligomer **1** with 1-phenyl-1-(1′-pyrenyl)ethene.[14,19] Subsequent protonation with methanol yielded the pyrene-capped oligomer as shown in eq 2. The oligomers synthesized thus had a $M_n$ of 1800 with 55% of the chains functionalized.




(2)

The pyrene-terminated oligomers prepared by either eq 1 or 2 were used to modify virgin polyethylene by entrapment functionalization.[13] In this entrapment functionalization process, a known amount of the pyrene functionalized cooligomers **4** or **5** was codissolved with high molecular weight high-density polyethylene at 105 °C in toluene. Cooling the solution precipitated the entrapment functionalized powder, and solution casting yielded films in which the pyrene labels were located at or near the surface (Figure 1). With block cooligomers as modificants, 0.5–5 wt % loaded entrapped powders were typically prepared. Studies with phenylpyrenylmethyl-terminated oligomers used powders that had ≤1.5 wt % loading of **5**. These powders were stored and used as needed in casting films from solutions of 1,2-dichlorobenzene at 135 °C. Steady-state fluorescence spectra of the resulting entrapment functionalized cast films were taken after the films had equilibrated in a specific solvent for ca. 2 h. Information about excimer formation and $I_1/I_3$ ratio as a function of solvent were obtained from this steady-state analysis. Quenching studies were performed by adding a quencher into the cuvette containing the film. Fluorescence spectra were recorded after the quenching agent was

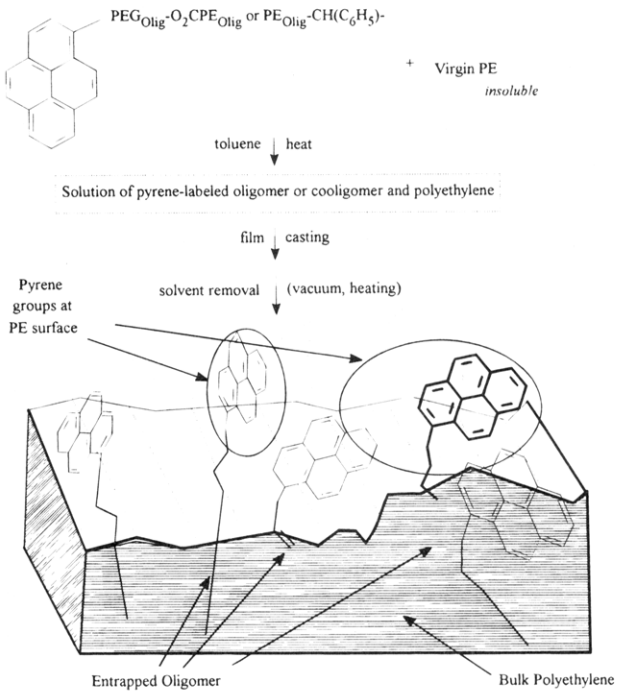



**Figure 1.** Schematic drawing of the entrapment functionalization process leading to pyrene-labeled polyethylene with pyrene groups distributed either as pyrene butyrate terminated $PE_{Olig}CO_2$–$PEG_{Olig}$ ester or as $PE_{Olig}$–CH(Ph)pyrene-terminated ethylene oligomers.

in contact with the film for at least 1 h. Experimental variables such as the weight percent loading of the oligomer as well as changes in the molecular weight of the poly(ethylene glycol) portion of the oligomer were examined. In the case of 1-phenyl-1-(1′-pyrenyl)ethene-terminated oligomers, poly(methacrylonitrile) was anionically grafted onto these oligomers once they were entrapped into the host high-density polyethylene. These grafting experiments used *n*-BuLi to generate a reactive lithiated surface to which a solution of methacrylonitrile was added.[14] Fluorescence spectra of the polymer film were then recorded before and after grafting, to study the changes induced in the pyrene groups due to surface grafting.

## Excimer Formation in Functionalized Films

Excimer formation is due to the interaction of an excited pyrene species with a pyrene molecule in its ground state. The interaction between the excited pyrene species and the pyrene in its ground state is both orientation and distance dependent. The required interplanar distance is about 3.5 Å.[23] Excimer formation in pyrene-labeled films was detected by the presence of a broad featureless band attributed to excimer fluorescence centered at 477 nm. None of the 1-phenyl-(1′-pyrenyl)-terminated polyethylene oligomers showed any excimer formation. However, they were all lightly loaded (≤1.5 wt %). Likewise the lightly loaded 0.5 wt % films of PE–($PE_{Olig}$–$PEG_{Olig}$–pyrene) did not show any excimer formation in the dry state or in the presence of solvents. The higher loaded (2–5 wt %) films, however, showed a small amount of excimer even in the dry state. A substantial increase in excimer formation in these cases occurred when these films were placed in a solvent. A plausible explanation of this effect would be that the solvent diffuses into the film and permits movement of these fluorescent groups leading to excimer formation.

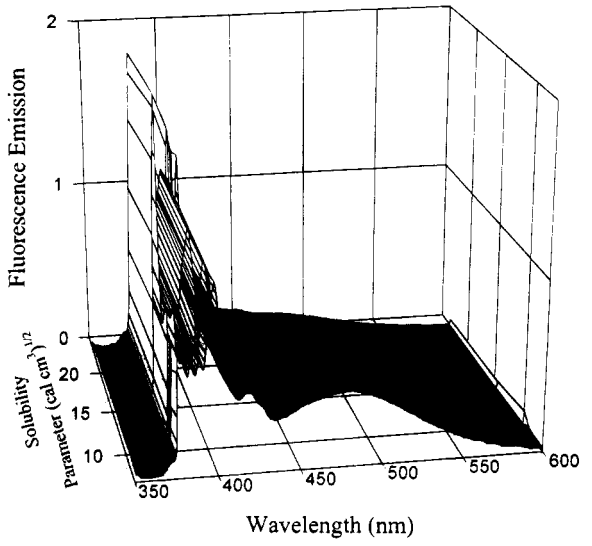



**Figure 2.** 3D plot of emission spectra of polyethylene films functionalized with 2.5 wt % pyrene (PE–($PE_{Olig}$–$PEG_{1000}$–pyrene)) suspended in different solvents showing a decrease in the excimer fluorescence for poorer solvents (solvents with higher solubility parameters).

The effect of solvents on the fluorescence spectra of a 2.5 wt % loaded PE–($PE_{Olig}$–$PEG_{1000}$–pyrene) film suspended in different solvents is shown in the 3D plot in Figure 2. In this plot, the fluorescence emission is plotted versus wavelength and suspending solvent's solubility parameter. The solvent's solubility parameter is most commonly used as an estimate of the ability of a solvent to dissolve a polymer.[25] The magnitude of this parameter depends on the structure of the solvent, hydrogen bonding interactions of the solvent, and other intermolecular forces. When the solubility parameter of the solvent matches that of the insoluble polymer, swelling should be maximized. Polyethylene (PE) has a solubility parameter of 8.3 $(cal/cm^3)^{1/2}$. Poly(ethylene glycol) (PEG) has a solubility parameter of 9.8 $(cal/cm^3)^{1/2}$. A solvent whose solubility parameter matches that of PE or PEG would not necessarily actually dissolve the polymer film at 25 °C. However, such a solvent should swell the polymer and the functionalized interface. Such swelling would increase entrapped polymer chain mobility and would permit the pyrene end groups of the chains to interact. This would lead to the observed increased excimer formation. Interestingly, this is the opposite of what would be expected for an end-labeled soluble polymer. In a dilute solution of a polymer in a good solvent, the polymer chain is in its extended form and the chain ends interact minimally to give a low excimer to monomer ratio. In a poor solvent, however, the polymer is in a coiled form, permitting better interaction with the chain ends and more excimer emission.[26] In a functionalized surface, however, the chains are constrained in absence of a solvent due to the lesser volume available for mobility. As the solvent swells the interface, the mobility of the terminal groups permits interaction and excimer formation. As the solubility parameter of the solvent deviates from that of the polymer, less swelling is reflected in less amount of excimer being formed. This is observed in Figure 2 where the excimer peak at 477 nm decreases in intensity for solvents that are poor solvents for the functionalized surface.

Films containing oligomers with pyrene ester terminated block cooligomers had an $I_e/Im$ ratio that varied with the size of the PEG group and with the solvent in the case of the cooligomer containing the $PEG_{1000}$ group. Specifically, while a 5 wt % PE–($PE_{Olig}$–$PEG_{600}$–pyrene) film had a relatively constant $I_e/I_m$ ratio of 0.2–0.3, a 5 wt % loaded PE–($PE_{Olig}$–$PEG_{1000}$–pyrene) film had a $I_e/I_m$ ratio that varied from 0.28 to 0.71 depending on solvent. In this latter case, the $I_e/I_m$ ratios were highest with a solvent whose solubility parameter matched that of the PEG group. The greater amount of excimer formation in the PE–($PE_{Olig}$–$PEG_{1000}$–Pyrene) film versus the 5 wt % PE–($PE_{Olig}$–$PEG_{600}$–pyrene) film is in agreement with our earlier study that showed that greater surface segregation was seen in entrapment of block cooligomers with larger PEG groups.[16] The greater sensitivity to solvent of the PE–($PE_{Olig}$–$PEG_{1000}$–pyrene) film also suggests that surfaces with larger poly(ethylene glycol) groups are more responsive to solvent.

## $I_1/I_3$ Measurements in Pyrene Functionalized Films

The steady-state emission spectra of pyrene and its derivatives have fine vibronic bands. The first singlet absorption corresponding to peak $I_1$ in pyrene is symmetry forbidden but is allowed in pyrene derivatives. Of more interest to this work is the fact that the intensity of the $I_1$ band is affected by solvents. Specifically, the $I_1$ band shows significant intensity enhancement in polar solvents because the dipole moment of the excited state for this transition is different from its ground state leading to solvation effects. Consequently, the emission maxima and yield depend on the polarity of the solvent. On the other hand, the $I_3$ peak is a peak that shows little variation in intensity with solvent. While a detailed interpretation of the magnitude of the $I_1/I_3$ ratio is complicated due to intricate solute–solvent interactions, this peak ratio has been used as a measure of the environmental micropolarity of a pyrene label. Changes in this intensity ratio also provide information about the medium in the vicinity of the pyrene in these functionalized films.[23]

While changes in the $I_1/I_3$ ratio are useful in the case of these surface-functionalized films, there are significant differences from similar studies in solution. A principle difference is that the $I_1/I_3$ ratios measured for these pyrene functionalized films suspended in solvents are composite ratios. They are the composite of the distribution of pyrene groups that was schematically illustrated in Figure 1. Simplistically, some pyrene moieties in these films are affected by solvent and some are not. The former pyrene groups $I_1/I_3$ ratio will change with solvent. The latter group's $I_1/I_3$ ratio would not. More realistically there is probably a continuum of effects ranging from one of these extreme conditions to the other.

The effect of solvents on this $I_1/I_3$ ratio for two comparably loaded films containing either a PE–($PE_{Olig}$–$PEG_{1000}$–pyrene) or a PE–($PE_{Olig}$–$PEG_{600}$–pyrene) block cooligomer is shown in Figure 3 as a function of solvent polarity as measured by the solvent dielectric constant. In both cases, the $I_1/I_3$ ratio increased to a higher value for more polar solvents. The magnitude of this higher value depended on the type and molecular weight of the entrapped oligomer. The magnitude of this change was attenuated for lower molecular weight PEG groups and for the phenylpyrenylmethyl-terminated entrapped oligomers and is in qualitative agreement with the premise that larger PEG blocks favor surface functionalization of the entrapment functionalized solvent-cast films.[16]

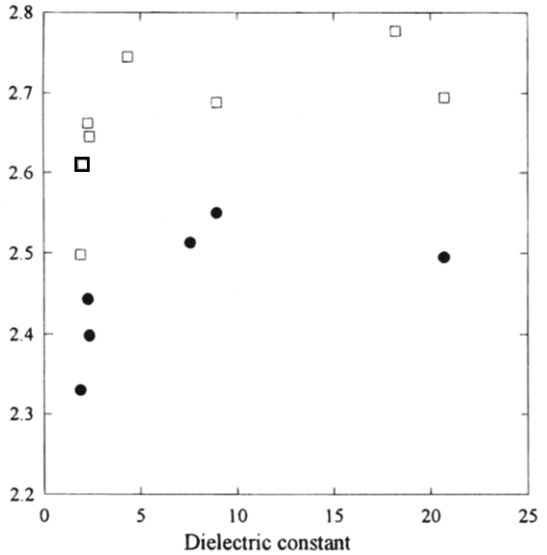



**Figure 3.** Effect of swelling solvents on the $I_1/I_3$ ratio for films entrapment functionalized with $PE_{Olig}$–$PEG_{Olig}$–pyrene block cooligomers containing different sized $PEG_{Olig}$ groups (●, PE–($PE_{Olig}$–$PEG_{2000}$–pyrene) block cooligomer; ○, PE–($PE_{Olig}$–$PEG_{600}$–pyrene) block cooligomer).

The $I_1/I_3$ ratio could also be correlated with the Lippert function $\Delta f$ which is given by eq 3.[27,28] A

$$\Delta f = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1) \qquad (3)$$

roughly linear correlation between $I_1/I_3$ and the Lippert function was seen for all entrapment functionalized films analyzed. A similar correlation of the Lippert function in the case of pyrenebutyric acid and for pyrene labels in self-assembled monolayers has been used previously as a measure of the polar environment of pyrene.[28,29]

Comparison of these values for the Lippert function and $I_1/I_3$ for two different loadings of a $PE_{Olig}$–$PEG_{400}$–pyrene film, a $PE_{Olig}$–$PEG_{2000}$–pyrene film, a $PE_{Olig}$–CH(Ph)pyrene film, and a $PE_{Olig}$–C(Ph)pyrene-*g*-poly(methacrylonitrile) film provided additional insights into the character of these functionalized solvated surfaces. These results are shown in Figure 4. The results show distinct differences between a 0.5 and a 5.0 wt % loaded $PE_{Olig}$–$PEG_{400}$–pyrene functionalized film. These data show that the more lightly loaded film containing 0.5 wt % block cooligomer had a higher $I_1/I_3$ ratio than the higher 5 wt % loaded film. While this may not seem to be the expected result, it actually agrees with our prior work with entrapment of simple $PE_{Olig}$–$PEG_{Olig}$ block cooligomers that showed a greater percentage of a more surface functionalized material at low loadings of the cooligomer.[16] Essentially what this shows is that a greater percentage of the pyrene groups in the lightly loaded film are in a more polar environment than was true for a film with the 5 wt % loading. Likewise, for a given loading, a larger PEG group in the block copolymer led to more surface functionalization. Finally, the pyrene groups of the entrapped $PE_{Olig}$–CH(Ph)pyrene oligomers are not as exposed to the changing solvent environments as are the pyrene groups of the entrapped $PE_{Olig}$–$PEG_{Olig}$–pyrene block cooligomers. Moreover, grafting (*vide infra*) of a short poly(methacrylonitrile) chain (degree of polymerization of ca. 60) onto the $PE_{Olig}$–CH(Ph)pyrene significantly changes the relationship between $I_1/I_3$ and the Lippert function.

The films containing $PE_{Olig}$–$PEG_{Olig}$ block cooligomers are in effect surface-grafted films with pyrene labels at

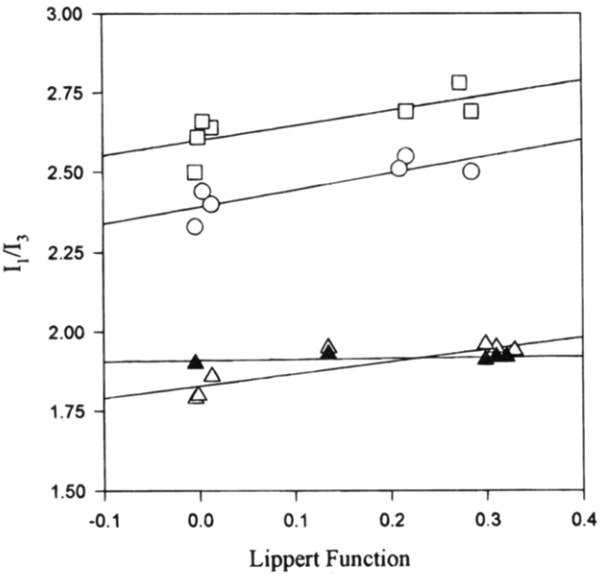
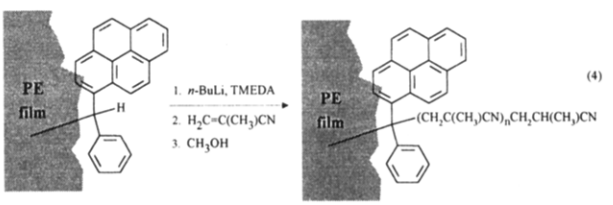



**Figure 4.** Plot of the Lippert function ($\Delta f$) of a group of solvents versus $I_1/I_3$ of various entrapment functionalized high-density polyethylene films; 0.5 wt % $PE_{Olig}$–$PEG_{400}$–pyrene in polyethylene (□), 5 wt % $PE_{Olig}$–$PEG_{400}$–pyrene in polyethylene (○); 1 wt % $PE_{Olig}$–CH(phenyl)pyrene in polyethylene (△), and $PE_{Olig}$–C(phenyl)pyrene-*g*-poly(methacrylonitrile) in polyethylene (▲).

the terminus of the polyethylene incompatible poly(ethylene glycol) graft. An alternative labeling situation would have the pyrene labels at the locus of the surface graft. We have prepared such a surface using the phenylpyrenylmethyl groups as initiator groups for anionic grafting as described previously. Using *n*-BuLi, we deprotonated the weakly acidic C–H. After removing any excess *n*–BuLi, a 4 M THF solution of methacrylonitrile was added to yield a poly(methacrylonitrile) graft with an approximate degree of polymerization of 60 (eq 4).




Unlike the $PE_{Olig}$–$PEG_{Olig}$ block cooligomer functionalized films discussed above, the film formed by the reaction in eq 4 had a layer of methacrylonitrile groups that could inhibit solvation and accessibility of the pyrene groups on the functionalized polyethylene surface. The consequence of this is illustrated by the data in the plot shown in Figure 4 and is reiterated by the results shown in Figure 5. Figure 5 shows the variation of the $I_1/I_3$ ratio with solvent before and after grafting. It illustrates the difference between a film where pyrene is the terminus versus the locus of a surface graft copolymer. Here the ungrafted film behaved similarly to the block coologimer functionalized films in Figure 3 in that the value for the $I_1/I_3$ ratio increased with more polar solvents, leveling off in the case of higher dielectric constant solvents. While the extent of change and the magnitude of the $I_1/I_3$ ratio was not as large as those for the $PE_{Olig}$–$PEG_{Olig}$–pyrene films, both this $PE_{Olig}$–CH(phenyl)pyrene and the $PE_{Olig}$–$PEG_{Olig}$–pyrene films had terminal pyrene groups. In constant, studies with the grafted film showed practically no dependency for

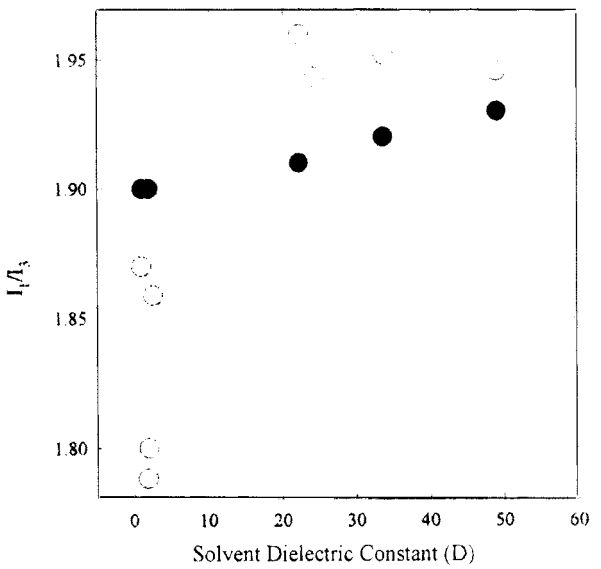



**Figure 5.** Plot of $I_1/I_3$ in different solvents for $PE_{Olig}$–CH(Ph)pyrene functionalized oligomers entrapped in high-density polyethylene before (○) and after (●) anionic grafting with methacrylonitrile showing the comparative lack of a solvent effect on the $I_1/I_3$ ratio after grafting.

the $I_1/I_3$ ratio on the type of solvent chosen for study. The pyrene groups are probably buried in a sheath of PMAN chains and do not interact with solvents. Further confirmation of this scenario was obtained in the quenching studies below wherein the extent of pyrene groups quenched was insensitive to the type of solvent after grafting.

## Anisotropy of Pyrene Fluorescence in Surface-Functionalized High-Density Polyethylene Films

Fluorescence depolarization is a technique that can measure the mobility of pyrene labels.[22,30] Freely rotating groups do not retain any memory of the orientation of the polarized excitation prior to emission. However, in the event of hindered rotation of the fluorophore, emission of light can occur with some degree of correlation with the plane polarized excitation. The extent of polarization is given by the factor $P$ (eq 5). A pyrene

$$P = \frac{I_{VV} - I_{VH}}{I_{VV} + I_{VH}} \tag{5}$$

$I_{VV}$ = emission intensity with vertically polarized excitation and vertically polarized emission

$I_{VH}$ = emission intensity with vertically polarized excitation and horizontally polarized emission

label with no mobility would have a value of $P = 1$, and a totally mobile pyrene would have a value of $P = 0$. Polarization like the $I_1/I_3$ values above should be composite values that reflect a range of different pyrenes, some of which are presumably more sensitive to solvent. The pyrene groups should be the same as those that exhibited excimer formation or a higher value of $I_1$. To avoid the latter problem, we studied polarization using the peak $I_3$. These studies and the values of $P$ measured were not corrected for intrinsic instrument polarization. As expected, higher extents of excimer formation were correlated with lower values of $P$. This trend is shown in Figure 6 for a 2.5 wt % loaded PE–($PE_{Olig}$–$PEG_{400}$–pyrene) film wherein the amount of excimer formed in a particular solvent is plotted as a function of anisotropy

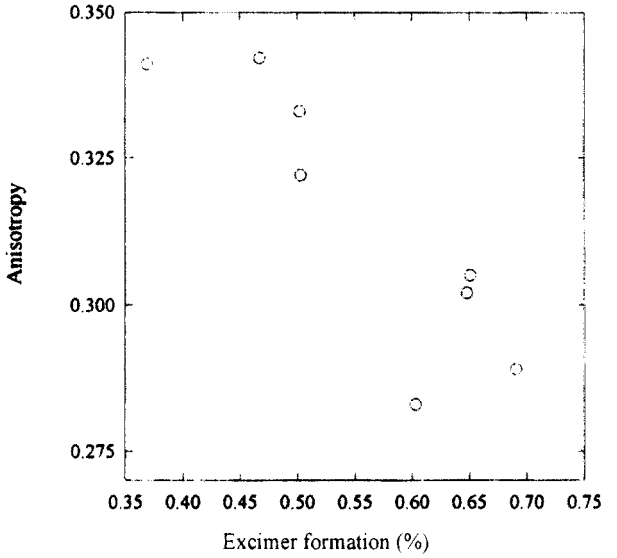



**Figure 6.** Plot of pyrene fluorescence anisotropy as a function of the percent excimer formation for a 2.5 wt % loaded PE–($PE_{Olig}$–$PEG_{400}$–pyrene) functionalized film in various solvents.

in the same solvent. These results agree qualitatively with each other other in that a higher amount of excimer formed corresponds to a lower value of $P$ and vice versa.

## Quenching Studies on Pyrene Functionalized Films

The excited state of a pyrene molecule can be rapidly deactivated in reactions involving suitable quencher molecules.[23,24] Here we have used quenching studies with amines to determine the number of accessible pyrene groups that can interact with the quencher in a given solvent. Different solvents swell polyethylene to different extents, and this quenching process can be crudely related to the depth of the polyethylene–solvent interface. Aromatic and aliphatic amines are efficient quenchers of aromatic hydrocarbons, and they are believed to effect quenching through formation of a charge-transfer complex. Here we used *N*,*N*-dimethylethanolamine as a quencher. This amine was previously used by Weiss to study dopant sites in a covalently modified low-density polyethylene film.[24]

These quenching studies were all performed on polyethylene entrapment functionalized with the phenylpyrenylmethyl-terminated oligomers. Quenching was followed by monitoring the decrease in the intensity of the $I_3$ peak as a function of the quencher concentration. Figure 7 shows the percentage of pyrene groups quenched at increasing concentrations of the quencher for a number of solvents. For all the solvents studied, there was an initial fast drop in the number of groups quenched. The curves then leveled off at a point that depended on both the swelling capability of the solvent and the type of solvent. In prior studies with dansyl-labeled films, we have shown that the fluorophores in such functionalized interfaces reside in three regions.[9] The first region consisted of groups which interacted with the solvent immediately and were in the outermost layer of the film. This was the region rapidly accessed and readily quenched even at low quencher concentrations. A second region was more affected by solvent–polymer interaction. The third region contained groups that were not accessible to a quencher that did not readily permeate into bulk high-density polyethylene.

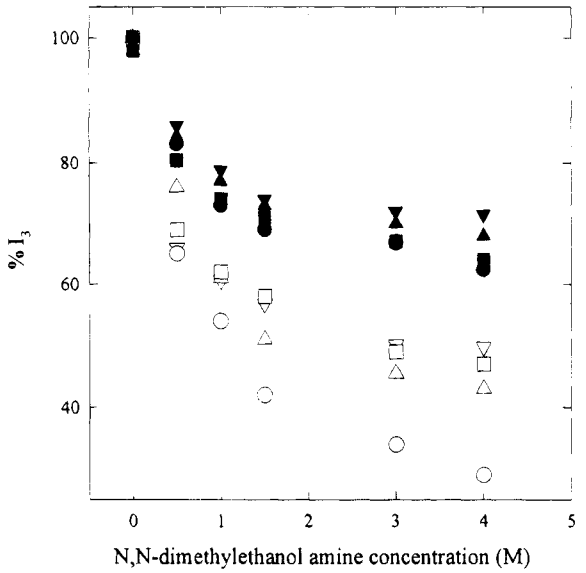



**Figure 7.** Fluorescence quenching of high-density polyethylene films containing $PE_{Olig}$–CH(Ph)pyrene that have been surface grafted with poly(methacrylonitrile) shown by changes in the relative fluorescence intensity of a film before by quenching using various concentrations of dimethylethanolamine in several solvents: ethanol (▽), cyclohexane (□), toluene (△), and THF (○) compared to quenching of the same films before grafting in ethanol (▼), cyclohexane (■), toluene (▲) and THF (●).

In this case, DMEA in THF was the most effective system, quenching about 71% of the fluorophores. This presumably reflected the swelling ability of THF for these interfaces and the modest polarity of THF that could facilitate the quenching process. Effects of changing solvent on the quenching of bound pyrenes were also observed with block cooligomers entrapped in high-density polyethylene. For example, DMEA in methylene chloride quenched about 62% of the groups in a 2.5 wt % loaded PE–$PEG_{1000}$–pyrene film, while a similar methanol solution quenched only 50% of the groups.

Figure 7 also shows that these surfaces allow us to examine the effects of a short graft on pyrene groups that were used as the initiator for the graft. We expected a PMAN graft to decrease the accessibility and extent of quenching of such pyrene groups. Indeed, we had earlier shown that the effects of solvent on the $I_1/I_3$ ratios were appreciably altered by the presence of a graft. After grafting, these ratios were insensitive to the type of solvent in which the grafted films were suspended. Similar behavior was observed in the extent of quenching in Figure 7. The differences seen in the amount of pyrene groups quenched at the high quencher concentration are in accord with the notion that an overlayer of PMAN grafts at least partially hide the pyrene groups and prevent them from interacting with the solvent or soluble reagents.

Quenching should also affect the $I_1/I_3$ ratio since quenched fluorophores are those that can interact with solvent. As noted above, the $I_1/I_3$ ratios we measure here are due to a mixture of fluorophores, some of which interact with solvent and some of which do not. If the ones that interact with solvent are removed from the picture through quenching, the only pyrene groups left would be those that do not interact much with the solvent. Thus, the $I_1/I_3$, ratio would reflect the environment of the remaining unquenched pyrene groups and should decrease. When we examined the $I_1/I_3$ ratio during the quenching process, the ratio dropped as the amount of pyrene quenched increased. This suggested that the unquenched pyrene was in a less polar environment. Indeed, the limiting values of the $I_1/I_3$ ratio when all the accessible groups were quenched by *N,N*-dimethylethanolamine were approximately the same irrespective of the type of solvent in which quenching was done. The fluorescence obtained at this stage is due to the groups buried deeper in the bulk polymer and inaccessible to the solvent and should have been in similar chemical environments irrespective of the solvent used for swelling.

## Conclusion

These fluorescence studies show how fluorescent terminal groups in an entrapment functionalized polyethylene can interact with solvents. They show both parallels and contrasts with the behavior of similar soluble fluorescent labels. Fluorescence spectroscopy, though not a surface spectroscopic technique, provides considerable information about the mobility and accessibility of functional groups in a polymer–solvent interface. Postpolymerization modification through surface grafting is shown to significantly affect these labels and to lead to surfaces whose reactivity contrasts with that of labels whose pyrene groups are located at a graft's terminus versus the graft's origin.

## Experimental Section

Ethylene and carbon dioxide were obtained from Matheson Co. Other chemicals and reagents were obtained from Aldrich Chemical Co. Hydrocarbon solvents were distilled under nitrogen from a purple solution or suspension of benzophenone and sodium prior to use. Other solvents were reagent grade and generally used without further purification. *N,N,N',N'*-Tetramethylethylenediamine was distilled from potassium metal and stored under nitrogen until use. Ethylene was reagent grade and was not further purified. All glassware was dried in an oven at 130 °C prior to use. Syringes were used to transfer water- and air-sensitive reagents. All polymer films were cast in an explosion-proof Friction-Aire oven maintained at 135 °C. Transmission infrared spectra of polymer powders were taken using thin translucent disks prepared by a pressed-disk technique. IR spectra were recorded on a Mattson Galaxy 4021 FT-IR spectrometer at room temperature at a resolution of 2 $cm^{-1}$. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Gemini 200-MHz NMR spectrometer or on a Varian XL-200 spectrometer. High-temperature NMR was recorded at 105 °C to maintain the polymer in solution. Chemical shifts are reported in ppm relative to HMDS. Number-average molecular weights of the oligomers were determined by $^1H$ NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard. Steady-state fluorescence spectra were recorded using a SLM Aminco SPF-500C spectrofluorometer. The excitation slit width was typically 4 nm, and the emission slit width was 2 nm. Other instrument parameters such as the voltage level or gain were kept constant through a set of experiments but were varied according to the requirements of the sample. Values for intensities of the $I_1$ or $I_3$ peak were calculated using the maxima for the peaks in each relevant spectrum. The high molecular weight high-density polyethylene used was obtained from Allied Corp. This polymer had an average molecular weight between $1.8 \times 10^5$ and $2 \times 10^5$. Any additives or impurities were removed from the polymer be repeatedly dissolving the polymer in fresh solvent and precipitating it at least six times prior to use. Poly(ethylene glycol)s were obtained from Aldrich Chemical Co. and used without further purification. The $M_n$ values of poly(ethylene glycol) were confirmed using $^1H$ NMR spectroscopy and end-group analysis.

**Preparation of Lithiated Ethylene Oligomer (1).** A dry 500-mL Fischer-Porter presure bottle equipped with a magnetic stirring bar was connected to a multiple-use (vacuum, nitrogen, and ethylene) pressure line through a pressure

coupling. This bottle was then evacuated and purged with nitrogen three times. Dry heptane (250 mL), 9.2 mL of 1.6 N *n*-butyllithium in hexane, and 2 mL of *N,N,N′,N′*-tetramethylethylenediamine were added successively by syringe. The bottle was pressurized with ethylene to 30 psig, and the oligomerization was carried out at this pressure. The reaction was continued for ca. 60 h after the lithiated ethylene oligomer precipitated.

**Preparation of Carboxyl-Terminated Ethylene Oligomer.** The suspension of the intermediate lithiated ethylene oligomer in heptane was cooled to −78 °C using a dry ice−acetone bath. Any ethylene in the reactor was removed, and dry $CO_2$ was introduced. The resulting suspension was then allowed to stir under 30 psi of $CO_2$, while the reaction mixture was warmed to room temperature. After stirring at room temperature for several hours, the product suspension was poured into 10% HCl. Filtration through a coarse fritted funnel yielded the crude product as a white powder. The product was placed in a jacketed Soxhlet extractor and extracted with hot toluene for 2 days. Extraction was facilitated by attaching a Dean−Stark trap to the apparatus to remove any water (from the HCl). The final product was recovered by cooling the hot toluene solution to precipitate the carboxyl-terminated oligomer. Filtering and vacuum drying yielded the final product (mp 120−124 °C). Esterification of this product with methyl alcohol and $^1$H NMR spectroscopic analysis of the ester indicated that the efficiency in carboxylation was about 61% and that the $M_n$ was 2250. The product carboxyl polymer had a distinctive carbonyl peak at 1710 cm$^{-1}$. On esterification the $\nu_{C=O}$ shifted to 1735 cm$^{-1}$. Prior work has shown that any contamination with the ketone byproduct (from the carboxylation) was evident at this point by the presence of a residual peak at 1705 cm$^{-1}$.[18]

**Preparation of the Mono(pyrenebutyryl ester)Derivative of Poly(ethylene glycol) (5).** Pyrenebutyric acid (0.5 g) was dissolved in benzene, and an excess of thionyl chloride (ca. 3 mL) was added. The mixture was refluxed for about 3 h and then cooled. The solvent was removed on a rotovap, and the solid residue was analyzed by IR spectroscopy to confirm that complete conversion of the carboxylic acid to the acid chloride had occurred. A 50-mL $CH_2Cl_2$ solution of a 10 mol excess of the poly(ethylene glycol) was prepared in a separate flask, and 200 mL of a $CH_2Cl_2$ solution of this acid chloride was then added dropwise to the poly(ethylene glycol) solution over a period of 1 h at 25 °C. The mixture was further stirred for about 2 h after the addition was complete and worked up by washing once with water, twice with 50 mL of saturated sodium bicarbonate, and then three times with 50-mL aliquots of distilled water. When necessary, a small amount of sodium chloride was added to effect a better solvent separation. The organic layer was dried over magnesium sulfate, and the solvent was removed to yield the product: IR (thin film) 3500, 3027, 2920, 2874, 1735, 1604, 1495, 1461, 1380, 1105, 710 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 8.1 (br), 4.15 (t), 3.38 (t), 2.5 (t), 2.2 (t), 3.65 (br). The purity of the monofunctionalized product was assayed by NMR spectroscopy by comparing of the integrals of the ester peak at $\delta$ 4.15, the methylene protons adjacent to the oxygen in the PEG chain (d 3.65), and the protons from pyrene. For example, a monopyrene derivative of PEG of molecular weight 400 had a ratio of 9:2:2:2:2:34 for the peaks at $\delta$ 8.1, 4.15, 3.38, 2.5, 2.2, and 3.65.

**Preparation of Polyethylene−Poly(ethylene glycol)−Pyrene.** The carboxylic acid terminated polyethylene oligomer (0.5 g) was placed in a 250-mL flask along with 100 mL of toluene. About 1 mL of thionyl chloride was added, and the solution was refluxed for 3 h. The solution was cooled, and the oligomer that precipitated out was isolated. IR spectroscopy confirmed conversion of the acid to the acid chloride (IR 1780 cm$^{-1}$). After addition of fresh toluene and the mono(pyrenebutyric ester) of poly(ethylene glycol), the solution was refluxed for 3 h. At that point, cooling precipitated the difunctionalized poly(ethylene glycol) **4**. Washing first with methanol and then with ether followed by vacuum drying yielded $PE_{Olig}$−$PEG_{Olig}$−pyrene block cooligomer: IR (KBr pellet) 3027, 2920, 2874, 1735, 1604, 1495, 1472, 1462, 1380, 1369, 1105, 730, 720 cm$^{-1}$, $^1$H NMR (105 °C, C-$D_8$) $\delta$ 0.9 (t), 1.4 (br s), 3.65 (br), 4.15 (t), 8.1 (br), 3.38 (t), 2.5 9t), 2.2 (t).

**Preparation of 1-Phenyl-1(1′-pyrenyl)polyethylene.** The suspension of oligomer **1** in heptane was allowed to settle. Then ethene was shut off, and the flask was pressurized to 10 psig with nitrogen. Any unreacted ethene and as much heptane as possible was removed by forced siphon. The 1-phenyl-1(1′-pyrenyl)ethene (1.5 equiv)[19] in 250 mL of THF was added. The resulting suspension was stirred for 52 h at −78 °C. The reaction mixture gradually changed from dark blue to black. The suspension was then transferred into a flame-dried 1000-mL round-bottomed flask under a constant flow of argon. The flask was quickly sealed, and the reaction was refluxed for 24 h under argon. The reaction mixture was quenched by addition of methanol. The solid was collected by filtration, washed with ethanol and ether, and then extracted with hot toluene using a Soxhlet apparatus. The extracted oligomer was again collected by filtration. The oligomer was then dissolved in hot toluene. The toluene was then cooled until the oligomer fell out of solution. The dissolution and precipitation process was repeated twice more in fresh toluene. The final precipitate was washed again with ethanol and ether and dried in vacuo for at least 24 h before any subsequent analysis. The product oligomer was characterized by $^1$H NMR spectroscopy (toluene-$d_8$ at 105 °C); $\delta$ 7.1−7.6 (m, phenyl), 7.8−8.3 (m, pyrene), 5.2 (t, CH), 1.2−1.9 ($CH_2$), 1.05 (t, $CH_3$).

**Grafting Reactions onto an Entrapment-Functionalized Surface.** The entrapped film (1 cm$^2$) was placed in a flame-dried 50-mL centrifuge tube that had been flushed with argon. The tube was sealed with a septum, and the tube was again gently flame-dried under an argon flow. The tube was placed under a positive pressure of argon and 15 mL of THF, freshly washed with lithiated Merrifield resin,[31] was added. Washing with THF that had been passed over a lithiated polymer ensured that the solvent was water- and oxygen-free. The centrifuge tube containing the film then cooled to 0 °C, and TMEDA (1.1 mmol) was added followed by 1.6 N *n*-BuLi (1 ml) to yield a ca. 0.04 N solution. The suspension was placed on a mechanical shaker and shaken for 30−120 min. The solution above the film was removed via a cannula. The faint pinkish film was then washed with oxygen- and water-free THF (5 mL) twice. Then a 4 M solution of methacrylonitrile in THF (30 mL) was added. The resulting suspension was then mechanically shaken for 8 h, at which point the polymerization was quenched by the addition of methanol. The film was removed and washed with acetone, ethanol, petroleum ether, and then ether. The film was then extracted with hot acetone using a Soxhlet apparatus for 6 h. The collected film was rinsed with acetone and then ether and finally dried in vacuo for 3 days.

**General Procedure for Entrapment Functionalization.** In a typical procedure, 100 mg of the pyrene-containing oligomer, 10 g of host high-density polyethylene, and 250 mL of toluene were placed in a 500-mL round-bottomed flask equipped with a magnetic stirring bar. After heating the suspension to 110 °C using an oil bath, a solution formed. The solution was stirred for 1 h at this temperature, and the oil bath was removed. After cooling to 25 °C, the mixture of polyethylene and the cooligomer which precipitated was recovered by filtration, washed with 150 mL of toluene, and dried under reduced pressure for 24 h. Similar procedures were used to prepare other loadings of the block cooligomer in polyethylene by varying the quantity of high-density polyethylene and the functionalized oligomer as desired.

**Preparation of Entrapment-Functionalized High-Density Polyethylene Films.** Films were cast by dissolving ca. 0.2 g of the entrapped oligomer in hot 1,2-dichlorobenzene. This solution was then poured into a hot flat-bottomed dish that was placed in a 135 °C explosion-proof Friction-Aire oven. The dish was covered with a plane of glass, and the solvent was allowed to evaporate over a period of about 1 h. The dish was removed from the oven and allowed to cool to room temperature in a dessicator under vacuum. Films were then placed in a vacuum oven maintained at 155 °C (0.05 Torr) for 30 min. Under these conditions, the polymer melted and the last traces of the solvent were removed. The polymer was

peeled off the glass dish, cut into rectangular strips, and analyzed. The absence of the casting solvent in the product film was verified by the absence of the strong aromatic and C–Cl stretches observed in dichlorobenzene in IR spectroscopy.

**Acknowledgment.** Support of this work by the National Science Foundation (Grant DMR-9308414) is gratefully acknowledged.

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