a century ago: Green, A. G.; Woodhead, A. E. *J. Chem. Soc., Trans.* **1910,** *97,* 2388.
(9) Wei, Y.; Focke, W. W.; Wnek, G E.; Ray, A.; MacDiarmid, A. G. *J. Phys. Chem.* **1989,** *93,* 495. Leclerc, M.; Guay, J.; Dao, L. H. *Macromolecules* **1989,** *22,* 649.
(10) MaCinnes, D., Jr.; Funt, B. L. *Synth. Met.* **1988,** *25,* 235. Manohar, S. K.; MacDiarmid, A. G.; Epstein, A. J. *Bull. Am. Phys. Soc.* (Abstract) **1989,** *34*(3), 583.
(11) MacDiarmid, A. G.; Chang, J. C.; Richter, A. F.; Somasiri, N. L. D.; Epstein, A. J. In *Conducting Polymers*; Alcacer, L., Ed.; D. Reidel Publications: Dordrecht, Holland, 1987.
(12) Wei, Y.; Tang X.; Sun, Y.; Focke, W. W. *J. Polym. Sci., Polym. Chem. Ed.* **1989,** *27,* 2385.
(13) Wei, Y.; Sun, Y.; Tang, X. *J. Phys. Chem.* **1989,** *93,* 4878. Wei, Y.; Sun, Y.; Patel, S.; Tang, X. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1989,** *30*(1), 228.
(14) Wei, Y.; Jang, G.-W.; Hsueh, K. F.; Hariharan, R.; Patel, S.; Chan, C. C.; Whitecar, C. *Polym. Mater. Sci. Eng.* **1989,** *61,* 905.
(15) Reynolds, J. R.; Poropatic, P. A.; Toyooka, R. L. *Macromolecules* **1987,** *20,* 958.
(16) Focke, W. W.; Wnek, G. E.; Wei, Y. *J. Phys. Chem.* **1987,** *91,* 5813.
(17) Tang, X.; Sun, Y.; Wei, Y. *Makromol. Chem., Rapid Commun.* **1988,** *9,* 829.
(18) Wudl, F.; Angus Jr., R. O.; Lu, F. L.; Allemand, P. M.; Vachon, D. J.; Nowak, M.; Z. X. Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987,** *109,* 3677. Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* **1988,** *24,* 231. Genies, E. M.; Lapkowski, M.; Penneau, J. F. *J. Electroanal. Chem.* **1988,** *249,* 97.
(19) Wei, Y.; Hsueh, K. F.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G., to be submitted for publication.
(20) Hofmann, A. W. *Proc. R. Soc. London* **1863,** *12,* 576. Cox, R. A.; Buncel, E. In *The Chemistry of Hydrazo, Azo and Azoxy Groups*; Patel, S., Ed.; Wiley: New York, 1975; Part 2, p 775.
(21) Breitenbach, M.; Heckner, K. H. *J. Electroanal. Chem.* **1971,** *29,* 306; **1973,** *43,* 267. Genies, E. M.; Lapkowski, M. *J. Electroanal. Chem.* **1987,** *236,* 189; 199.
(22) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975.

Registry No. (Aniline)(*o*-toluidine) (copolymer), 124287-76-9; (aniline)(*m*-toluidine) (copolymer), 124287-77-0; *m*-toluidine, 108-44-1; aniline, 62-53-3; *o*-toluidine, 95-53-4.

Effect of Solvent Polarity on Functionalized Polyethylene–Solution Interfaces

David E. Bergbreiter* and Marc D. Hein

Texas A&M University, Department of Chemistry, College Station, Texas 77843.
Received May 1, 1989; Revised Manuscript Received August 16, 1989

ABSTRACT: Entrapment functionalized films containing dansyl fluorescent labels were prepared and changes in the polymer–solution interface were investigated as a function of solvent polarity. Changes in the emission maximum, the extent of fluorescence quenching, and the rate of fluorescence quenching showed that the polymer–solution interface depth varied depending on the polarity of the solvent used. Functional groups in the polymer–solution interface existed in one of three types of chemical environments—the bulk of the polymer where functional groups were unreactive to reagents in solution and in which they did not interact with solvent, an interfacial region where soluble reagents could react with the functionalized polymer to varying extents but in which the reactivity of external reagents was approximately the same regardless of the external solvent, and a highly solvated region where the functional groups acted as if they were in solution and where the polyethylene-bound dansyl were readily accessible to reagents in solution.

Polymer surfaces play an important role in many polymer applications including adhesion, composite formation, biocompatibility, mass transport, and biodegradation.[1-4] Surface modification of preformed polymers is a practical and useful method of altering the surface properties of a polymer without changing the polymer's bulk properties. Examples of this approach for the functionalization of hydrocarbon polymers include the use of chromic[5-11] or nitric acid etching[12] and corona discharge treatments.[13-16] We have previously described an alternative to these chemical procedures in which terminally functionalized ethylene oligomers are entrapped from solutions of such oligomers and additive-free polyethylene to form functionalized polyethylene powders or films.[17,18] This procedure, which we have called entrapment functionalization, has proven to be useful both in preparation of functionalized polyethylenes and as a technique to facilitate the use of homogeneous catalysts.[19-22] One advantage of entrapment functionalization is that we can prepare entrapment functionalized polyethylene films selectively and reproducibly by controlling conditions such as the method of precipitation, the crystallinity of the host polymer, the size of the functional group, the polarity of the functional group, and the extent of branching in the ethylene oligomer.[18] Therefore, consecutive samples may be prepared with similar distributions and concentrations of functional groups. Further, since we have a measure of control over the degree of surface functionalization, we can prepare functionalized polymers that are suitable for probing the solid–liquid interfaces involving polyethylene and organic solvents.

One poorly understood aspect of polymer surface chemistry is the question of exactly what constitutes a polymer surface. Complicating this question are subtle effects such as the degree to which such a surface changes with time, heating, or different chemical environments. The case of a non-cross-linked polymer like polyethylene suspended in various organic solvents is one example of a situation in which the term "surface" is ambiguous. In our prior work we have described this surface as the region

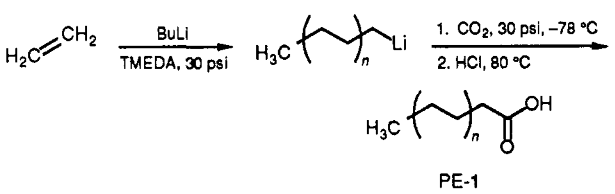
0024-9297/90/2223-0764$02.50/0

or interface in which functional groups bound to the polymer can readily react with solvents and reagents in solution. Such a surface or interface is a much broader phase boundary than the phase boundary encountered in dealing with polyethylene–water interfaces, which Whitesides has studied in some detail.[5–11] Further, different solvents will define different polyethylene–solution interfaces depending upon the solvent's interaction with the functionalized polymer surface. A variety of changes can be envisioned in response to changes in the identity of the suspending solvent such as an increase or decrease in the depth of the interface, a change in the effective viscosity of the interface, an altered reactivity of functional groups versus their reactivity in homogeneous solution or bulk polymer, and a restructuring of the polymer interface. Spectroscopic investigations using ESR,[6,17,18,22] UV–visible,[23–25] and fluorescence[26–28] spectroscopy have proven to be useful methods of probing structural and chemical changes in many polymeric systems and each of these techniques should be useful in studying these solid–liquid interfaces. Solvatochromic shifts in the emission spectra of fluorescent labels in polymers have been used to advantage in prior work to probe both solvation and reactivity.[29–31] Here we describe our initial studies using these same fluorescent probes attached to linear ethylene oligomers (M_n ca. 2000) to examine the effects of organic solvents on functionalized polyethylene films prepared by entrapment functionalization.

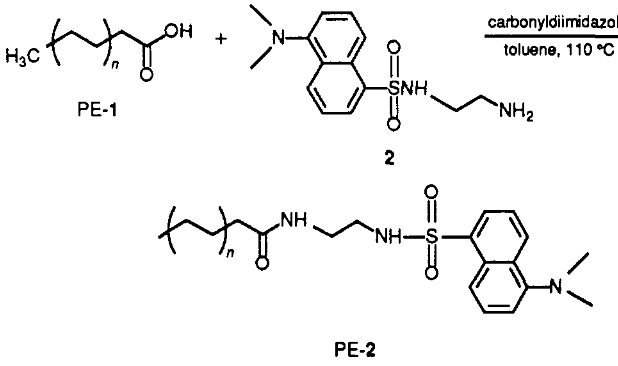
This paper discusses results we obtained using dansyl ([5-(dimethylamino)-1-naphthyl]sulfonyl)-labeled polyethylene films prepared by entrapment functionalization to observe solvent effects upon the accessibility and reactivity of functional groups at polyethylene–solvent interfaces. Our results show that the functional groups exist in an interfacial region that is sensitive to changes induced by the choice of the solvent in which the film is suspended. Kinetic studies of the rate of protonation, the extent of protonation, and the λ_{max} of the emission show that these dansyl groups do not exist in a uniform environment. Our results can be interpreted in terms of the interface being qualitatively divided into three regions. First, the entrapped fluorescent labels are located in a bulk region where they react only slowly if at all with soluble reagents and where solvent interactions with the fluorescent probe are minimal. Second, there is an interfacial region where soluble reagents can react with the functionalized polymer to varying extents but in which the reactivity of external reagents is approximately the same regardless of the external solvent. Third, a portion of the fluorescent groups are located in a highly solvated region where the functional groups react as if they were in solution and where they experience a more solution-like environment.

Results and Discussion

Terminally carboxylated ethylene oligomer (PE-1) was prepared as outlined in eq 1. This strictly linear carboxylated ethylene oligomer was further derivatized to form the dansyl-labeled oligomer PE-2 (eq 2). Dissolution of oligomer PE-2 with a 100-fold excess of additive-free polyethylene (M_w of ca. 190 000, melt index of 0.96) in toluene at 110 °C followed by cooling resulted in coprecipitation of the polyethylene and the dansyl-labeled oligomer to form an entrapment functionalized polyethylene powder containing PE-2. Films (ca. 15 μm thick) of the entrapment functionalized polyethylene were then solvent cast from o-dichlorobenzene solutions of this polymer and fluorescent labeled oligomer.



(1)



(2)

The dansyl-labeled polyethylene films so prepared are indistinguishable from unfunctionalized polyethylene films under room light. Under UV radiation they exhibit a blue-green fluorescence indicative of dansyl labels. Absorbance spectra of the 1% functionalized films were not obtained due to the low concentration of functional groups. However, an absorbance spectrum of the dansyl-labeled ethylene oligomer was identical with that observed for the dansyl-labeled octadecanoic acid and octadecylamine, $C_{17}H_{35}CONHCH_2CH_2NHSO_2C_{10}H_6N(CH_3)_2$ ($C_{17}H_{35}CO$-2) and $C_{18}H_{37}NHSO_2C_{10}H_6N(CH_3)_2$ ($C_{18}H_{37}$NH-DANS). Emission spectra of the dansyl-labeled films were also similar to spectra obtained from $C_{17}H_{35}CO$-2 and $C_{18}H_{37}$NH-DANS. Characteristic shifts in λ_{max} with varying solvent polarity were observed for both soluble analogues and dansyl-labeled films.[29–31]

Qualitatively the shifts in λ_{max} show the dependence of the polyethylene–solution interface upon solvent polarity. Figure 1 shows the changes observed in the emission maxima versus solvent dielectric constant. With soluble analogues a continuous increase in λ_{max} was observed from nonpolar to polar solvent. In entrapment functionalized films, λ_{max} was at 458 nm in cyclohexane suspensions. Similarly, solutions of $C_{18}H_{37}$NH-DANS had a λ_{max} of 449 nm. However, unlike $C_{18}H_{37}$NH-DANS, a maximum was observed in dichloromethane. With solvents more polar than dichloromethane, λ_{max} gradually decreased until a λ_{max} of 458 nm was observed in an aqueous suspension of PE-2. This last value is characteristic of dansyl labels in a nonpolar environment. Whitesides has reported similar but less dramatic changes in λ_{max} with dansyl-labeled polyethylene films prepared by chromic acid etching.[8] Two differences between the two types of films are evident here. Functional groups in entrapment functionalized films exist in a much more nonpolar environment than dansyl labels in etched films as evident by an emission maximum that is as much as 30 nm lower (Table I). This is probably due to the more polar surface of etched films, which could include ketone, aldehyde, and either unreacted carboxylate or ester functionalities. Second, the oxidized films reported by Whitesides are comparatively less sensitive to changes in solvent polarity showing a total shift over the range of solvents used of only 15 nm. Entrapment functionalized films show a greater sensitivity to solvent polarity showing shifts in λ_{max} of approximately 30 nm with the same solvents. Although the emission maxima in Whitesides films started out at much higher wavelengths and were less sensitive

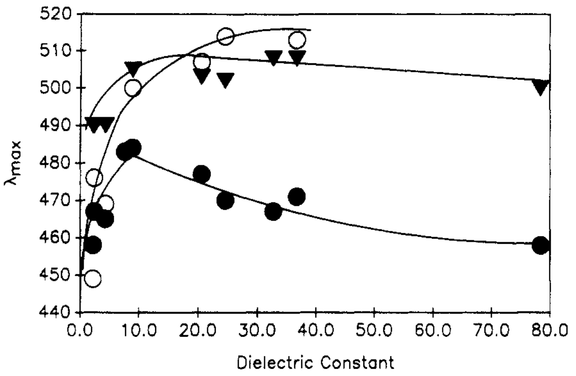


Figure 1. Plot of the observed emission maximum (in nanometers) as a function of the dielectric constant: (○) dansyl-labeled octadecylamine ($C_{18}H_{37}NH$-DANS), (●) dansyl-labeled entrapment functionalized polyethylene film (polyethylene-containing PE-2), (▽) dansyl-labeled etched polyethylene film (from data in ref 8).

Table I
Observed Emission Maxima for Dansyl-Labeled Compounds[a]

solvent	dielectric constant	emission max, nm octadecylamine	entrapped	etched[b]
cyclohexane	2.220	449	458	490
toluene	2.381	476	467	490
diethyl ether	4.335	469	465	490
tetrahydrofuran	7.58		483	
dichloromethane	8.93	500	484	505
acetone	20.56	507	477	503
ethanol	24.55	514	470	502
methanol	32.66		467	508
dimethylformamide	36.71	513	471	508
water	78.39		458	500

[a] Fluorescence spectra were measured at 25 °C with excitation at 350 nm. Values for dielectric constants were taken from ref 33. [b] Reported emission maxima for etched polyethylene films listed by Whitesides in ref 8.

to changes in solvent polarity due to the more polar nature of the etched surfaces, the same qualitative changes were seen in switching from nonpolar to polar solvents.

One feature of dansyl labels is that the fluorescence is readily quenched by acid. We used this to measure the kinetic differences between polyethylene–solution interfaces with different solvents. Two series of related solvents were chosen with differing polarities along with toluene and two chlorinated solvents. The results from these studies, which illustrate the extent to which solvent can affect chemistry at these functionalized polyethylene solution interfaces, are listed in Table II. The experiments were conducted by suspending a film in a solution containing a standard amount of HCl. Acid solutions were prepared by adding equimolar amounts of acetyl chloride and methanol to the appropriate solvent and diluting to the desired volume, except in water, ethanol, butanol, and octanol, in which cases the methanol was omitted. The resulting HCl solution was then added to a cuvette containing the dansyl-labeled film. The extent of quenching was determined by measuring the decrease in fluorescence intensity over a period of approximately 20 h.[32] No loss of fluorescence intensity was seen in control experiments in which HCl was absent.

The plots of I/I_0 (Figure 2) show that the extent of protonation varied depending on the dielectric constant of the solvent used. In the most polar solvent studied, water, 24% of the dansyl groups in the film were protonated. Similar extents of protonation were seen in methanol and ethanol. However, as the solvents became more nonpolar, a significant change in the extent of fluorescence quenching is observed. This is best illustrated by comparing the series of hydroxylic solvents in which the extent of quenching varied from 24% in water to 60% in octanol. Ethers gave rise to the points that do not fit well on the curve shown in Figure 2. While the extent of protonation also varied with solvent in these ethers, the maximum extent of protonation was seen with THF, the most polar ether solvent. In the case of halogenated solvents and toluene, the percent of unreacted dansyl groups was consistently low.

Table II
Extent and Rate of Fluorescence Quenching of Dansyl-Labeled Polyethylene Films[a]

solvent	dielectric constant	$10^{-3}k$, s^{-1}	rel population, %, region 1	2	3	film thickness, μm
hydroxylic solvents						
water	78.39	1.27	7	17	76	14.5
methanol	32.66	2.88	4	26	70	21.5
ethanol	24.55	3.21	3	33	64	9
butanol	17.51	6.81	10	43	47	
octanol	10.37	8.36	6	54	40	28
ethereal solvents						
tetrahydrofuran	7.58	3.31	34	28	38	14
dimethoxyethane	7.20	4.79	34	27	39	14.5
ethyl ether	4.335	6.72	26	24	50	17
butyl ether	3.083	4.20	25	52	23	
hydrocarbon and chlorinated hydrocarbon solvents						
dichloromethane	8.93	7.06	67	24	9	20
chloroform	4.806	22.2	95	5	7	18
toluene	2.381	2.46	42	46	12	11

[a] Quenching was studied at 25 °C by using a 1.3 × 10^{-2} M solution of HCl (generated from ROH + CH_3COCl). Values for the dielectric constants for the solvents shown were taken from ref 33.

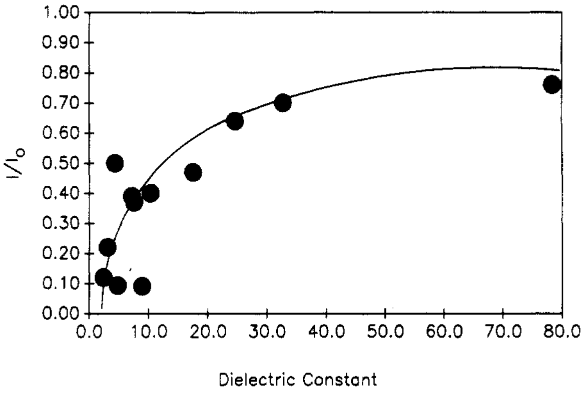


Figure 2. Plot of the observed extent of fluorescence quenching of dansyl labels in entrapment functionalized polyethylene films by HCl versus the dielectric constant of the suspending solvent.

One possible explanation for these results would be that the solvent chosen affected the equilibrium between HCl and the protonated dansyl fluorophore. We attempted to eliminate this possibility by our choice of experimental conditions. In the case of the protonation of films, we used a large excess of HCl, typically about an 8000:1 molar excess. However, in the case of CH_2Cl_2, THF, and ethanol we ran a second series of protonations. In these three cases, we added a sample of $C_{18}H_{37}NH$-DANS equivalent to about 0.5% of the original amount of HCl (i.e., a 200:1 molar ratio of HCl to $C_{18}H_{37}NH$-DANS). Even under these conditions where the concentration of dansyl group is more than a factor of 10 less, substantial or complete protonation of the soluble label occurred. Specifically, there was >99% quenching in CH_2Cl_2, 70%

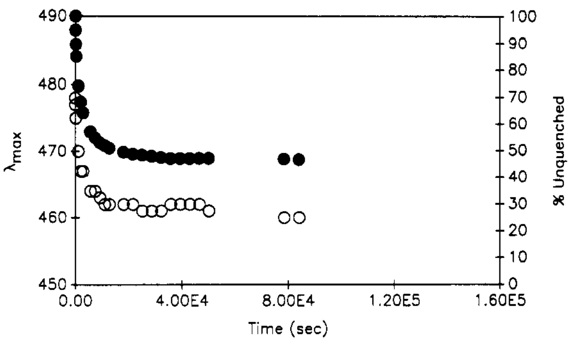


Figure 3. Plot of observed changes in emission maximum (○) (in nanometers) and the percent of unquenched dansyl labels (●) versus time.

quenching in THF, and 86% quenching in ethanol. These results suggest that solvent effects on the protonation of a dansyl label have at most a small effect on the relative populations shown in Table II. However, increasing concentrations of HCl in solution do affect the amount of protonation. For this reason, the data in Table II were all obtained with the same amount of soluble acid (except for the dibutyl ether data in which the HCl concentration was a factor of 2 greater).

Film thickness could have a large effect on the results reported in Table II. However, the examples listed in this table all have similar film thicknesses, which were on the order of 15 ± 5 μm. Additional experiments carried out with thinner films (5–10 μm) showed trends similar to those listed in Table II and described in the figures above. However, some differences in the extent of protonation were noted in that thinner films generally reacted to a greater extent.

A reasonable explanation of these results would be that it is only the dansyl groups at the surface and in the solvent-swollen interface that are being protonated. The unreacted dansyl groups that remain after the protonation reaction is complete would then presumably be those located in the bulk polymer, which are unaffected by solvent. This premise was supported by protonation experiments in which a change in λ_{max} was seen during the course of the protonation. These results, which are summarized in Figure 3 graphically, show that these dansyl groups exist in a range of chemical environments in the polyethylene–solvent interface that have varying accessibility to solvent, which parallels their reactivity toward reagents in solution. For example, consecutive scans of the emission spectrum of a dansyl-labeled film suspended in butanol during the protonation experiment show that as more of the functional groups were protonated, the emission maximum shifts to lower wavelengths until it levels off at a level like that seen for a dry film (or for a film in cyclohexane suspension). This shift in λ_{max} is in accord with the presumption that the functional groups that do not react with HCl in these solvents are those that exist in the most nonpolar environment, i.e., bulk polyethylene, and are unaffected by solvent.

The kinetics of these protonation reactions (Figure 4 and Table II) provide further insight into the reactivity of dansyl groups in these polyethylene–solvent interfaces. As can be seen from the representative kinetic plots shown in Figure 4, the rate of protonation was not a simple first-order reaction. Instead, the kinetic plots in Figure 4 (and for the other solvents in Table II) consisted of two separate regions. The first part of the protonation reaction was in most cases too fast to examine by our procedures. This phase of the reaction was typically complete within 300 s. A second, slower pseudo-first-order reaction was then observed. Rate constants obtained from data after 500 s are listed in Table II. We suggest that this behavior is due to the functional group's location in two chemically different environments.

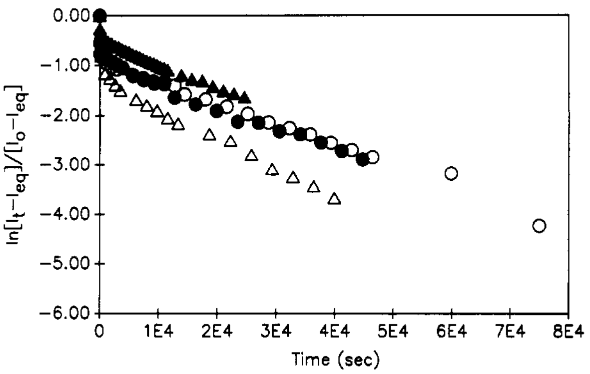


Figure 4. Plots of the rate of protonation of dansyl-labeled entrapment functionalized polyethylene films in ethereal solvents: (●) tetrahydrofuran, (○) diethyl ether, (△) dimethoxyethane, and (▲) dibutyl ether.

Different chemical environments in a functionalized polyethylene film suspended in a solvent could arise for several reasons. For example, differences in polarity, ion-solvation ability, viscosity, and the degree of swelling by solvent could each be contributing factors producing different chemical environments. We believe the simplest interpretation of our results is a picture in which these effects combine to produce polyethylene–solution interfaces in which there are three chemically and kinetically distinctive domains. Region 1 is a highly solvated region. Functional groups existing in this region were readily accessible to reagents in solution and experience a solution-like environment. Region 2 is a region that may contain some solvent molecules. However, the functional groups in this region experience a more polymer-like environment with diminished access to soluble reagents possibly due to diffusional restriction imposed on such reagents by the polymer chains. Plausibly the polymer chains in this region would be less mobile, perhaps because these chains are adjacent to crystalline regions of the polymer. Region 3 would be best described as bulk polymer. Functional groups in this region are inaccessible to solvent and reagents. Although the dimensions of each of the regions varied depending upon the particular solvent chosen, each polyethylene–solvent system studied contained some functional groups in each of these regions.

The actual dimensions of the regions cannot be defined from these experiments. However, we were able to estimate the relative populations of dansyl labels in each region in any given solvent suspension under our conditions from the extent of protonation and changes in the rate of protonation. In all of the cases, there was a distinct change in the rate of protonation after 200–400 s. Thus, we measured the I/I_0 value after ca. 300 s and at the point at which the protonation reaction had essentially ceased.[32] The values of I/I_0 measured were then used as estimates of the percent of dansyl groups that had been quenched. Such estimates are qualitative and contain some intrinsic errors in that they assume that dansyl groups in each region fluoresce with equal efficiency. Nonetheless, the estimates of populations derived in this manner, which are listed in Table II, do provide a consistent picture of a polyethylene interface that varies appreciably in depth depending on solvent. Comparison of the relative populations in the hydroxyl-containing solvents is illustrative. In these cases, more dansyl groups react in the more organic alcohols. However, in ethereal solvents, which are all less polar, the situation changes. As one changes from THF to diethyl ether to dibutyl ether the overall extent of reaction begins to decrease. A possible explanation would be that there is an optimum value for solvent polarity in these oxygenated solvents that facilitates reaction. In the case of the two chlorinated solvents and for toluene, essentially all the entrapped dansyl groups are protonated. Evidently these solvents swell polyethylene to a sufficient extent for nearly complete access by HCl to the entrapped fluorophores. However, even in these cases, a measurable amount of dansyl groups do not become quenched showing that there are regions of polyethylene in which HCl is kinetically unreactive under our conditions.

The observed rate constants listed in Table II also support this description. In particular, the rate constant for the second stage of the protonation reaction shows only a modest sensitivity to changes in polarity of the solvent used. This suggests that solvent does not markedly affect the rate of this second stage of the protonation reaction. In fact all of the rate constants except that for chloroform are in the range $(1.2-8.3) \times 10^{-3}$ s^{-1}. The small differences that are seen are best illustrated by the changes seen among the hydroxylic solvents. In this series of solvents there is a regular increase in the rate constant for the protonation reaction with decreasing solvent polarity. However, it is also likely that significant amount of this difference could be due to differences in acid strength (or identity) in these different solvents.

Larger effects are seen in the greater amounts of initial protonation in the non-oxygen containing solvents. This may reflect the identity of the acidic species present. In oxygenated solvents, protonated solvent is the likely acid. However, in chloroform, methylene chloride, and toluene the proton donor may be the more reactive HCl. This could also explain the greater extent of protonation in the last three solvents since HCl diffusion into polyethylene may be much more facile than that of protonated solvent.

Summary

The results described demonstrate that polyethylene–solvent interfaces contain a variety of chemical environments. The dimensions of the polyethylene interface change with the introduction of various polarity solvents. Functional groups located at the interface experience a range of chemical environments. These environments can be qualitatively described as three different regions varying only in the degree of solvation or swelling of the polymer interface. The evidence for this heterogeneity of microenvironments is seen both in qualitative observations of shifts in λ_{max} and in non-first-order kinetics in the protonation experiments.

These observations are in contrast to the results observed in etched films by Whitesides and co-workers. In etched systems, the functional groups were insensitive to changes in solvent polarity and appeared to experience one homogeneous environment. This suggests that entrapment functionalized films are a good alternative method of preparing functionalized polyethylene surfaces allowing the preparation of similar surfaces obtained by other more common methods. However, some of the properties of entrapment functionalized films are quite different from those of films prepared by surface oxidation. In general we feel that entrapment functionalization incorporates functional groups into regions much deeper in the polymer interface than surface oxidation procedures. This difference allows the probing of changes in polyethylene–solution interfaces that may not be observed in other systems.

The polyethylene–solution interface is a heterogeneous medium that is important to many polymer applications. The effects of the interface upon molecular interactions is still poorly understood. The work described here, although qualitative in many respects, demonstrates the need to understand how simple changes such as the changing of solvent polarity can dramatically effect the polymer interface.

Experimental Section

General Methods. Ethylene and carbon dioxide gases were purchased from Matheson Co. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was distilled from potassium metal and stored over potassium metal under a nitrogen atmosphere until used. Carbonyldiimidazole was obtained from Fluka Chemical Co. *n*-Butyllithium was purchased from Aldrich Chemical Co. as a 1.6 N solution in hexanes. This solution was periodically titrated with a xylene solution of *N*-phenyl-1-naphthylamine and 2-butanol.[34] The column for GPC analysis was 30 cm long and 7.8 mm in diameter and packed with fully porous highly cross-linked styrene–divinylbenzene copolymer (Waters, 500-Å ultra STYRAGEL). GPC analysis was carried out with degassed toluene at room temperature. Toluene and heptane were distilled from sodium benzophenone ketyl under a nitrogen atmosphere. All other solvents were ACS reagent grade and were used without further purification.

Polymer Materials. The high molecular weight polyethylene used throughout these experiments was obtained from Allied Corp. This polymer had an average molecular weight between 180 000 and 200 000 with a melt index of 0.96. Short-chain oligomers were removed from the sample by repeatedly dissolving the polymer in fresh solvent and precipitating it until no soluble materials could be detected in the solvent at room temperature by GPC with RI detection.

Instrumentation. All ^1H NMR spectra of polymer samples were taken in toluene-d_8. Samples consisted of 15–20 mg of polymer in approximately 0.5 mL of solvent with 4 mg of 1,1,2,2-tetrachloroethane as an internal standard. All spectra of polymer samples were taken on a Varian XL-200 or XL-400 NMR at 105 °C. All other NMR data were collected on a Varian XL-200E NMR at room temperature. UV–visible spectra were obtained by using a Perkin-Elmer Model 552 or Lambda 4 spectrophotometer. IR spectra were obtained on an IBM IR44 FT/IR. Fluorescence spectra were obtained on a SLM-Aminco SPF-500 C spectrofluorometer. All polymer films were cast in an explosion-proof Friction-Aire oven.

Preparation of carboxyl-terminated ethylene oligomer was accomplished according to a literature procedure.[35]

Preparation of 1-(Dimethylamino)-5-naphthalenesulfonyl Octadecylamine. Octadecylamine (4.86 g, 30 mmol) was dissolved in 75 mL of methylene chloride in a 250-mL, round-bottomed, three-necked flask equipped with a magnetic stir bar, a reflux condenser, and an addition funnel. The apparatus was purged with argon for 15 min and 1.62 g of dansyl chloride dissolved in 50 mL of methylene chloride was added to the dropping funnel. The dansyl solution was slowly added to the octadecylamine solution over a 10-min period. The reaction was allowed to stir for 3 h and worked up by extracting once with 500 mL of 1 N NaOH and four times with 500 mL of water. The solution was dried over Na_2SO_4 and concentrated under vacuum to yield a crude product, which was purified by column chromatography with silica gel (ethyl acetate elution). The fluorescent fraction was collected and dried to yield 2.51 g of product: mp 66–68 °C (lit.[36] mp 69.5–71.0 °C); ^1H NMR ($CDCl_3$) δ 0.9 (t), 1.3 (br m), 2.9 (m), 4.65 (t), 7.2 (d), 7.6 (q), 8.3 (t), 8.6 (d).

Preparation of [[1-(dimethylamino)-5-naphthyl]sulfonyl]ethylenediamine was accomplished according to a literature procedure.[8]

Preparation of Dansylethylenediamine-Labeled Octadecanoic Acid. Octadecanoic acid (0.2 g, 0.7 mmol) and 0.13 g (0.8 mmol) of carbonyldiimidazole were added to a 150-mL, three-necked, round-bottomed flask equipped with a magnetic stir bar. The apparatus was purged with argon and 20 mL of toluene was added. After heating to reflux for 14 h, 0.3 g of dansylethylenediamine was added to the mixture and the reaction was refluxed for an additional 24 h. The reaction mixture was worked up after cooling to room temperature by first adding 100 mL of methylene chloride and then extracting with three 500-mL portions of water and once with 500 mL of saturated $NaHCO_3$. The organic layer was then dried and concentrated under vacuum to yield a crude product. Further purification was accomplished by recrystallization from 80% methanol and 20% water to yield 0.274 g of a tan colored solid (54% yield) having mp 88-90 °C: ^1H NMR (toluene-d_8) δ 0.9 (t), 1.3 (br s), 1.7 (t), 2.5 (s), 2.6 (m), 2.8 (m), 4.9 (m), 5.4 (), 6.8 (d), 7.4 (t), 8.2 (d) and 8.6 (d); HRMS 559.3869, calcd for $C_{32}H_{53}O_3N_3S$ 559.3807.

Preparation of Dansylethylenediamine-Labeled Carboxylated Ethylene Oligomer. Carboxyl-terminated ethylene oligomer (2.0 g, 1.24 mmol of CO_2H) and 0.3 g (1.8 mmol) of carbonyldiimidazole were placed in a 250-mL, three-necked, round-bottomed flask equipped with a magnetic stir bar and a reflux condenser. Addition of 100 mL of toluene and heating to reflux dissolved the oligomer. The 0.505 g (1.7 mmol) of dansylethylenediamine was added and the reaction allowed to reflux for an additional 3 h. At this time, the reaction mixture was cooled to precipitate the dansyl-labeled oligomer, which was collected by suction filtration. The crude oligomer product was redissolved in toluene and precipitated a second time to yield 1.52 g of product: ^1H NMR (toluene-d_8) δ 0.9 (t), 1.3 (br s), 1.7 (t), 2.6 (s), 2.7 (br s), 2.9 (q), 4.9 (br s), 7.2 (t), 7.35 (t), 8.2 (d), 8.4 (d), 8.5 (d). From end-group analysis the molecular weight was calculated to be 2050 g/mol with a loading of 0.18 mmol/g.

Preparation of Entrapment Functionalized Polyethylene Powders. Polyethylene powders containing PE-2 were prepared by cooling a 110 °C toluene solution of 1 part of functionalized ethylene oligomer to 100 parts of virgin high molecular weight polyethylene. Any loosely adsorbed dye was removed by Soxhlet extraction with methylene chloride for 96 h.

Preparation of Entrapment Functionalized Polyethylene Films. A solution of 0.13 g of entrapped oligomer in polyethylene was prepared by using 25 mL of 1,2-dichlorobenzene at 140 °C. Upon dissolution of the polymer, the solution was immediately poured into a Petri dish maintained at 135 °C in an explosion-proof Friction-Aire oven. The dish was covered with a pane of glass and solvent was allowed to evaporate. The Petri dish was removed from the oven and allowed to cool to room temperature. The film was then removed from the bottom of the dish in 1-in. square pieces with forceps and stored in a capped scintillation vial. Film thickness was nominally 15 μm and is listed in Table II.

General Fluorescence Measurements. Solution samples were prepared from a concentrated stock solution of the soluble fluorophore in methylene chloride. Aliquots of the stock solution were then added to a volumetric flask. The flask was purged with argon until all the solvent evaporated. Then the aliquot was diluted to the desired volume with the appropriate solvent. A small aliquot of the diluted sample was then transferred to a cuvette and the emission spectrum was obtained between 375 and 600 nm (excitation at 350 nm, 5-nm excitation and emission slit). Fluorescence spectra of functionalized films were obtained by using a triangular cuvette with the film resting against the diagonal face. The diagonal face of the cuvette was placed so that reflected light did not reach the detector.

Procedure for Fluorescence Quenching of Entrapment Functionalized Polyethylene Films. Polyethylene films containing PE-2 were suspended in the solvent of choice and allowed to equilibrate for a minimum of 15 min. After the emission spectrum was recorded, the solvent was removed and replaced with an HCl solution prepared by dissolving 0.1 g (1.3 mmol) and 0.041 g (1.3 mmol) of acetyl chloride and methanol, respectively, in 100 mL of the chosen solvent. Methanol was omitted for other hydroxylic solvents. Emission spectra were periodically recorded over a period of 20 h at which point changes in emission intensity had essentially stopped occurring.

Acknowledgment. Support of this research by the National Science Foundation (DMR-8605941) and the Texas Advanced Technology Research Program is gratefully acknowledged. We also thank Mark Espenscheid for his assistance in measuring film thicknesses.

References and Notes

(1) *Polymer Surfaces and Interfaces*; Feast, W. J., Munro, H. S., Eds.; John Wiley & Sons: Chichester, 1987.
(2) Wu, S. *Polymer Interfaces and Adhesion*; Marcel Decker: New York, 1982.
(3) *Surface and Interfacial Aspects of Biomedical Polyers*; Andrade, J. D., Ed.; Plenum: New York, 1985; Vol. 1.
(4) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1986**, *3*, 932-950.
(5) Rasmussen, J. R., Stedronsky, E. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4736-4745.
(6) Rasmussen, J. R.; Bergbreiter, D. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 4746-4756.
(7) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725-740.
(8) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1986**, *2*, 266-281.
(9) Holmes-Farley, S. R.; Whitesides, G. M. *Langmuir* **1987**, *3*, 62-76.
(10) Holmes-Farley, S. R.; Reamey, R. H.; Nuzzo, R.; McCarthy, T. J.; Whitesides, G. M. *Langmuir* **1987**, *3*, 799-815.
(11) Holmes-Farley, S. R.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1988**, *4*, 921-927.
(12) Melby, L. R. *Macromolecules* **1978**, *11*, 50-56.
(13) Brewis, D. M.; Briggs, D. *Polymer* **1981**, *22*, 7-16.
(14) Briggs, D. J. Adhesion **1982**, *13*, 287-301.
(15) Nuzzo, R. G.; Smolinsky, G. *Macromolecules* **1984**, *17*, 1013-1019.
(16) Clark, D. T.; Dilks, A.; Shuttleworth, D. In *Polymer Surfaces*; Clark, D. T., Ed.; John Wiley & Sons: New York, 1978; Chapter 9.
(17) Bergbreiter, D. E.; Chen, Z.; Hu.-P. *Macromolecules* **1984**, *17*, 2111-2114.
(18) Bergbreiter, D. E.; Hu.-P.; Hein, M. D. *Macromolecules* **1989**, *22*, 654-662.
(19) Bergbreiter, D. E.; Chandran, R. *J. Am. Chem. Soc.* **1987**, *1*, 174-179.
(20) Bergbreiter, D. E.; Blanton, J. R. *J. Org. Chem.* **1985**, *50*, 5828-5833.
(21) Bergbreiter, D. E.; Hein, M. D.; Huang, K. *Macromolecules* **1988**, *21*, 3331-3333.
(22) Chandar, P.; Somasundaran, P.; Turro, N. J.; Waterman, K. C. *Langmuir* **1987**, *3*, 298-300.
(23) Preist, W. J.; Sifain, M. M. *J. Polym. Sci., Part A-1* **1986**, *9*, 3161-3168.
(24) Dubini-Paglia, E.; Beltrame, P. L.; Marcandalli, B. *J. Appl. Polym. Sci.* **1987**, *33*, 2965-2974.
(25) Dubini-Paglia, E.; Beltrame, P. L.; Marcandalli, B.; Cartini, P.; Seves, A.; Vicini, L. *J. Appl. Polym. Sci.* **1986**, *31*, 1251-1260.
(26) *Photophysics of Polymers*; Hoyle, C. E., Torkelson, J. M., Eds.; ACS Symposium Series 358, American Chemical Society: Washington, DC, 1987.
(27) Chandar, P.; Somasundaran, P.; Turro, N. J. *Macromolecules* **1988**, *21*, 950-953.
(28) Morawetz, H. *Makromol. Chem., Suppl.* **1985**, *13*, 67-74.
(29) Li, Y.-H.; Chan, L.-M.; Tyer, L.; Moodey, R. T.; Himel, C. M.; Hercules, D. M. *J. Am. Chem. Soc.* **1975**, *97*, 3118-3126.
(30) Shea, K. J.; Okahata, Y.; Dougherty, T. K. *Macromolecules* **1984**, *17*, 296-300.
(31) Shea, K. J.; Stoddard, G. J.; Sasaki, D. Y. *ACS Symp. Ser.* **1987**, *358*, 97-106.
(32) We used I/I_0 as the extent of fluorescence quenching where I_0 was the initial emission intensity observed and I represented the observed emission intensity at a given time.
(33) Dielectric constants were abstracted from the compilation of solvent properties in: *Techniques of Organic Chemistry*, 3rd ed.; Riddick, J. F., Bunger, W. B., Eds.; Wiley-Interscience: New York, 1970; Vol. II, Organic Solvents.
(34) Bergbreiter, D. E.; Pendergrass, E. *J. Org. Chem.* **1981**, *46*, 219-220.
(35) Bergbreiter, D. E.; Blanton, J. R.; Chandran, R.; Hein, M. D.; Huang, K.-J.; Treadwell, D. R.; Walker, S. A. *J. Polym. Sci., Polym. Chem.*, in press.
(36) Romero, A.; Sunamoto, J.; Fendler, J. H. In *Colloid and Interface Science*; Kerker, M., Ed.; Proceedings of the International Conference on Colloids and Surfaces, 50th, San Juan, P.R.; Academic Press: New York, 1976; Vol. V, pp 111-118.