silylene),[17] and poly(di-*n*-propylsilylene)[17] where trans conformations have been documented yet the absorption maxima were found at 342, 332, and 344 nm, respectively. In addition, the λ_{max} in poly(di-*n*-tetradecylsilylene) is 347 nm, even though its conformation has been reported as tgtg′.[18] These results demonstrate the problem in correlating the UV absorption maxima with specific conformations or with lengths of conformational sequences.

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(11) A film of the polysilylene cast from hexane onto a sheet of quartz was placed in an optical high-pressure cell (Nova-Swiss, Effretikon, Switzerland) filled with ethanol as the pressure transmitting medium. This apparatus was positioned in the optical path of a Uvikon Model 860 spectrophotometer with a temperature-regulated adapter. The temperature of the pressure cell was measured with a copper–constantan thermocouple located in a small hole in the cell; the temperature at this point was found to accurately measure the temperature within the pressure cell. The pressure within the cell was monitored with a temperature-compensated Bourdon-tube style gauge (Heise, Inc., Newtown, CT). For each polysilylene spectrum the background absorption due to the quartz sheet was measured separately under the same experimental conditions and then subtracted from the original spectrum. This procedure has been found to give accurate and reproducible results.

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Azo Dye Stereoisomerization at Polyethylene–Solution Interfaces

The extent to which solvents interact with polymers is an important parameter that can affect many aspects of a polymer's behavior. However, while many aspects of the behavior of polymers in solution are well established, there is less known about how solid polymers and in particular how surface functionalized polymers behave in contact with solvents. This is due, in part, to the problems of synthesizing such interfaces and of monitoring the chemistry and dynamics of molecules at such interfaces. More recently, details about the chemistry of macromolecules and solvents at solid–liquid interfaces are in part being addressed by recent developments in studies of Å-level interactions of polymers adsorbed on mica surfaces, in various physical studies of interfaces, and in studies of organic thin films.[1–4] Studies that yield similar information about functional group behavior for a functionalized polymer's solid–liquid interface are also actively being pursued by several groups.[5,6] Here we describe experiments which show that thermal geometric isomerization of an azo dye can be used to probe solvent–polymer interaction at functionalized polymer–solvent interfaces.

Geometric isomerization of azo dyes is a facile reaction and occurs both thermally and photochemically.[7] Such isomerizations have been studied for small molecules in solution and for macromolecular derivatives in either the solid state or solution. In solution, such isomerizations follow simple first-order kinetics. However, in polymeric solids more complicated kinetics are seen.[7–12] Typically the isomerization under these conditions proceeds by two or more first-order processes. The most common observation of an initial fast first-order isomerization followed by a second slower first-order isomerization reportedly only occurs below T_g. Similar isomerizations also occur in dye-labeled chromic acid etched and entrapment-functionalized polyethylene.[9,10,12] Further, the extent of isomerization can be correlated with the behavior of other probes of solvent–polymer interactions at functionalized polyethylene–solution interfaces.[13,14] While we have examined both chromic acid etched high density polyethylene labeled with an azo dye and entrapment-functionalized polyethylene that incorporates an azo dye and seen similar behavior for each system, we have used entrapment-functionalized materials for quantitative studies. This is primarily because quantitative studies with a labeled chromic acid etched polymer are frustrated by the small amount of chromophore present. Comparison of isomerization data of an entrapment-functionalized polymer with rotational correlation times measured for ESR spin labels of similarly functionalized polyethylene suspended in the same solvents shows that the extent of the initial, faster stage of the isomerization is correlated with these τ_C values.[13] However, the total amount of isomerization seen is better correlated with solvation of these interfaces as measured with a fluorescence probe.[14]

In previous work we had reported that terminally functionalized ethylene oligomers can be blended with additive-free polyethylene to produce functionalized polyethylene powders and films. The product films and powders have been shown to form such that the terminal functional groups are largely accessible to solvent and reagents in solution. The degree to which the product films and powders are "surface" functionalized depends on various experimental parameters that have been discussed in a prior paper. Spectroscopic and chemical behavior of the product-functionalized polymer parallel that of similar derivatized etched polyethylene films although the depth

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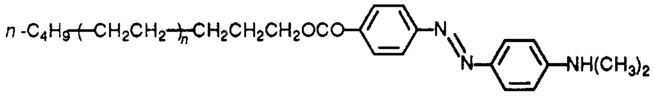
of functionalization in entrapment-functionalized materials is greater than that seen in a classical etching reaction.[13-15] ^{13}C solid-state NMR spectra, infrared spectra, and thermal analysis comparisons of a sample of entrapment-functionalized polymer and the starting polymer do not show any differences, suggesting that changes in polymer bulk morphology on entrapment are negligible. We believe that this reflects cocrystallization of the very crystalline terminally functionalized linear oligomers and high density polyethylene. In this work we have used the azo dye 1



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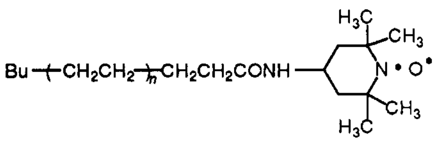
which we previously showed can be easily synthesized and entrapped in polyethylene.[15,16] We previously used the resulting functionalized polyethylenes to probe Brønsted acidity at polyethylene solutions interfaces.[16] However, during these studies we noted that 10-μm thick films containing 1, PE/1, had unexpected behavior in a UV–visible spectrometer. When such films were placed in a cuvette and scanned repeatedly for several hours, a gradual *increase* in the absorption at 428 nm was noted along with a *decrease* in absorbance at 350 nm. A single isosbestic point was present at 380 nm. After no further change was noted in the UV spectrum of PE/1, the cuvette was removed from the spectrometer. After being left standing in room light for 12 h or after irradiation with a tungsten lamp, it was found that the UV spectrum of PE/1 was the same as that of the original sample before it had been placed in the spectrometer. Further experiments showed that these changes in the spectrum of PE/1 occurred whenever PE/1 was removed from room light. These changes are due to geometric isomerization of the entrapped azo dye in the dark and its' subsequent equilibration in room light to a different E/Z mixture and were fully reversible. The observed kinetic behavior was apparently not due to simple solvent swelling of the film since isomerized films that were reequilibrated with irradiation and kept in solvent showed reproducible kinetic behavior in subsequent isomerizations. Films were in any case suspended in solvent for ca. 30 min before isomerization began. Finally, we observed the same sort of kinetics in isomerization of PE/1 films in the absence of solvent though the isomerization was slower the absence of solvent.

The rate of this isomerization was followed by plotting ln $[(A_\infty - A_t)/(A_\infty - A_0)]$ versus time. The resulting plots superficially consisted of two first-order plots with a faster reaction for the first 40–50 min of the reaction. The initial rate in these isomerizations was approximately 4 times faster than the slower second stage of the isomerizations. The second slower rate varied in a narrow range from 0.8×10^{-2} to 1.2×10^{-2} min^{-1} for a range of solvents from water to heptane. These data were used in several ways as a measure of solvent interaction with functional groups in the interface of these functionalized polyethylenes in contact with solvent. First, we compared the amount of isomerization that had occurred in the first 50 min and the total amount of dye isomerized with rotational correlation times measured for a similar nitroxyl terminated ethylene oligomer 2 entrapped in high density polyethylene. The



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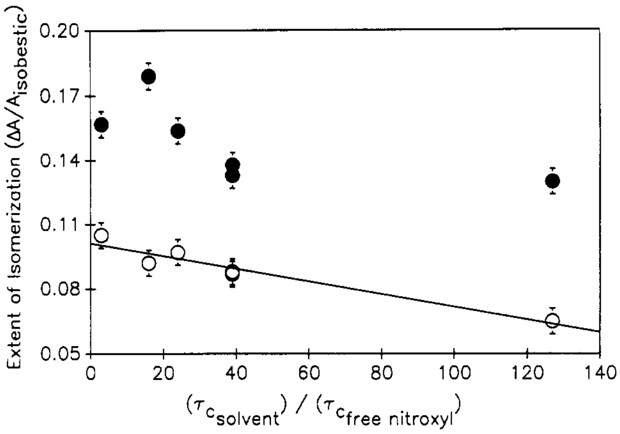
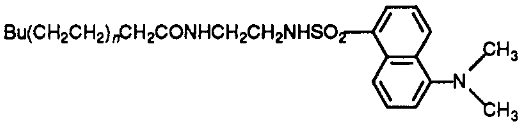


Figure 1. Extent of isomerization of PE/1 after 50 min (○) and after 500 min (●) as determined by the change in absorbance measured at 428 nm in various solvents suspensions plotted versus the rotational correlation time for samples of PE/2 suspended in the same solvents.

extent of isomerization in these cases was measured by determining the ΔA at 50 min, the total ΔA, and correcting these absorbance values for the amount of sample by dividing these numbers by the measured absorbance at the isosbestic point. We have previously shown that rotational correlation times of entrapped nitroxyl groups correlate with their reactivity toward reagents external to polyethylene.[13] The resulting plots of isomerization at 50 min or total isomerization versus τ_C are shown in Figure 1. Two aspects of this figure are noteworthy: (1) the evident correlation between the molecular mobility of entrapped groups measured by ESR and the extent of isomerization of PE/2 at 50 min and (2) the fact that the total amount of isomerization of PE/2 depends on solvent although not in the same manner that the initial isomerization does. This suggests that azo dye isomerization can be used as a measure of interaction between solvents and functional groups at functionalized polyethylene–solution interfaces.

The amount of entrapped azo dye that isomerizes either initially or totally was not correlated to solvent dielectric constant. However, there was a modest correlation between the total amount of dye that isomerizes (ΔA_{total}) and the extent of reaction of suspensions of a similar oligomer with solutions of HCl. These protonations involved an oligomer like 1 but which had a dansyl label attached it. This dansyl-labeled oligomer (3) was entrapped in the



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same type of polyethylene film and suspended in the solutions of HCl in the same solvents. The correlation between the measured amount of initial isomerization ($\Delta A_{50\,\text{min}}$) and the extent of protonation of a dansyl label was somewhat poorer. These data which are shown in Figure 2 suggest that the end groups of these labeled oligomers can interact with solvents or with solutions of reagents like HCl but still not be located at the surface or near some free volume in the solid polymer film.

Finally, these azo dye isomerizations studied in some detail for entrapment-functionalized films can also be used in studying functionalized polyethylene produced by oxidative etching with CrO_3/H_2SO_4.[17] Qualitatively, dry films exhibit the same behavior as the entrapment-functionalized films in that two kinetic regimes for isomerization are seen. However, the total change in absorbance in these

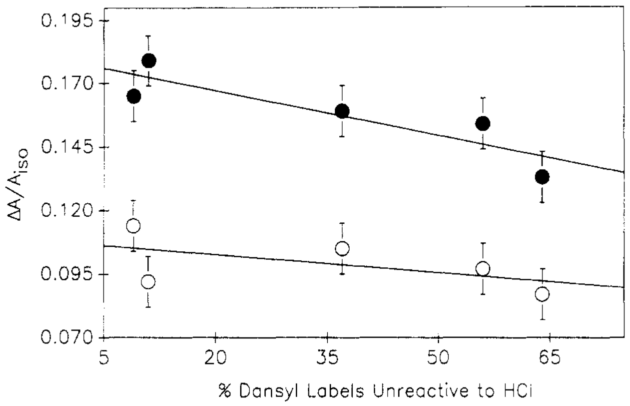

Figure 2. Extent of isomerization of PE/1 after 50 min (○) and after 500 min (●) as determined by the change in absorbance at 428 nm in various solvents suspensions plotted versus the extent of reaction of the dansyl labels of PE/3 with HCl in the same solvent suspensions.

cases is quite small (ca. 0.002 absorbance unit). Nonetheless, the data are good enough to show that isomerization is about 4 times faster in the presence of solvent than for dry films.

In summary, photoisomerization of azo dyes entrapped in polyethylene shows a modest dependence on the nature of the solvent in contact with the functionalized polymer. Good correlations are obtained between the initial amount of isomerization and prior ESR and fluorescence studies of functional group behavior for functionalized polymers suspended in these same solvents. Similar kinetic behavior are seen with both etched polyethylenes and entrapment-functionalized polyethylene films though the low loading of the former films frustrates quantitative analysis in that case.

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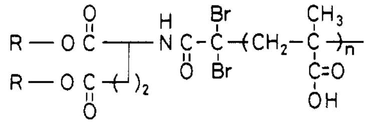
Chain-Length Effects of Poly(ethylene glycol) on a Monolayer of a Poly(methacrylic acid)-Based Amphiphile at the Air–Water Interface

In this report we show that the newly prepared amphiphile 1 composed of two long alkyl chains and a poly(methacrylic acid) segment forms a stable surface monolayer which is significantly affected by variation of the pH in the subphase and by the addition of poly(ethylene glycol) (PEG) to the subphase and that such a monolayer responds to the chain length of PEG in the subphase as a result of a polymer–polymer interaction based on hydrogen bonding at the air–water interface.



1 ; R = $C_{18}H_{37}$—
n = 55

$HO{+}CH_2CH_2O{+}_mH$ PEG
m = 4 - 191

We have reported that amphiphilic block polymers of poly(acrylic acid-*block*-styrene) (PAA-PSt) and poly(oxyethylene-*block*-styrene) (POE-PSt), prepared by using the catalytic system of halo-terminated polymer and manganese carbonyl ($Mn_2(CO)_{10}$), can form stable surface monolayers which are affected by the chain length of the PSt segment, by variation of the pH in the subphase and by addition of a water-soluble polymer to the subphase.[1,2] In particular, POE-PSt monolayers formed an interpolymer complex with PAA in the subphase through hydrogen bonding, and such complexation was reversibly controlled by pH change.[2] Interpolymer complexations of PMAA and PEG through hydrogen bonding have been extensively investigated in an aqueous medium.[3,4] However, the polymer–polymer interaction at the air–water interface has not yet been established. The π–A isotherm measurement is a useful tool for detecting molecular interactions at the air–water interface due to its high sensitivity to the monolayer state. In the present study, we employ PMAA-containing amphiphile 1 as a molecular recognizable monolayer component and studied the effects of chain length of PEG as an additive in the subphase on the surface monolayer of 1 by using surface pressure (π)–area (*A*) isotherm measurements.