Surface Selectivity in Blending Polyethylene–Poly(ethylene glycol) Block Cooligomers into High-Density Polyethylene

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ABSTRACT: Functionalization of polyethylene with block cooligomers of polyethylene and poly(ethylene glycol) is described. Poly(ethylene glycol) of different molecular weights was used. The block cooligomers of polyethylene and poly(ethylene glycol) were codissolved with additive-free polyethylene and then precipitated to obtain entrapment-functionalized powders. These powders contained 0.3–15 wt % of the cooligomer in the host high-density polyethylene and contained a mixture of the block cooligomer and virgin polyethylene. Solvent casting using these powders was used to produce polymer films which were analyzed by contact angle, XPS, and ATR-IR spectroscopy. These analyses showed that the poly(ethylene glycol) units ended up primarily at the outermost layers of the film. Further, the extent of segregation of these block cooligomers to the edges of these films increased as the weight percent loading of the cooligomer decreased. Block cooligomers with large poly(ethylene glycol) groups had a greater selectivity for the surface than similar block cooligomers with smaller poly(ethylene glycol) groups.

The surface composition and structure of solid organic polymers influence many of their properties and applications.[1-3] Examples of technologically important applications affected by a polymer's surface composition include wetting, permeability, adhesion, friction, dyeing, and biocompatibility. In these sorts of applications, modification of the surface of a polymer can be used to alter a polymer's interaction with a contacting solid, liquid, or gas. A process that is selective for the surface of a polymer is of particular interest in that it leaves the bulk physical properties of the polymer intact. Much of the focus of the current interest in surface functionalization of polymers aims toward these objectives, typically through modification of an existing polymer film. We have been exploring the potential and applications of an alternative approach we have termed entrapment functionalization, a method where small amounts of modified oligomers are mixed with unmodified polymer resin to produce directly a surface-modified film or powder. Our approach differs from the conventional approach in that it combines a preformed terminally functionalized oligomer with virgin polymer to directly produce a functionalized film. Our prior work has demonstrated that this entrapment-functionalization procedure using end-functionalized ethylene oligomers does lead to surface-modified polyethylene films and powders.[4-7] This prior work indicates that the interaction of the oligomeric ethylene chains with the host polymer is large enough that these groups do not readily extract from the polymer as would a low molecular weight additive. Further, by controlling the microstructure of the oligomer, the end-group size and polyethylene compatibility, and the experimental details of the entrapment process, we can achieve modest to good surface selectivity. We demonstrated the surface selectivity of these processes by the facile interaction of spectroscopic labels with solvent or with reagents which do not diffuse into polyethylene. However, entrapment functionalization is less surface selective than many etching or plasma modifications in that the interface or surface of an entrapment-functionalized polymer film is broader and deeper than the functionalized interface produced by derivatization of a preformed film. Here we describe extension of these entrapment-functionalization procedures to include blending of asymmetric AB block cooligomers into polyethylene. A combination of contact-angle measurements, XPS spectroscopy, and ATR-IR spectroscopy have been used to show that block cooligomers of ethylene and ethylene glycol can be blended into virgin polyethylene to produce, after solvent casting, films with nearly all poly(ethylene glycol) groups of the PEG portion of the block cooligomer being located at the cast film's surface volume.

Since polyethylene by itself does not have any functional groups other than C–C or C–H bonds, existing derivatization techniques are often chemically harsh. In most cases, derivatization of the surface involves reactions which produce chain scission. Procedures involving chromic acid etching,[8,9] sulfonation,[10] and plasma treatments[11] are common synthetic examples. Surface selectivity in these cases results from diffusion of a soluble reagent from a polar solution to the interface or from diffusion of a highly reactive gaseous reagent to the polymer surface. High surface selectivity is often possible although the product functionalized polymer's surface may only have limited thermal stability.[12-14] Subsequent chemistry can be used to transform these initial surface-functionalized polyethylenes into a host of other groups although this subsequent chemistry is complicated by analytical problems, by the presence of multiple types of functional groups, and by possible spatial heterogeneity in the distribution of functional groups both within the interface and across the surface of the product polyethylene film.[8,15] Nonetheless, most studies on the surface chemistry of functionalized polyethylene films and powders have relied on derivatizations using these sorts of procedures.

It is important to realize that the term "surface" is itself ambiguous with regard to an organic polymer. The definition of what constitutes the "surface" of a polymer like polyethylene depends largely on what phenomena one chooses to study and on the experimental conditions of the determination. For example, water contact angles have been shown to be quite selective, responding to functional groups in the outer 5 Å of the polymer.[16] Vacuum techniques like XPS are less surface selective and detect groups in the top ca. 50 Å of a surface.[17] ATR-IR spectroscopy (attenuated total reflectance IR spectroscopy) is much less surface selective. Depending on the wavelength of the incident radiation, it analyzes about the top 1 μm of the polymer surface.[18] These techniques all involve analysis of the polymer as an air– or vacuum–solid interface or involve the use of a solvent which is a

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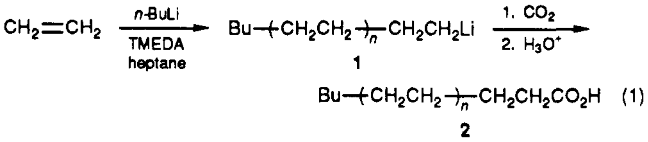
poor solvent for the substrate polymer. All of these techniques analyze what is in practice a surface volume, an interface whose depth depends on the analytical method. The comparative importance of functional groups in the surface defined by contact angle, XPS, or ATR-IR in interfacial chemistry is also unclear. In a practical sense, the depth of functional groups which interact with solvents or reagents for a functionalized polymer like polyethylene depends on the conditions in which an organic solvent or reagent is present. Such depths are either unknown or more difficult to define. However, reagents which are known to permeate polyethylene are known to react readily with functional groups located below the 50-Å XPS interface. Recent studies by Lee have shown that adhesion which is a technological problem of interest in surface-modified polymers may be significantly affected by groups at depths of >1000 Å.[19] The studies described here have examined these various-depth regimes in a block cooligomer entrapment-functionalized film using a combination of analytical techniques.

The studies described below detail the results of entrapping small amounts of an AB block cooligomer of polyethylene and poly(ethylene glycol) (PE-PEG) into an excess of virgin high-density polyethylene. Various sized poly(ethylene glycol) blocks and varying amounts of the AB cooligomer have been used and the cast films from these PE-PEG cooligomers have been studied using contact-angle measurements, variable-angle XPS, and variable-angle ATR-IR spectroscopy. These analyses showed that the PEG groups were primarily in the outermost layers of the product film and that the extent of segregation of these PE-PEG cooligomers to the edges of the film increased as the weight percent of the PE-PEG in the host polyethylene decreased. Block PE-PEG cooligomers having larger PEG blocks also had greater selectivity for the surface than similar block cooligomers with smaller PEG groups.

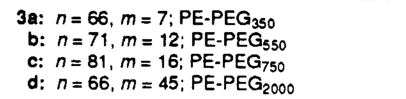
Results and Discussion

The block cooligomers used in this study were all prepared the same way starting with a terminally carboxylated polyethylene which itself had been prepared by anionic oligomerization of ethylene initiated by *n*-BuLi–TMEDA and by quenching with CO_2 (eq 1).[20,21] The efficiency of the carbonation varied from 57 to 81% for different oligomerizations. Typically about 60% of the chains were functionalized on quenching as determined by ^1H NMR spectroscopy of a methyl ester derivative of 2.



$$CH_2{=}CH_2 \xrightarrow[\text{TMEDA, heptane}]{n\text{-BuLi}} Bu{-}(CH_2CH_2)_n{-}CH_2CH_2Li\ \mathbf{1} \xrightarrow[2.\ H_3O^+]{1.\ CO_2} Bu{-}(CH_2CH_2)_n{-}CH_2CH_2CO_2H\ \mathbf{2} \qquad (1)$$

Asymmetric AB block cooligomers were prepared by coupling 2 and commercially available monomethyl ether terminated poly(ethylene glycol)s of varying M_n via an ester bond. This was accomplished according to eq 2 using an acid catalyst such as *p*-toluenesulfonic acid. After the esterification reaction, the untreated poly(ethylene glycol) stayed in solution while the cooligomer precipitated out. The cooligomers prepared were characterized using IR spectroscopy and ^1H NMR spectroscopy at 105 °C. The loading and the molecular weight of the product was calculated by integrating the methylene protons adjacent to the ester linkage ($\delta = 4.15$), the methoxy protons ($\delta = 3.15$), and the methyl protons at the other end of the chain ($\delta = 0.9$) relative to a known amount of internal standard (1,1,2,2-tetrachloroethane).



$$Bu{-}(CH_2CH_2)_n{-}CH_2CH_2CO_2H + H{-}(OCH_2CH_2)_m{-}OCH_3 \xrightarrow[\text{refluxing toluene}]{p\text{-TsOH}} n\text{-}C_4H_9{-}(CH_2CH_2)_n{-}CH_2CH_2COOCH_2CH_2{-}(OCH_2CH_2)_{m-1}{-}OCH_3 \qquad (2)$$

3a: $n = 66$, $m = 7$; PE-PEG$_{350}$
b: $n = 71$, $m = 12$; PE-PEG$_{550}$
c: $n = 81$, $m = 16$; PE-PEG$_{750}$
d: $n = 66$, $m = 45$; PE-PEG$_{2000}$

These copolymers were entrapped in virgin polyethylene by thermal precipitation.[5,22] A measured quantity of the oligomer and high molecular weight polyethylene were dissolved in toluene at 105 °C and the solution was cooled to precipitate the entrapped polymer. Experimentally we found it more convenient to make up a larger sample of mixtures of block cooligomer and host polyethylene in the form of entrapment-functionalized powders. These powder were then stored and used as needed in casting films of entrapped functionalized polyethylene. Alternatively, one could weigh out a desired amount of block cooligomer and virgin polyethylene and directly cast an entrapment-functionalized film. Films were cast from 1,2-dichlorobenzene solution at 135 °C. Most of the casting solvent was removed at 135 °C. Any residue was removed by placing the film in its original glass dish in a vacuum oven at 155 °C for 30 min. The film thickness (t) of the product films

$$t = 10\,000/\Delta\lambda \qquad (3)$$

was measured from the wavelength difference ($\Delta\lambda$ in cm^{-1}) between interference fringe peaks seen in transmission IR spectroscopy and was typically 45 ± 5 μm. Thinner films could be prepared using less powder, but thin films adhered too strongly to the glass dish to be removed for analysis without cohesive failure of the film. Typically the product films were carefully peeled from the glass dish, cut into pieces, and analyzed.

The contact angle of a water drop on a polymer surface measures the hydrophobicity/hydrophilicity of the surface. A low-energy surface is hydrophobic and has a high contact angle while a high-energy surface has a low contact angle with water and is hydrophilic. Water contact angles have been shown to be very sensitive to the nature of functional groups at the top few angstroms of a functionalized polyethylene. Surface hydrophilicity has also been correlated to the presence of poly(ethylene glycol) oligomer in two specific studies from Whitesides' group.[8,23] In the first of these studies, polyethylene etched with CrO_3–H_2SO_4 was esterified with PEG groups. With smaller PEG units on the polyethylene ($-[CH_2CH_2O]_nCH_2CH_2OH$; $n = 7$–9) that had terminal hydroxyl groups, these systems had advancing water contact angles of ca. 40°. However, the Θ_a values of this surface gradually increased as the size of the PEG block increased until the Θ_a value approached 80° ($-[CH_2CH_2O]_nCH_2CH_2OH$; $n \geq 100$). This change was attributed to a diminished contribution of the terminal hydroxyl to the surface's hydrophilicity. Presumably this latter surface would better resemble the glass side of the films we have prepared. A better defined self-assembled monolayer of HO-PEG-modified alkanethiols on gold had a somewhat lower contact angle of ca. 30° with a similar-sized hydroxyl-terminated polyethylene glycol.[23] The systems described here are less well-defined systems than either of those studied by Whitesides. While our entrapment-functionalized materials have essentially just two types of functional groups, namely the polar portion contributed by the polyethylene glycol units and the non-

Table I
Contact Angle on the Glass Side of Cast Entrapment-Functionalized Polyethylene Films[a]

molecular weight of PEG in copolymer	loading of copolymer,[b] wt %	contact angle,[c] deg	
		glass side of film	air side of film
no added PEG	no added PEG	96	105
PEG_{350}	15.3	83	100
	10.0	83	102
	8.0	84	101
	2.3	89	103
	1.1	90	102
PEG_{750}	15.3	69	102
	7.1	73	104
	4.8	84	103
	2.5	88	101
	0.7	90	103
PEG_{2000}	16.2	65	102
	9.0	65	103
	6.0	67	104
	4.4	69	104
	3.6	76	103
	2.2	79	106

[a] The films were prepared at 135 °C from a solution of 0.21 g of entrapment-functionalized powder in 25 mL of *o*-dichlorobenzene. The solvent removal was complete on the basis of IR spectroscopy. [b] The weight percent of the cooligomer was based on the weight of the functionalized cooligomer and the weight of the polyethylene used to prepare the entrapped powder. [c] This was a static (Young's) contact angle measured on a sessile drop under 100% relative humidity and has an error or ±3°.

polar portion by polyethylene units, they are certainly not as well-ordered as are those in a self-assembled monolayer. On the basis of prior studies,[4-7] the PEG groups introduced by entrapment functionalization are likely to be located in an interface extending from the outermost surface of these films to regions substantially beneath the contact-angle surface. A further difference is that the materials we have studied contain a terminal OCH_3 group. Substitution of a methoxy group for a hydroxy group would increase the value for Θ_a and lead to surfaces for the PE-PEG_{2000} films which were more comparable to the PEG-containing polyethylenes ($PE/{-}[CH_2CH_2O]_nCH_2CH_2OH$; n = 40–60) studied by Whitesides. Considering these differences, the results of the contact-angle studies summarized in Table I proved informative. The data in this table are static contact angles (Young's angle) and are comparable to but usually slightly less than an advancing angle. There are several significant features about the contact-angle data. First, the contact angles for the glass side of the films were uniformly much less than the contact angle found for the air-film interface. We believe that this reflects a preferential migration of PEG blocks to the contact-angle interface when the film is heated on the glass. Glass is a high-energy substrate while the interface with air represents a low-energy substrate. Thus poly(ethylene glycol) is expected to be in contact with the glass side of the film and polyethylene would be less likely to be at the air–film interface. This behavior is precedented both for a number of other pure polymers and polymer mixtures and blends. For example, contact-angle measurements on pure poly(methyl methacrylate) (PMMA) cast against glass had lower contact angles on the glass–film interface than the air–film interface.[24] The contact angle of high molecular weight PMMA on the glass–film interface was 73° and 82° on the air–film interface. Similar studies have been performed on other blends by Teyssie's group.[25] In all of these cases, there is a preferential segregation of the low-energy polymer or component to the lower energy air–film interface versus a higher energy interface.[26,27]

The data in Table I also show that there was an effect of the weight percent of PE-PEG and the size of the PEG block in the entrapped PE-PEG cooligomer on the extent to which PEG groups were located at the polymer surface. Contact angles at similar weight percentages of PE-PEG were generally lower for films in which the PEG portion of the PE-PEG was larger. Contact angles also gradually increased as the weight percent of the PE-PEG decreased. However, the glass side surfaces always remained significantly more hydrophilic than the starting polyethylene cast under the same conditions, even with low weight percent PEG contents.

In summary, the contact-angle data suggest that some of the PEG groups were located at the outer few angstroms of the film surfaces. The amount of PEG groups at this interface was greatest as expected at the glass–polymer interface. It was also greatest for the larger PEG groups and for higher loadings of PEG. However, for each size PEG the contact angle decrease leveled off by the time the PE-PEG content had increased to about 5% (by weight). Comparison of the contact angle for these PEG-modified polyethylenes with an etched polyethylene with PEG groups at the interface suggests that 2–6% of a PE-PEG diblock cooligomer was needed to produce the same density of polar groups at the surface as in oxidative etching of a preformed film, assuming the PEG groups in our systems had a similar effect as those in Whitesides' work. However, in our case, we only achieved these comparable water wettabilities when we used larger PEG blocks and when we examined the glass side of films cast on and annealed against glass. Contact angles at the air–film surface were largely unchanged although XPS and ATR-IR studies (vide infra) showed that PE-PEG groups were located just below the contact-angle interface.

X-ray photoelectron spectroscopy (XPS) is another spectroscopic tool for studying in detail the surface of a functionalized polyethylene film. Its use as a quantitative tool to analyze the elemental composition of the surface of polymers is well-established. While the depth of analysis will vary with the material studied, it is clearly less than 100 Å. Indeed, with a well-defined system of hydrocarbon films on gold the attenuation length of photoelectrons with energies of 940 eV was less than 30 Å.[17] With the inclusion of variable-angle studies, XPS also provides a measure of depth profiling for functional groups as well. While the only atoms present in our samples were carbon and oxygen, XPS has nonetheless proven useful as a way to verify the trends in surface selectivity seen both in the contact-angle experiments described above and in the IR experiments described below.

Figure 1 shows the results of XPS experiments carried out on three films—the air side of a cast film containing 0.86% PE-PEG_{750}, the glass side of a cast film containing 0.86% PE-PEG_{750}, and the glass side of a cast film containing 12.3% PE-PEG_{750}. In the figure, we have plotted the change in area ratios of the O_{1s} to C_{1s} peaks as a function of the incident angle of the X-rays. The O/C ratios for each film were normalized to the ratio seen for the 82° angle. Since the low angles represent a more surface selective analysis, the data are in effect a profile of the O/C ratio in the outermost 50 Å of these cast films. The results shown in Figure 1 suggest that similar depth profiles are seen for the air and glass sides of the film with a 0.86% loading of PE-PEG_{750} and for the glass side of the 12.3% loaded PE-PEG_{750} film. In each case, the O/C ratio increased, indicating that there was a gradient with increasing concentration of PEG at the surface. Similar gradients are seen in the ATR-IR studies described below

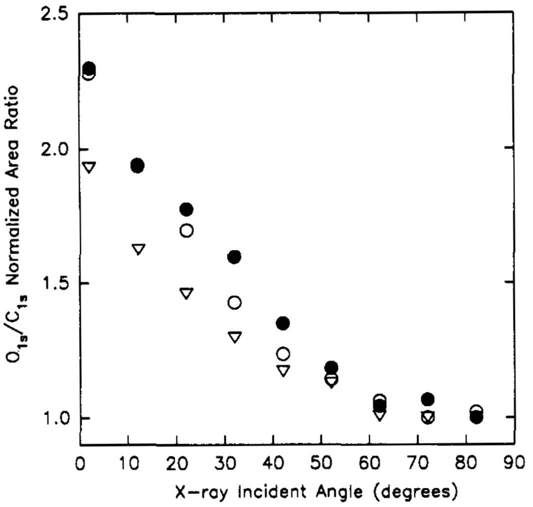


Figure 1. Plot of the O_{1s}/C_{1s} peak area ratio versus X-ray incident angle for XPS spectra of the glass side (●) and air side (○) of films having 0.86% loading of PE-PEG$_{750}$ cast from o-dichlorobenzene at 135 °C and annealed at 155 °C. In addition, the O/C area ratio for the glass side of a film with a 12.3% loading of PE-PEG$_{750}$ is plotted versus the X-ray incident angle (▽). The O/C ratios were normalized to their value at 82°.

in that segregation of PEG groups to the surface is more pronounced with more lightly loaded films. There is little difference in the concentration gradient for the PEG groups in the outermost 50 Å of these films between the glass side and air side of the 0.86% PE-PEG$_{750}$ loaded film. Correction of the O/C area ratios for the 82° angle data for the sensitivity of O_{1s} and C_{1s} gave values of O/C of 0.20 (glass, 0.86% PE-PEG$_{750}$), 0.14 (air, 0.86% PE-PEG$_{750}$), and 0.17 (glass, 12.3% PE-PEG$_{750}$). These values, which should represent the amount of PEG in the outermost 50 Å, indicate that there is more PEG$_{750}$ in this region for the glass side of the film than for the air side of the film. They also indicate that the concentration gradient for PEG groups in the outermost 50 Å of the glass side of the 0.86% PE-PEG$_{750}$ film is greater than that of the glass side of the 12.3% PE-PEG$_{750}$ film. Contact-angle data suggest that the 12.3% PE-PEG$_{750}$ film should have more PEG at the contact-angle interface (the outermost 5 Å) than the 0.86% PE-PEG$_{750}$ film. However, the O/C area ratios for the 0.86% and 12.3% PE-PEG$_{750}$ containing films from a glancing (2°) angle experiment were the same within experimental error. This discrepancy presumably reflects some contamination of the 0.86% PE-PEG$_{750}$ film or a subtle difference in composition of the sub-contact-angle interface for these films. A similar variable-angle study of the glass side of films containing 0.5% PE-PEG$_{2000}$ and 16.3% PE-PEG$_{2000}$ also showed an increase in the O_{1s}/C_{1s} area ratios of 151% and 138% (0.18–0.28 and 0.13–0.18, respectively) as the incident X-ray angle changed from 82° to 2°, respectively.

Blank runs using pure PEG$_{750}$ cast on a copper XPS sample support showed no variation of the O/C ratio with X-ray incident angle. In this case, the O/C area ratio corrected for the number of scans and element sensitivity was between 0.45 and 0.47. The calculated O/C ratio for PEG$_{750}$ (ca. $C_{33}H_{68}O_{17}$) is 0.51.

Our most extensive studies of these entrapment functionalized films used ATR-IR spectroscopy. While the sampling depth of ATR-IR spectroscopy (ca. 1 μm depending on the frequency of the incident radiation) is much deeper than that of XPS, it was the only conveniently available technique to study functional groups in these polymers at depths greater than 100 Å. Initially we examined transmission IR spectra of entrapment-functionalized powders to construct a calibration curve so that we could determine the amount of block cooligomer present in the polymer ATR-IR interface. To do this, we analyzed a series of transmission spectra for a given type of PEG present at varied loading. For each loading we determined the absorbances of the peaks at 1105 cm^{-1}, which corresponded to the C–O stretch of poly(ethylene glycol), and at 1369 cm^{-1}, which was a polyethylene peak. A calibration curve was then constructed with the ratio of the absorbances along the ordinate and $C_{\text{PE-PEG}}/C_{\text{PE}}$ along the abscissa where $C_{\text{PE-PEG}}$ and C_{PE} were the weight percent of the copolymer and virgin polyethylene in the entrapped mixture. Here 1 wt % of the copolymer corresponded to 1 g of the cooligomer added to 99 g of virgin polyethylene. Calibration plots were prepared for PE-PEG cooligomers prepared using methoxy-terminated poly(ethylene glycol) of molecular weight 350, 550, 750, and 2000.

Attenuated total reflectance IR spectroscopy (ATR-IR) has long been used for qualitative analysis of polymer surfaces. Recent efforts have emphasized applications of this technique for quantitative analysis of polymer components.[28,29] Quantitative analysis is important especially for polymer films in which two or more components are present, and the composition of the surface layer is different from that of the bulk. The major problem faced in quantitative analysis using this type of spectroscopy is the necessity of achieving good contact between the polymer film and the internal reflection element.[30] This is an essential factor in obtaining reproducible results. To minimize the impact of this intrinsic problem in measurement of absolute absorbance, we used the technique of band ratioing, which provides an internal standard. The advantages of this technique in quantitative analysis using ATR-IR spectroscopy has been previously described.[31] In our experiments, we checked the reproducibility of our results by ratioing the peaks of interest, removing the sample, replacing it, and analyzing again to replicate the results. The ratios of the two measurements were within 5%. We also used a variable-angle ATR-IR apparatus to study spectra of films taken with varying angles of incidence of the IR radiation. The ability to record spectra with varying angles of incidence allows the study of the structural gradient of the film. Zerbi and others have used this technique to study the variation of crystallinity with depth in commercial polyethylene.[32] All of these ATR-IR studies were carried out for both the air and glass sides of the cast films.

ATR-IR spectra of cast films were run for each mixture of block cooligomer and host polyethylene using 45° KRS-5 or Zn–Se crystals. The ratio of the absorbances at 1105–1369 cm^{-1} were determined for each film. Since the extent of excursion of the evanescent wave from the crystal in ATR-IR spectroscopy is a direct function of the wavelength of the incident beam, the ratios obtained from the ATR-IR spectra were corrected for this effect.[18] The ratio of the weight percent of the cooligomer at the surface to polyethylene at the surface ($C_{\text{PE-PEG(s)}}/C_{\text{PE(s)}}$) was determined from the calibration plot (the subscript s denotes surface measurement). Since $C_{\text{PE-PEG(s)}}$ and $C_{\text{PE(s)}}$ are weight percents and since the only species present were polyethylene (PE) and the cooligomer (PE-PEG), the sum of these weight percents equals 100 (eq 4). The weight

$$C_{\text{PE-PEG(s)}} + C_{\text{PE(s)}} = 100 \tag{4}$$

percent of PE-PEG at the surface (PE-PEG$_{(s)}$) with respect to the total amount of material at the surface was

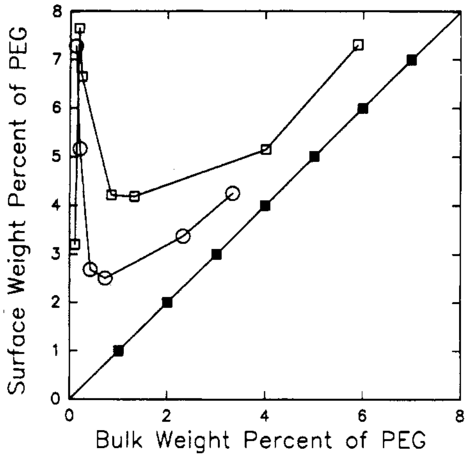


Figure 2. Plot of a non-surface-selective distribution of the weight percent of $PEG_{(s)}$ versus $PEG_{(bulk)}$ (■), the weight percent of $PEG_{750(s)}$ versus $PEG_{750(bulk)}$ (○), and the weight percent of $PEG_{2000(s)}$ versus $PEG_{2000(bulk)}$ (□).

determined using eq 4 and the $C_{PE\text{-}PEG(s)}/C_{PE(s)}$ ratio was then determined from the calibration curve.

The weight percent of $PE\text{-}PEG_{(s)}$ was further related to the weight percent of $PEG_{(s)}$ by a factor which depended on the size and efficiency of functionalization of the oligomer chains. This factor was calculated from the molecular weight of the polyethylene portion of the PE-PEG oligomer and the percentage of chains functionalized with PEG and the PEG molecular weight. These numbers were determined by ^1H NMR spectroscopy (cf. Experimental Section). Using these data, the weight percent of PEG at the surface and in the bulk was calculated from the relevant PE-PEG weight percents measured from IR and initial weights, respectively.

A plot of the surface weight percent of PEG to bulk weight percent of PEG for the glass side of cast films containing cooligomers with PEG groups of molecular weights 750 and 2000 is shown in Figure 2. In the absence of surface effects, the $PEG_{(s)}$ should have been equal to the $PEG_{(bulk)}$. The comparison of the $PEG_{2000(s)}$ and $PEG_{750(s)}$ to this normal distribution shown in Figure 2 indicates that there is a tendency for the PEG groups to concentrate at the surface. However, this effect was most pronounced at weight percents of PEG of less than 2 wt %. At higher overall loadings, the amount of PEG at the surface corresponded more closely to that expected for a normal distribution of PEG throughout the film, although the $PEG_{(s)}$ in our experiments always exceeded the $PEG_{(bulk)}$. The most interesting aspect of these data is the observation that when the loading of PEG was decreased there was a gradual deviation from the normal behavior in that the weight percent of PEG at the surface increased as the bulk loading decreased. The weight percent of PEG at the surface increased with decreased loading until a stage is reached when there is insufficient PEG content for any substantial amount to be on the surface. The implication of these data is that at low loadings of the oligomer there is a tendency for segregation and most of the oligomeric units end up on or near the surface of the film. We have rationalized this effect on the basis that the known segregation of a functionalized ethylene oligomer to the surface of a cast film at low weight percents[4-7] reinforces the expected phase segregation of PEG and produces enhanced surface selectivity. At higher weight percentages of oligomer, a more normal distribution due to phase segregation of PEG throughout the bulk polymer is obtained. This normal distribution might take the form of PEG aggregates throughout the film. Above a certain concentration, PEG groups would phase separate into the bulk because the surface volume is limited. Below this concentration, the surface volume can accomodate essentially all of the block cooligomer present. Similar studies of films containing $PE\text{-}PEG_{350}$ and $PE\text{-}PEG_{550}$ oligomers also showed that, at low total weight percentages of PEG, the weight percentage of PEG at the ATR-IR surface was also increased relative to what would have been expected.

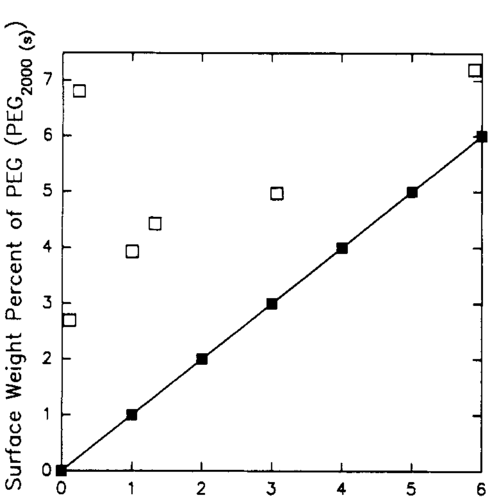


Figure 3. Plot of the surface weight percent of PEG ($PEG_{(s)}$) versus the bulk weight percent of PEG ($PEG_{(bulk)}$) for equal amounts of PEG at the surface and bulk (■) and for the air surface of $PE\text{-}PEG_{2000}$ films (□) cast from o-dichlorobenzene at 135 °C.

Conversion of the weight percent data in Figure 2 to a mole ratio of $moles_{PE\text{-}PEG}/moles_{PE}$ at the surface overemphasizes the surface selectivity but is nonetheless interesting. In the case of $PE\text{-}PEG_{2000}$ (0.65%) and $PE\text{-}PEG_{750}$ (0.48%), these mole ratios approached 10/1.

While the general effect of surfactant selectivity at low loadings is common for all the oligomers, comparison of the data for the various molecular weights of PEG shows that there were some differences. Specifically, the surface segregation of PEG_{2000} seems more important than that for PEG_{750} in Figure 2. The variation probably reflects the extent to which phase separation occurs between PEG of different molecular weights. Both a PEG_{750} and PEG_{2000} oligomer are hydrophilic and incompatible with the host polyethylene. The small differences between $PE\text{-}PEG_{750}$ and $PE\text{-}PEG_{2000}$ presumably reflect the greater PEG character of the latter block cooligomer. In this explanation, the difference would be that high molecular weight PEG is more phase separated than PEG of lower molecular weight.

Further confirmation of the surface selectivity of low-loadings PEG was seen in a graph of the PEG_s versus PEG_{bulk} for the air side of a film containing $PE\text{-}PEG_{2000}$ in Figure 3. Just as in Figure 2, there was an enhancement of the amount of PEG at the surface. This enhanced surface concentration was present at all loadings of PE-PEG and was more pronounced for lower loadings. While there were small differences in the weight percent of PEG at the air side and glass side for a given bulk concentration of PE-PEG, these differences were within experimental error, suggesting that the air and glass sides of the film were comparable so far as an ATR-IR analysis is concerned. Apparently while the casting interface (glass versus air) is perturbed on the basis of the data in Table I, the deeper surface volume sampled by ATR-IR is less affected.

To further confirm that we have more PEG at low loadings on the surface, we performed depth studies on

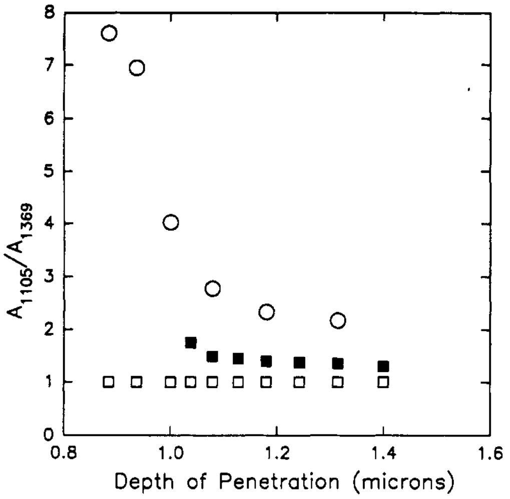


Figure 4. Plot of the ratio of the absorbance at 1105 cm^{-1} to the absorbance at 1369 cm^{-1} (A_{1105}/A_{1369}) using variable-angle ATR-IR spectroscopy to sample the polymer film at varying depths to show the relative increase in absorbance of the PEG peak (1105 cm^{-1}) at shallower depths.

our films. The depth of penetration of the excursion wave in ATR spectra is given by eq 5.[18] On the basis of this

$$d_p = \frac{\lambda}{2\pi n_1 [\sin^2 \Theta - (n_2/n_1)^2]^{1/2}} \tag{5}$$

λ = the wavelength of the radiation in microns

d_p = the depth of penetration of the IR radiation

n_1 = the reactive index of the ATR crystal

n_2 = the refractive index of the polymer film

Θ = the angle of incidence of the IR beam on the ATR crystal

equation, the depth of penetration for different angles and for the wavelengths of interest were calculated. Then the ratio of absorbances due to the doublets at 1369 and 1352 cm^{-1} (peaks from polyethylene) and the ratio of absorbances due to the peaks at 1105 and 1263 cm^{-1} [peaks from poly(ethylene glycol)] were calculated. Both the ratio of A_{1369}/A_{1352} and the ratio of A_{1105}/A_{1263} were independent of the depth of analysis. However, the ratio of A_{1105}/A_{1352} and A_{1105}/A_{1369} did increase as the depth of analysis decreased. This effect is shown in Figure 4 both for the glass side of a 0.65 wt % PE-PEG_{2000}/PE film and for a 12.3 wt % PE-PEG_{750}/PE film. Figure 5 shows a similar graph comparing two PE-PEG_{2000} films with 0.65 and 16.2 wt % of oligomer. If there was no surface selectivity, these ratios should not change (they should equal 1). There is a somewhat larger change for the PE-PEG_{2000} film than for the PE-PEG_{750} film and for the film with a lower PE-PEG loading, supporting the general trend described above which indicated that selective surface segregation of PEG groups did occur and that such effects were greatest at low weight percent PEG loadings and with higher PEG molecular weights.

Finally, chemical etching of a film containing 4.4 wt % PE-PEG_{750} was used to confirm the gross distribution of PEG groups deduced from the above spectroscopic studies. In this experiment, a film containing PE-PEG was immersed in an oxidizing mixture containing CrO_3, sulfuric acid, and water in a 14/21/9 (w/w/w) mixture for 10 min at 50 °C. Analysis of the product film by transmission IR spectroscopy showed that no PEG groups remained, indicating that >90% of the PEG groups which had been entrapped as PE-PEG block cooligomers had been chemically removed. The film thickness as measured by the interference fringe peaks was 45 μm. The lack of change in film thickness during this oxidation coupled with the loss of the IR signals due to the PEG groups support the implication of the ATR-IR experiments that >90% of the PEG groups were located in the outermost few microns of the film.

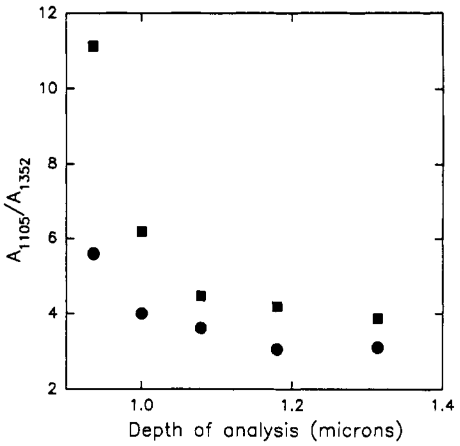


Figure 5. Plot of the ratio of the absorbance at 1105 cm^{-1} to the absorbance at 1352 cm^{-1} (A_{1105}/A_{1352}) using variable-angle ATR-IR spectroscopy to sample the polymer film at varying depths to show the relative increase in absorbance of the PEG peak (1105 cm^{-1}) at shallower depths for a 0.65 wt % PE-PEG_{2000} (■) and a 16.2 wt % PE-PEG_{2000} film (●).

Conclusions

Entrapment functionalization is a surface-selective method. It provides the equivalent of a grafted film through a blendinglike procedure. The selectivity is highest at low loadings of the cooligomer. Enhanced selectivity is observed with high molecular weight poly(ethylene glycol). There is apparently no detectable difference with respect to the hydrophilic groups between the glass and air side of the film as detected by ATR. However, the two surfaces behave quite differently in the contact angle interface which is reflected to a certain extent in XPS studies.

Note Added in Proof: Tensile properties of cast films of pure polyethylene and of polyethylene containing 1% PE-PEG_{2000} were comparable (3037 and 3259 psi tensile strength, respectively), showing that entrapment did not produce a significant change in bulk film properties.

Experimental Section

General Methods. Ethylene and carbon dioxide were obtained from Matheson Co. Other chemicals and reagents were obtained from Aldrich Chemical Co. Hydrocarbon solvent was 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.

Transmission IR spectra of polymer powders (i.e., polyethylene or entrapment-functionalized polyethylene or copolymer) were taken using thin translucent disks prepared by a pressed-disk technique. IR spectra were recorded on Mattson Galaxy 4021 FT IR spectrometer. The spectrometer was purged with nitrogen on a continuous basis. ATR spectra were recorded in the same spectrometer using either a Wilks Model 10 ATR accessory with a 45 ° KRS-5 crystal or a Seagull accessory obtained from Harrick Scientific Co. with a Zn–Se crystal. Spectra were recorded at 1 cm^{-1} resolution using a Hg–Cd–Te detector. XPS spectra were recorded on a Hewlett-Packard 5950A ESCA spectrometer using a 600-W Al $K\alpha$ source. Samples were mounted on a copper plate using double-sided Scotch tape. ^1H NMR spectra were recorded on a Gemini 200 200-MHz NMR spectrometer at 105 °C in C_7D_8 and chemical shifts are reported relative to HMDS. Contact-angle measurements were determined using a Ramè-Hart contact-angle goniometer at 100% relative humidity at ambient temperature. All measurements were performed using the sessile drop method with doubly distilled water. Measurements were made with drops of 1-μL volume after ca. 15 s and reported values were the average of eight measurements at various places on the same film sample. The values of contact angle measurements varied by ±3°.

Polymer Materials. The high molecular weight host polyethylene used was obtained from Allied Corp. This polymer had an average molecular weight of between 1.8×10^6 and 2×10^6. Short-chain oligomers were removed from the polymer 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. Poly(ethylene glycol) samples were obtained from Aldrich Chemical Co. and used without further purification. The M_n value for the methoxy-terminated poly(ethylene glycol) was confirmed by end-group analysis using ^1H NMR spectroscopy.

Preparation of Lithiated Ethylene Oligomer (1).[21] A dry 500-mL Fischer–Porter pressure both 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 evacuated and purged with N_2 three times. Dry heptane (250 mL), 9.2 mL of 1.6 N *n*-BuLi in hexane, and 2 mL of *N,N,N′,N′*-tetramethylenediamine 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 initially homogenous. After 30 min, 1 precipitated. The reaction was continued for 60 h.

Preparation of Carboxyl-Terminated Ethylene Oligomer 2. The suspension of oligomer 1 in heptane was cooled to −78 °C using a dry ice–acetone bath. Any ethylene in the reactor was removed by applying a vacuum 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 added to a glass thimble in a jacketed Soxhlet extractor and extracted with hot toluene for 2 days. Extraction was facilitated by attaching a trap to the apparatus to remove any water (from the HCl). The final product was recovered by cooling the hot toluene solution to precipitate 2. Filtering and vacuum drying yielded the final product (mp 120–124 °C). Esterification of this product with methyl alcohol yielded a methyl ester that was analyzed by ^1H NMR spectroscopy. End-group analysis of this ester indicated that the efficiency in the carboxylation was typically 61% and that the M_n was 2250. The product polymer was also characterized by IR spectroscopy and had a distinctive carbonyl peak at 1710 cm^{-1}. On esterification, the $\nu_{C=O}$ shifted to 1735 cm^{-1}. Prior work had shown that any contamination with ketone byproduct (from the carboxylation) was evident at this point by the presence of a residual carbonyl peak at 1705 cm^{-1}.[21]

Preparation of Block Copolymer (PE-PEG). To about 0.5 g of carboxylic acid terminated polyethylene was added about 2 g of monomethoxy-terminated poly(ethylene glycol) and 0.1 g of *p*-toluenesulfonic acid. The contents of the flask were refluxed in 100 mL of toluene overnight. The resulting solution was cooled and the copolymer precipitated out. The PE-PEG copolymer was separated from the toluene solvent by centrifugation. Ether was added to the resulting solid and the final product was isolated by filtration and then dried overnight under vacuum. The block cooligomer so formed was characterized by IR and NMR spectroscopy: IR (KBr pellet) 1735, 1472, 1462, 1369, 1105, 730, and 720 cm^{-1}; ^1H NMR (105 °C, C_7D_8) 0.9 (t), 1.4 (br s), 3.15 (s), 3.4 (t), and 4.15 (t). The area ratio of the peaks at δ 3.15 to those at δ 4.15 was 3/2. The peak ratio of δ 3.4 to δ 3.15 depended on the oligomer size but was the same in the block cooligomer as it was in the poly(ethylene glycol) used to prepare the particular oligomer. This indicates that there was no unreacted poly(ethylene glycol) present. These area ratios, the area of the methyl group at δ 0.9, and the area of a known amount of added internal standard 1,1,2,2-tetrachloroethane were used to measure the M_n values listed in Table II.

Table II
Molecular Weights of PE-PEG Cooligomers

starting PEG-OCH_3[a]	PE-PEG-OCH_3 cooligomer[b]	% chains functionalized[c]
350	2215	58
550	2550	60
750	3070	57
2000	3841	81

[a] The M_n of the pure poly(ethylene glycol) was determined by ^1H NMR spectroscopy based on the integrals for the methylene groups adjacent to the oxygen and the terminal methoxy groups. [b] The M_n of the cooligomer was determined using a known amount of 1,1,2,2-tetrachloroethane as an internal standard for ^1H NMR spectroscopy. [c] The percentage of chains functionalized derives from the efficiency of the initial carboxylation. The other chains present were H-terminated ethylene oligomers.

General Procedure for Entrapment Functionalization.[4] In a typical procedure, 100 mg of the PE-PEG cooligomer prepared above was added to 10 g of host high-density polyethylene in a 100-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 PE-PEG cooligomer which precipitated was recovered by filtration and washed with 150 mL of toluene and dried under reduced pressure for 24 h. Similar procedures were used to prepare other loadings of PE-PEG in polyethylene varying the quantity of high density polyethylene and functionalized oligomer as necessary.

Preparation of Entrapment-Functionalized Polyethylene Films. A solution of the PE-PEG oligomer entrapped in polyethylene (0.2 g) (this is equivalent to using a weighed amount of the pure block cooligomer with a weighed amount of pure polyethylene) was prepared using 30 mL of 1,2-dichlorobenzene at 140 °C. Upon dissolution of the polymer, the solution was immediately poured into a flat-bottomed dish maintained at 135 °C in an explosion-proof Friction-Aire oven. The dish was covered with a pane of glass and the solvent was allowed to evaporate. The dish was removed from the oven and allowed to cool to room temperature. It was then placed in a vacuum oven and maintained at 155 °C and 0.05 Torr for 30 min. Under these conditions, the polymer was in the form of a melt 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 casting solvent in the product film was verified by IR spectroscopy by the absence of the strong aromatic and C–Cl stretches observed in dichlorobenzene. IR spectroscopy also showed no −OH stretching.

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