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Polypropylene Surface Modification by Entrapment Functionalization

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ABSTRACT: A new approach to prepare surface-functionalized polypropylene using block cooligomers of propylene and acrylate esters is described. Using boron-promoted radical polymerization and a vinyl-terminated polypropylene oligomer, block cooligomers of propylene and *tert*-butyl acrylate were prepared. Codissolution of such cooligomers with excess isotactic polypropylene and film casting produced functionalized films. Acidolysis of the *tert*-butyl esters at the surface of these films produced a poly(acrylic acid)-grafted polypropylene film that could be further modified chemically. Incorporation of pH-sensitive dyes into this poly(acrylic acid) surface in turn produced films whose reactivity in proton-transfer chemistry in various solvent suspensions was studied as a function of solvent.

Polyolefins and polypropylene in particular are of increasing interest because of developments in metallocene polymerization chemistry. However, while new polymerization chemistry affords new routes to new types of polyolefin homo- and copolymers, many applications of polyolefins entail postpolymerization modification procedures. Surface modifications to increase surface reactivity or hydrophilicity are examples of such postpolymerization chemistry.[1−3] Here we describe our initial work leading to new surface modification chemistry applicable to polypropylene. The approach described here uses a blending methodology we have termed entrapment functionalization.[1] It uses terminally functionalized polypropylene oligomers available through metallocene chemistry as starting materials to prepare block copolymers that in turn are mixed with a host polypropylene to prepare a modified, solvent-cast film.

Polypropylene surface modification has been accomplished in the past by a variety of procedures.[3−9] Plasma oxidations are generally applicable methods that serve to introduce various oxygen, nitrogen, and halogen functionalities.[1,4,5] Solution oxidations using reactive oxidants have successfully produced oxygenated and sulfonated surfaces.[6,7] Once functionalized, radical grafting has been used as a second stage method to produce a modified surface.[3,8,9] The goal in many of these cases is to introduce high concentrations of functional groups or high densities of graft copolymer. In the case of solution-phase oxidations, the reactivity of polypropylene toward ablative etching chemistry is a problem in this regard. Here we describe our work on an alternative surface modification technique that relies on mixing small amounts of a preformed polypropylene block cooligomer with an excess of a host polypropylene to produce a surface-modified polypropylene film that is in turn amenable to further chemistry.

In our prior work, we have shown that mixing terminally functionalized oligomers of ethylene with a large excess of a host polyethylene leads to “surface” functionalized polyethylene powder precipitates or solvent-cast films using the approach shown in Scheme 1.[1,10,11]

Since this mixing approach to polyethylene functionalization is a general approach, we expected it to be applicable to other polyolefins including polypropylene. The ready availability of polypropylene oligomers with defined stereochemistry and terminal functionality has prompted us to test this hypothesis. The results described here show both that vinyl-terminated polypropylenes can be readily modified to produce terminally functionalized polypropylene oligomers and that the entrapment chemistry illustrated in Scheme 1 is indeed applicable to polypropylene functionalization.

Results and Discussion

The success of the blending approach in our past work in polyethylene functionalization relies in large part on the availability of appropriately terminally functionalized polyethylene oligomers.[12−14] In our previous work on polyethylene surface modification by entrapment functionalization, the necessary polyethylene oligomers were prepared by anionic oligomerization of ethylene.[12] Further elaboration of the product terminally functionalized ethylene oligomers with simple functional groups or polymers then produced materials suitable for entrapment chemistry using high molecular weight polyethylene as a host matrix. However, polypropylene oligomers could not be synthesized by the anionic method used for polyethylene. Propylene has acidic, allylic C−H’s that preclude this anionic chemistry. Moreover, polypropylene oligomers are not readily available via radical polymerization chemistry.

Functionalized polypropylene oligomers can be prepared by thermolytic cracking of polypropylene. Simple cracking of polypropylene leads to vinyl-terminated oligomers.[15] A practical functionalized polypropylene can also be prepared by high-temperature grafting of polypropylene with maleic anhydride—a reaction that can form anhydride-terminated oligomers.[16,17]

Metallocene polymerization is a more practical synthetic route leading to functional polypropylene oligomers. Metallocene catalysts produce highly isotactic or syndiotactic polymer with excellent physical attributes. Moreover, these polymerizations can produce lower molecular weight polypropylene with terminal double bonds.[18−20]

While any of the procedures described above should, in principle, be useful as a route to oligomers for the chemistry described herein, we have concentrated on using oligomers derived from metallocene polymeriza-

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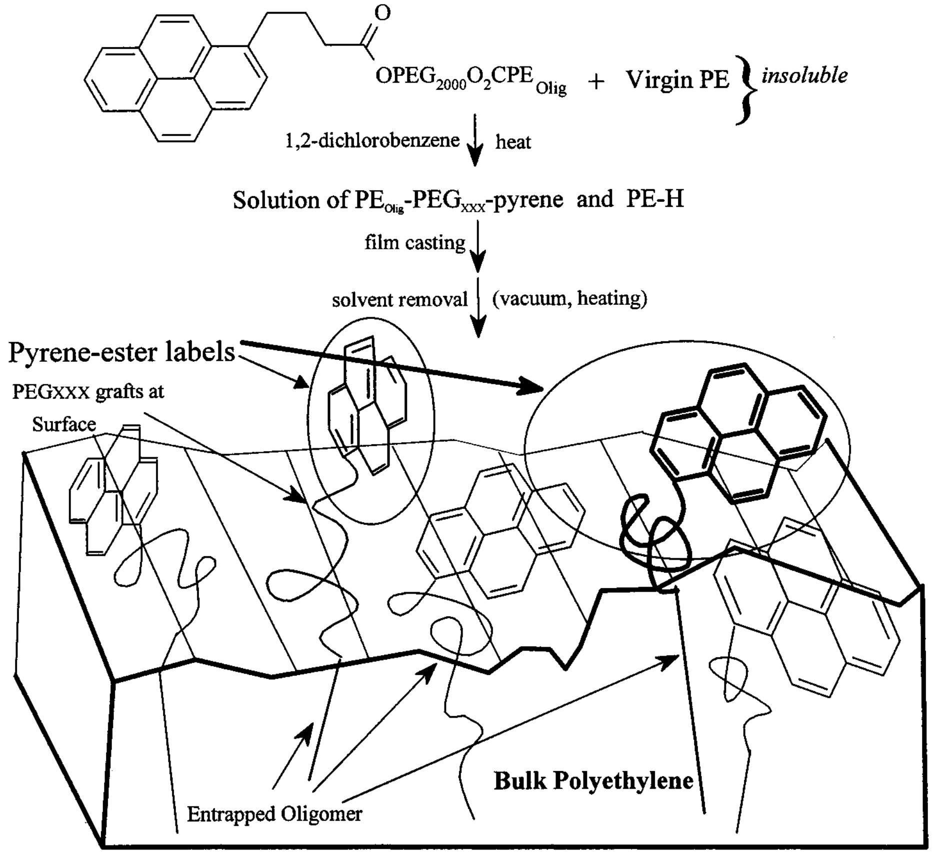
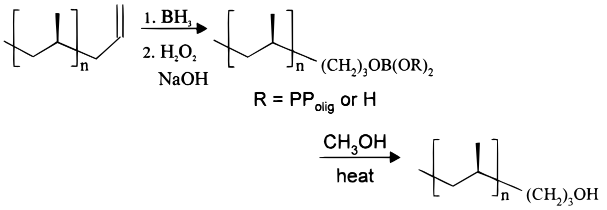
Scheme 1. Entrapment Functionalization of Labeled Block Cooligomers as a Route to Surface-Functionalized Polyethylene Films



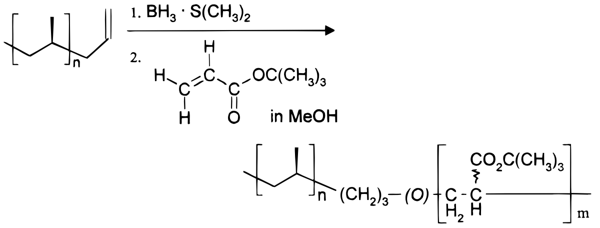
tion. Such vinyl-terminated polypropylene oligomers produced by metallocene polymerization appropriate for this chemistry were obtained as a gift from Exxon.[21] Three different samples of polypropylene oligomers were provided and had weight average molecular weights of 2000, 3000, and 8500, respectively, as determined by Exxon. For further studies, the sample of M_w 3000 was chosen due to its solubility characteristics and moderate chain length that makes end group analysis more facile.

Polypropylene oligomer modification was achieved by hydroboration.[22] To judge the effectiveness of this chemistry, we first hydroborated the oligomer with BH_3-SMe_2 and then oxidized the resulting oligomeric alkylborane with alkaline hydrogen peroxide. The initial product was a boric acid ester. Transesterification with methanol produced trimethoxy borate and a hydroxymethyl-terminated polypropylene oligomer whose M_n corresponded to that measured for the starting vinyl-terminated oligomer based on ^1H NMR spectroscopic analysis (eq 1). Model reactions such as esterification (acetic anhydride) or ether formation (tetrahydropyranyl ether) show that this hydroxymethyl-terminated oligomer could itself serve as a route to diblock copolymers or as a synthetic precursor for a radical initiator for subsequent polymerization. However, given the intermediacy of an alkylborane intermediate in this chemistry and the known utility of alkylboranes as initiators for radical polymerizations,[23-25] we chose to use reactions of the intermediate borane as a route to diblock cooligomers of polypropylene.



(1)

Our initial work leading to diblock cooligomers of polypropylene from a polypropylene borane intermediate has been confined to formation of acrylate cooligomers and largely to poly(*tert*-butyl acrylate)-*co*-polypropylene cooligomers. Poly(*tert*-butyl acrylate) was of specific interest because this acrylate ester is easily hydrolyzed to form a poly(acrylic acid) that can in turn be further derivatized.[4,26] The desired block cooligomers were prepared using the chemistry described in eq 2.



(2)

The terminally unsaturated polypropylene oligomers were first dissolved in toluene at 85 °C and then were allowed to react with excess borane dimethyl sulfide (2% in toluene). The solution was stirred for 15 min, after which a solution of methanol and *tert*-butyl acrylate monomer was added. After 1 h at 85 °C, solvent, residual monomer, trimethoxyborate, and methanol were removed under reduced pressure using a rotary evaporator. The crude block cooligomer was then dried under vacuum overnight.

Table 1. Graft Polymerization of *tert*-Butyl Acrylate Monomers onto Vinyl-Terminated Polypropylene via an Intermediate Polypropyl Borane Using Adventitious Oxygen Initiation[a]

TBA:PP-CH=CH$_2$ (equiv:equiv)	PTBA graft length in cooligomer product
102:1	47.0
82:1	34.0
61:1	31.0
51:1	19.0
43:1	10.0
40:1	8.5
36:1	6.4

[a] Graft polymerizations were carried out according to the procedure described in the Experimental Section, and the product block cooligomers were analyzed by ^{1}H NMR spectroscopy at 100 °C in toluene-d_8 by comparing the integrals for the methine protons of the *tert*-butyl acrylate block (δ 2.5) with the signals due to the polypropylene methyl groups (δ 1).

The product block cooligomers were characterized by high-temperature ^{1}H NMR spectroscopy using toluene-d_8 as solvent. The relative chain lengths of the polypropylene and poly(*tert*-butyl acrylate) blocks were determined by using the ^{1}H integration from the pendant methyl groups of polypropylene at δ 1 vs the relative integration of the methine protons of the *tert*-butyl acrylate segment δ 2.5.

As shown in Table 1, there was a roughly linear relationship between the chain length of the *tert*-butyl acrylate segment of the copolymer and the concentration of *tert*-butyl acrylate monomer present in the reaction vessel. Thus, by adjusting the concentration of monomer, *tert*-butyl acrylate chains of various lengths could be polymerized from the terminus of the polypropylene oligomers. In the entrapment experiments, diblock cooligomers used for entrapment functionalization contained a polypropylene segment consisting of 35 repeat units, on the basis of NMR and molecular weight data provided with the oligomers, and a poly(*tert*-butyl acrylate) segment with a chain length of 47 repeat units, as determined by NMR spectroscopy as described previously.

Teroligomers of methyl acrylate, *tert*-butyl acrylate, and polypropylene could also be prepared by borane-initiated radical polymerization. These experiments such as the simpler grafting in Table 1 showed that the extent of acrylate grafting onto polypropylene roughly paralleled the ratio of acrylate monomer to vinyl-terminated polypropylene. Moreover, cooligomerizations of methyl acrylate and *tert*-butyl acrylate onto these vinyl-terminated polypropylenes showed that the ratio of methyl acrylate/*tert*-butyl acrylate in the product teroligomer also paralleled the ratio of the starting acrylate ester monomers.[27]

We tried two approaches to synthesize surface-functionalized polypropylene films using the oligomers listed in Table 1. The first approach used acidolysis of the poly(*tert*-butyl acrylate)-*co*-polypropylene cooliogmer to form a polypropylene-*co*-poly(acrylic acid) block cooligomer (PP$_{\mathrm{Olig}}$-*co*-PAA$_{\mathrm{Olig}}$). As expected, acidolysis of this diblock cooligomer using *p*-TsOH in benzene at 60 °C was successful as judged by the disappearance of the $\nu_{\mathrm{C=O}}$ ester absorbance at 1728 cm^{-1} and the appearance of a new, broader $\nu_{\mathrm{C=O}}$ acid absorbance peak at 1710 cm^{-1} in the FTIR spectrum of the cooligomer. Confirming IR evidence for hydrolysis was seen in the reduction of the C–O stretch at 1150 cm^{-1} on going from the ester- to acid-containing graft. However, while the hydrolysis of the poly(*tert*-butyl acrylate) graft was facile, as expected, the PP$_{\mathrm{Olig}}$-*co*-PAA$_{\mathrm{Olig}}$ block cooligomer was insoluble in solvents that the host polypropylene dissolved in, precluding entrapment functionalization. Therefore, entrapment experiments and other syntheses focused on acrylate ester–propylene block cooligomers.

Fortunately, blending of the poly(*tert*-butyl acrylate)-*co*-polypropylene followed by hydrolysis was more successful as a route to polypropylene films functionalized with accessible, reactive poly(acrylic acid) grafts. These successful entrapment experiments involved mixing 3 wt % of the diblock cooligomer with virgin polypropylene. Heating in *o*-dichlorobenzene produced a homogeneous polymer solution that was in turn transferred to a preheated casting dish and placed in an explosion-proof oven for removal of solvent at 135 °C. After the casting solvent had been removed (this was confirmed by the absence of absorptions due to *o*-dichlorobenzene at 748 cm^{-1} in the IR spectrum of the film), the polymer film was then removed from the casting dish and cut into 3 × 1 cm strips for further experimentation. The films prepared by this solvent casting were determined to be 20 μm thick based on the amount of polypropylene used and the dimensions of the casting dish. This thickness estimate was confirmed by physical measurement of the thickness of a multiply folded film using a micrometer.

Transmission Fourier transform infrared (FTIR) and attenuated total reflectance infrared (ATR-IR) spectroscopic studies of the polymer film after entrapment showed the distinctive carbonyl stretch associated with the ester of the *tert*-butyl acrylate groups at 1728 cm^{-1}. Moreover, comparison of transmission IR vs ATR-IR spectra provided evidence of an enhanced presence of *tert*-butyl acrylate functionalities at the film surface. By looking at the ratio of the relative areas for aliphatic C–H stretching at 2900 cm^{-1} to the area of the $\nu_{\mathrm{C=O}}$ stretch at 1728 cm^{-1} compared to the area in the ATR-IR (3.6) and transmission IR spectrums (161.2), it was evident that the more surface selective ATR-IR spectrum showed a greater abundance of carbonyl groups relative to the aliphatic absorbance expected for bulk polymer. This 45-fold enhancement of *tert*-butyoxycarbonyl groups at the ATR-IR surface of these films was in agreement with our prior work on entrapment-functionalized polymer surfaces functionalized with poly(ethylene oxide)–polyethylene block cooligomers where IR spectra also indicated modest surface selectivity in diblock cooligomer entrapment.[10]

The *tert*-butyl acrylate ester groups in the entrapment-functionalized polypropylene film were then hydrolyzed by placing the film in a solution of benzene and excess *p*-toluenesulfonic acid for 4 h at 60 °C. Hydrolysis of the ester was confirmed by a shift and broadening of the ester carbonyl from 1728 to 1710 cm^{-1} and by the reduction of the ester C–O stretch at 1150 cm^{-1}. Further evidence for the presence of carboxylic acid groups was provided by results from treatment of the hydrolyzed film with sodium ethoxide in ethanol or ammonium hydroxide in THF. Deprotonation led to nearly complete reduction of the carbonyl stretch at 1710 cm^{-1} and formation of a new broad peak at 1565 cm^{-1} commensurate with the formation of the carboxylate anion even in the case of the poorer solvent ethanol.

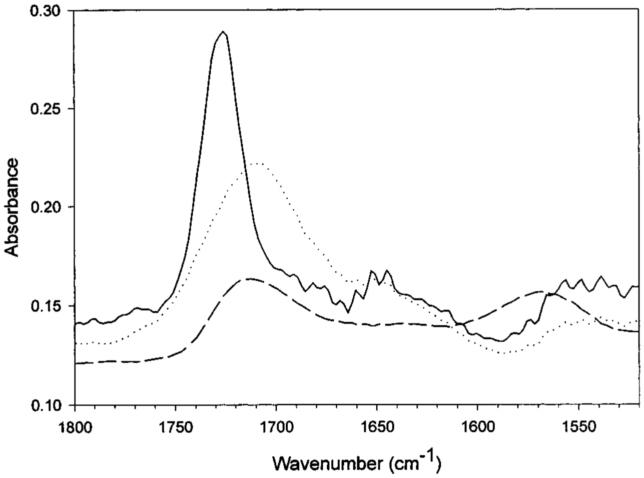


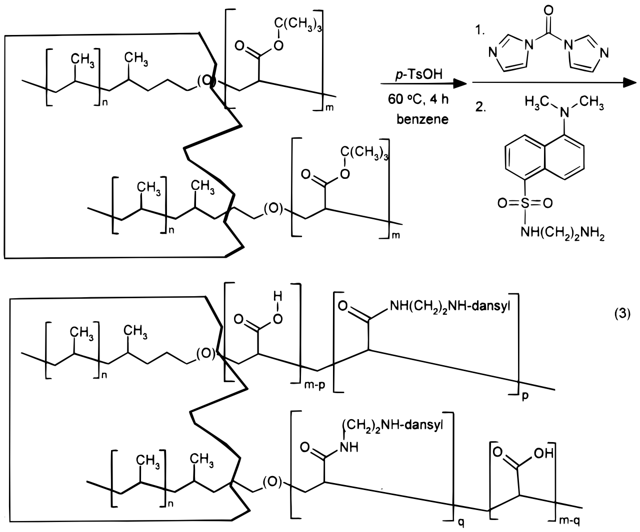
Figure 1. FT-IR transmission spectra of polypropylene functionalized with PP$_{Olig}$-*co*-TBA$_{Olig}$ (—), PP$_{Olig}$-*co*-PAA$_{Olig}$ (• • •), and PP$_{Olig}$-*co*-PAA$_{Olig}$-Na$^+$ (- - -).

While the above experiments confirm incorporation of the block copolymers and supported the expectation that some surface selectivity had occurred in the functionalization/fabrication process, contact angle analysis of the films containing poly(acrylate ester) or poly(acrylic acid) did not show changes consistent with significant changes in the outermost 5 Å of these polypropylene films in water. Specifically, a polypropylene film cast as described above without any cooligomer had a θ_a of 108°. Films containing PP$_{Olig}$-*co*-PTBA$_{Olig}$, PP$_{Olig}$-*co*-PAA$_{Olig}$ (after hydrolysis of the *tert*-butyl ester), or PP$_{Olig}$-*co*-PAA$_{Olig}$-NH_4+ (after hydrolysis and treatment with $NH_4 + OH^-$ in THF) had experimentally indistinguishable θ_a values of 112, 113, and 114°.

The contact angle experiments indicate that the polar block of the PP$_{Olig}$-*co*-PTBA$_{Olig}$ or the PP$_{Olig}$-*co*-PAA$_{Olig}$ cooligomers are buried below the outermost 5 Å of the cast films. However, our other experiments (e.g., Figure 1) suggested that these polar groups were accessible to reagents when these functionalized PP films were suspended in solvents that do not swell polypropylene. The ambiguities between these experiments arise from the ambiguities associated with the question of what constitutes surface functionalization of a polymer film when a film is immersed in a solvent. This reflects the fact that the surface of a functional polymer film—especially the surface of a functionalized polymer film in contact with a condensed phase—is not easily defined. We and others have discussed this issue previously.[28,29] Experiments below probe these questions for these polypropylene films by attaching fluorescent probes to the carboxylic acid groups of the block cooligomer. The results show that these entrapment films are indeed "surface" functionalized if one considers reactivity toward polar reagents as opposed to just contact angle analysis.

Many types of probe molecules have been used previously to characterize polymer surfaces. UV/visible chromophores, spin labels, and fluorescent molecules are a few of the common types of probes that have been used. For our purposes, the fluorescent probe, dansyl, was chosen as a suitable tool for characterization of the film surface since it could be used to probe solvation (solvatochromic shifts in fluorescence λ_{max}) and reactivity (protonation/deprotonation effects on dansyl fluorescence intensity).[30]

PP$_{Olig}$-*co*-PAA$_{Olig}$ block cooligomers entrapped in polypropylene were coupled to a dansylated amine by an amide bond using the chemistry shown in eq 3. The product dansyl-labeled films were cleaned by Soxhlet extraction with CH_2Cl_2 for 12 h. The entrapment-functionalized polypropylene films created in this manner fluoresced bright blue/green when irradiated with UV light. Control experiments wherein the dansylamine in CH_2Cl_2 was exposed to films containing unactivated PP$_{Olig}$-*co*-PAA$_{Olig}$ block cooligomers showed no fluorescence. Transmission and ATR-IR spectra of the PP$_{Olig}$-*co*-PAA$_{Olig}$-CONH$(CH_2)_2$NH-dansyl product showed a ca. 25% decrease (average of three runs) in the intensity of the carboxyl peaks after this labeling procedure and indicated the presence of amide. The presence of peaks attributable to the dansyl group at 570 and 630 cm^{-1} along with the intense fluorescence of the dansyl-labeled films confirmed covalent labeling of the PAA grafts. However, while we were able to qualitatively confirm incorporation of dansyl labels, overlap of the carbonyl peaks in the IR spectra precluded an accurate quantitative assessment of the extent of functionalization. Solely on the basis of the decrease in the $-CO_2H$ intensity, we can, however, estimate that ca. 25% of the carboxyl groups are labeled.



(3)

Several fluorescence studies were used to examine solvation and reactivity at these functionalized polypropylene/solvent interfaces. These include both solvatochromic studies of the effect of solvent on the λ_{max} of the entrapped PP$_{Olig}$-*co*-PAA$_{Olig}$-CONH$(CH_2)_2$NH-dansyl and studies of the reactivity of the PP$_{Olig}$-*co*-PAA$_{Olig}$-CONH$(CH_2)_2$NH-dansyl toward acidic alcohol solutions. In the latter case, we were able to study the reversibility of dansyl protonation in PP$_{Olig}$-*co*-PAA$_{Olig}$-CONH$(CH_2)_2$-NH-dansyl.

Our initial studies suspended a polypropylene film containing PP$_{Olig}$-*co*-PAA$_{Olig}$-CONH$(CH_2)_2$NH-dansyl in various solvents to examine solvation. The sensitivity of dansyl groups to solvent polarity is well established in other studies and represents a simple way to test how a functionalized polymer interface swells in different solvents.[30] In the case of dansyl-functionalized polypropylene films, the λ_{max} of the entrapped dansyl group did shift as the environment was changed from air to water and through methanol, ethanol, 2-propanol, and *tert*-butyl alcohol. The shifts in λ_{max} for these solvents represents a change in the environment in which the dansyl species are located, providing direct evidence that at least a portion of the dansyl groups in the polypropylene film containing PP_{Olig}-*co*-PAA_{Olig}-CONH-$(CH_2)_2$NH-dansyl are at the solvent/polymer interface. The emission maxima of these dansyl-labeled polypropylene films containing cooligomers PP_{Olig}-*co*-PAA_{Olig}-$CONH(CH_2)_2$NH-dansyl suspended in various solvents varied in the following way: air, $\lambda_{max} = 495$ nm; water, $\lambda_{max} = 493$ nm; methanol, $\lambda_{max} = 508$ nm; ethanol, $\lambda_{max} = 500$ nm; 2-propanol, $\lambda_{max} = 490$ nm; and *tert*-butyl alcohol, $\lambda_{max} = 490$ nm. Interestingly, while the series of alcohol solvents exhibit successive bathochromic shifts in λ_{max}, water is more like air as a solvent. This suggests little solvation of the surface by water, a conclusion in accord with the contact angle data reported above. However, solvation by alcohols is evident, accounting for the reactivity of the bound carboxyl groups and of the dansyl groups in such solvents. To further test the solvatochromic shifts associated with the polarity of the local environment of the dansyl probes, coderivatized surfaces containing dansyl/ethanolamine and dansy/taurine (2-aminoethansulfonic acid), respectively, were prepared. After activation of the PAA graft segments with CDI, a 1:1 (mol/mol) solution of dansyl and either taurine or ethanolamine was added to the suspended film. The λ_{max} of the washed and dried product films were compared to those containing only dansyl. The films containing dansyl and the more polar hydroxyl and sulfonic acid functionalities of the ethanolamine and taurine showed shifts in λ_{max} in air from 495 nm for the film containing only dansyl to 505 nm for the films containing the more polar substituents, suggesting the dansyl probes were indeed residing in a more polar local environment. The extent of the reactivity and accessibility of the dansyl probes in the dansyl-derivatized films were tested using protonation experiments, as described below.

When dansyl is protonated, its fluorescent properties are quenched. Therefore, by utilizing various acidic solvents, insight into the polymer/solvent interface can be gained by relating the quenching ability of a given solvent to the properties of that solvent. For example, if the fluorescence was rapidly and completely quenched in an acidic solvent, it could be inferred that all of the dansyl groups must be easily accessible to reagents in that solvent. Moreover, if a solvent were chosen that is not expected to penetrate into the bulk polypropylene, this would imply that the dansyl groups were all at the film/solvent interface. Conversely, if only an acidic-containing solvent considered to be a good solvent for polypropylene were to decrease the fluorescence intensity, it may be concluded that the dansyl groups reside in a more interior position that is only accessible when the polymer is swollen by a solvent capable of penetrating the bulk polypropylene.

Our ester hydrolysis experiments above already confirmed that toluene was a suitable solvent for modification of the block cooliogmers. Indeed, dansyl-labeled films reacted readily with acids in solvents such as toluene and THF on the basis of the visual decrease in fluorescence for films after exposure to acid in these solvents. To test surface selectivity in the reactivity of the dansyl-functionalized films, we therefore monitored the protonation of the dansyl groups as a function of time by monitoring the decrease in fluorescence intensity when polypropylene films functionalized with PP_{Olig}-*co*-PAA_{Olig}-$CONH(CH_2)_2$NH-dansyl cooligomers were suspended in alcohol solvents containing HCl. These alcohol solvents are not good solvents for bulk polypropylene but apparently are good solvents for the dansyl-modified interfacial region of these dansyl-modified PAA-grafted polypropylene films (vide infra).

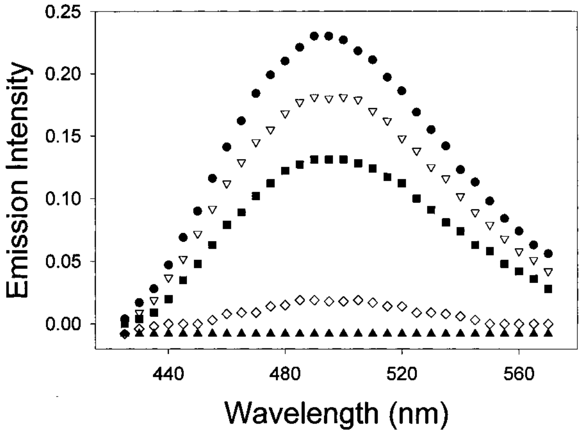


Figure 2. Changes in fluorescence for films containing PP_{Olig}-*co*-PAA_{Olig}-$CONH(CH_2)_2$NH-dansyl on exposure to *tert*-butyl alcohol containing 1% HCl (from addition of CH_3COCl) over the course of 40 min: $t = 0$ min (●); $t = 5$ min (▽); $t = 15$ min (■); $t = 30$ min (◇); $t = 40$ min (▲).

It is known that the fluorescence of dansyl groups is quenched by protonation of the $-N(CH_3)_2$ groups. The acidic alcohol solutions were prepared by adding 1 vol % of acetyl chloride to neat alcohol. Methanol, ethanol, and *tert*-butyl alcohol were all used as alcohol solvents. The resulting alcoholic solutions of HCl were then used in studies of a given dansyl film. In these fluorescence studies, the absolute fluorescence intensity varied from run-to-run even in the absence of HCl due to changes in fluorescence intensity when these flexible films were placed in the spectrometer. Thus, studies of the extent of protonation and of the rate of protonation were consistently made on the same film without removing the film from the spectrometer. Acidic *tert*-butyl alcohol showed complete protonation of the dansyl groups within 40 min, as determined by the fluorescence intensity dropping to zero over that time span (Figure 2). Methanolic HCl in contrast only protonated ca. 90% of the dansyl groups over a 48 h period. This suggests that methanol, being a more polar solvent, did not come into contact with all of the dansyl groups as a result of poorer solvation along the polymer/solvent interface. Ethanolic HCl was intermediate in its behavior.

The reversibility of these reactions was tested as shown in Figure 3, where polypropylene films containing PP_{Olig}-*co*-PAA_{Olig}-$CONH(CH_2)_2$NH-dansyl cooligomers were successively protonated and deprotonated. Figure 3 illustrates the results obtained when a film was suspended alternately in acidic and basic *tert*-butyl alcohol. When these solutions were alternated, the fluorescence intensity alternated from zero to a value that was roughly 60−80% of the intensity of the functionalized film's fluorescence in pure *tert*-butyl alcohol. Similar experiments in other “good” solvents such as THF show behavior analogous to the reversible protonation/deprotonation chemistry illustrated in Figure 3.

Conclusion

These experiments show that surface functionalization of polypropylene films using block cooligomers of polypropylene and *tert*-butyl acrylate by the blending

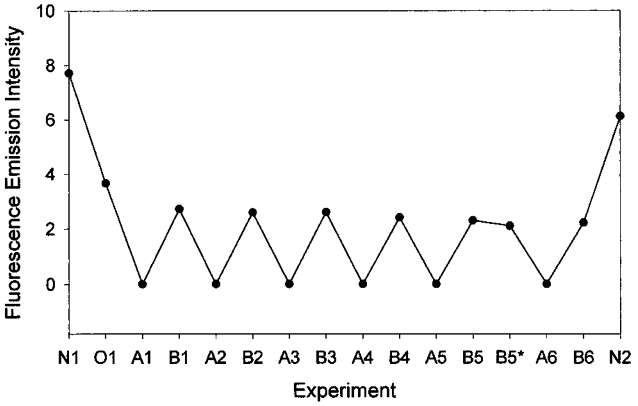


Figure 3. Exposure of polypropylene films containing PP$_{\mathrm{Olig}}$-*co*-PAA$_{\mathrm{Olig}}$-CONH(CH$_2$)$_2$NH-dansyl to *tert*-butyl alcohol solutions containing 1% HCl (from acetyl chloride addition) (A1, A2, A3, ..., A6) or 1% triethylamine (B1, B2, B3, ..., B6). The fluorescence of a neutral film in air before and after the series of protonation/deprotonation experiments (N1, N2) and for the film in pure *tert*-butyl alcohol solvent (O1) is also shown. Point B5* corresponds to an experiment where the film was left in base overnight (without illumination) to see if there was an intensity change after prolonged exposure.

process, which we call entrapment functionalization, is feasible. The product film surfaces have been studied after hydrolysis of the acid-labile *tert*-butyl ester groups. A substantial portion of the acid groups of the PAA grafts so formed are accessible to base. The resulting carboxylate groups can then be reprotonated on treatment with acid. When the PAA graft is labeled with a fluorescent dansyl probe, the probe is found to be responsive to changes in solvent. In the presence of acid and solvents such as *tert*-butyl alcohol or THF, these dansyl groups can be reproducibly protonated and deprotonated with HCl and Et$_3$N, respectively. In methanolic HCl, the protonation chemistry also occurs with ca. 90% of the dansyl groups being protonated. However, the reaction is much slower. Alcohols of intermediate polarity exhibit intermediate behavior. The results suggest that this synthetic procedure is a viable route to modify surface properties of polypropylene films. While this single blending step does not affect water wettability, our results indicate that further modification of these PAA-grafted polypropylene films is facile. Ongoing work in our laboratory aims to exploit the reactivity of these anchored polyfunctional oligomers in further surface modification, grafting, and synthesis.

Experimental Section

General Procedures. Solvents used in air-sensitive chemistry were prepurified by distillation from a suspension of sodium–benzophenone under N$_2$ prior to use. Other chemicals, reagents, and solvents were obtained from Aldrich Chemical Co. and used as received. IR spectra were recorded using a Mattson Galaxy Model 4021 FT IR spectrometer that was continuously purged with N$_2$. ATR spectra were recorded using the same spectrometer either with a Wilks Model 10 ATR accessory and a 45° KRS-5 crystal or a Seagull accessory (Harrick Scientific Co.) and a Zn–Se crystal. ^{1}H NMR spectra were obtained using either a 200 or 300 MHz NMR Varian Gemini or Unity spectrometer. Contact angle measurements were obtained using an automated First Ten Angstroms contact angle goniometer. The estimated error in contact angle measurements is ±3°. Chemical shifts are reported relative to HMDS.

Hydroboration/Oxidation of Terminally Unsaturated Polypropylene Oligomers. Terminally unsaturated polypropylene oligomer (0.5 g, $M_w = 3000$, $M_n/M_w = 1.8$, as determined by Exxon) was added to a two-necked 250-mL round-bottomed flask equipped with a condenser and stir bar. Distilled toluene (30 mL) was added by syringe, and the flask containing the solvent and oligomer was immersed in an oil bath. The polypropylene dissolved as the flask was heated to 85 °C. After complete dissolution, BH$_3$·S(CH$_3$)$_2$ (0.5 mL, 2M in toluene) was added dropwise. After 15 min, a solution of H$_2$O$_2$ (2 mL, 30%) and NaOH (2 mL, 3M) was added dropwise to the solution of the oligomeric borane. The mixture was stirred vigorously for 1 h. The aqueous layer was then removed, and solvent was removed by rotary evaporation under reduced pressure. The initial product from this procedure was an oligomeric borate ester. The oligomeric alcohol product was obtained from this ester by transesterification in refluxing methanol. The product was characterized by ^{1}H NMR spectroscopy; (toluene-d_8) δ 3.1–3.3, 1.65, 1.35, 0.97.

Preparation of PP$_{\mathrm{Olig}}$-*co*-PTBA$_{\mathrm{Olig}}$. A terminally unsaturated polypropylene oligomer was treated with borane dimethyl sulfide as described above. Then a solution of *tert*-butyl acrylate (3–10 mL depending on desired PTBA chain length) and methanol (0.5 mL, 12 mmol) was added by syringe. The solution was allowed to stir at 85 °C for 1 h. After cooling, solvent and excess reagents were removed at reduced pressure. The product cooligomers were dried under vacuum (0.1 mmHg) overnight and characterized by ^{1}H NMR spectroscopy at 100 °C (toluene-d_8): δ 2.5, 1.65, 1.5, 1.35, and 0.97.

General Procedure for Film Casting. Polypropylene films were prepared by dissolving 0.22 g of material (97 wt % Fortilene 9600 polypropylene and 3% PP$_{\mathrm{Olig}}$-*co*-PTBA$_{\mathrm{Olig}}$) in *o*-dichlorobenzene (25 mL) in a 50-mL beaker. The hot polymer solution was then poured into a 13.5-cm round Pyrex dish, which had been preheated to 130 °C. The hot casting dish containing the polymer solution was placed in an explosion proof oven at 135 °C for 45 min to evaporate the casting solvent. The film and dish were then cooled, and the film was removed and cut into 1-cm by 3-cm strips for further analysis and chemistry. The presence of the cooligomer in the product film was confirmed by ATR-IR or FTIR spectroscopy ($\nu_{\mathrm{C=O}}$, 1728 cm^{-1}; $\nu_{\mathrm{C-O}}$, 1150 cm^{-1}).

Hydrolysis of PP$_{\mathrm{Olig}}$-*co*-PTBA$_{\mathrm{Olig}}$/PP Films. A 3-cm by 1-cm segment of the polypropylene film containing entrapped PP$_{\mathrm{Olig}}$-*co*-PTBA$_{\mathrm{Olig}}$ cooligomer was placed in a 100-mL, round-bottomed flask containing benzene (50 mL) and *p*-toluenesulfonic acid (1.0 g, 5.3 mmol). The flask and contents were heated with gentle stirring in an oil bath to 60 °C for a period of 4 h. The film was removed and washed with methylene chloride. Hydrolysis was confirmed by ATR-IR spectroscopy (broad $\nu_{\mathrm{C=O}}$, 1710 cm^{-1}; disappearance of $\nu_{\mathrm{C-O}}$, 1150 cm^{-1}).

Deprotonation of PP$_{\mathrm{Olig}}$-*co*-PAA$_{\mathrm{Olig}}$/PP Films. A 3-cm by 1-cm segment of the polypropylene film containing entrapped PP$_{\mathrm{Olig}}$-*co*-PAA$_{\mathrm{Olig}}$/PP prepared by the procedure described above was placed in a solution of THF and NH$_4$OH (100 mL, 1% v/v NH$_4$OH) for 5 min. Alternatively, deprotonation was achieved by suspending the film in a solution of ethanol and sodium ethoxide for 12 h. The film was removed and washed with methylene chloride. The presence of the carboxylate was determined by ATR-IR spectroscopy (disappearance of $\nu_{\mathrm{C=O}}$, 1710 cm^{-1}; appearance of carboxylate stretch at 1595 cm^{-1}).

Preparation of Sulfonamide Amine 1. A three-necked, round-bottomed flask purged with nitrogen and equipped with a magnetic stir bar and an addition funnel was charged with ethylenediamine (33 mL, 494 mmol) and CH$_2$Cl$_2$ (50 mL). Dansyl chloride (2.0 g, 7.4 mmol) was dissolved in CH$_2$Cl$_2$ (20 mL) and transferred to the addition funnel. The dansyl chloride solution was added over 15 min to the ethylenediamine solution with rapid stirring. After 4 h of stirring at room temperature, the solution was transferred to a separatory funnel and washed with three portions of water (100 mL). The second washing required approximately 20 mL of saturated NaCl solution to eliminate an emulsion that had formed. The CH$_2$Cl$_2$ layer was then dried with MgSO$_4$. Solvent was removed by rotary evaporation under vacuum and the product was isolated in the form of yellow-green crystals after drying under vacuum overnight (2.06 g, 87%, melting point 149–151

°C (lit.[29] 150.5−151.5 °C); ^{1}H NMR ($CDCl_3$) δ 2.7 (2 H, t), 2.9 (10 H, m), 7.15 (1 H, d), 7.5 (2 H, m), 8.25 (2 H, m), 8.5 (1 H, d). The product is light sensitive and turns yellow brown upon prolonged exposure to fluorescent lighting.

Procedure for Coupling of the Dansyl-Labeled Amine 1 to PP_{Olig}-*co*-PAA_{Olig}/PP Films. One piece of PP_{Olig}-*co*-PAA_{Olig}/PP film was immersed in CH_2Cl_2 (50 mL) in a dry 100-mL round-bottomed flask equipped with a stir bar. Carbonyldiimidazole (CDI) (0.5 g, 3.1 mmol) was added and allowed to react with the suspended polymer film for 5 h. After this time, **1** (0.5 g, 1.7 mmol) was added. This solution stirred for 16 h at room temperature. The film was then removed from the reaction solution and washed with methylene chloride by Soxhlet extraction overnight. ATR-IR spectroscopy showed a diminished $\nu_{C=O}$ intensity at 1710 cm^{-1} as well as the appearance of small peaks at 570 and 630 cm^{-1}.

Fluorescence Quenching Experiments. Experiments were preformed using an SPF-Aminco SPF500 fluorometer. Excitation and emission band-pass widths were 5 and 2 nm, respectively. Measurements were taken at 27 °C between 425 and 575 nm with a scan rate of 5 nm/s to minimize photochemical bleaching of the films. The films were positioned diagonally in a quartz fluorescence cuvette with the aid of a Teflon support. Solvents were obtained from Aldrich and were used as received. Acidic and basic solutions were prepared by adding 1 vol % of acetyl chloride or triethylamine, respectively, to make a 100-mL solution of acidic or basic alcoholic solvent that was then used for all experiments. Since the fluorescence intensity was sensitive to the position of the film, fluorescence data were obtained without removing the film or cuvette during the course of the experiment.

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