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Hyperbranched Grafting on Oxidized Polyethylene Surfaces

David E. Bergbreiter,* Justine G. Franchina, and Konrad Kabza

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

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ABSTRACT: A new method to prepare functional grafts on polyethylene is described. In this chemistry, a terminally functionalized poly(*tert*-butyl acrylate) is first attached to an oxidized polyethylene film. Subsequent hydrolysis of the *tert*-butyl esters at room temperature then produces a film with some poly(acrylic acid) grafts. Although this initial graft is present at low density, repetition of this process through 2−4 more cycles produces a heavily grafted polyethylene that exhibits much of the same chemistry seen for hyperbranched poly(acrylic acid) grafts on more defined inorganic surfaces. The resulting grafts are more effective platforms for further ionic modification of polyethylene than simple oxidized polyethylene.

Introduction

Surface modification of organic polymer surfaces continues to be an important area because of the many cases where a polymer's surface properties affect its utility. Over the past few years there has been considerable interest in developing effective and selective procedures to usefully modify the surface of common polymers.[1−4] Likewise, there is increasing interest in organic thin film chemistry where thin films are supported on more defined inorganic surfaces.[5,6] In prior work, we have developed a new technique called hyperbranched grafting for thin film synthesis on gold, aluminum, silicon, and glass.[7,8] Here we show that similar hyperbranched grafting with α,ω-diaminopoly(*tert*-butyl acrylate) is also suitable for modification of softer, less-defined polymer surfaces. Using oxidized polyethylene as a substrate, hyperbranched chemistry affords a covalently modified polyethylene film containing significant amounts of grafted poly(acrylic acid). By using a polymeric reagent for the modification step, we ensure surface selectivity. By using repetitive cycles of grafting, we ensure a highly functionalized product as measured by the extent of coverage of an underlying polymer. In addition to spectroscopically characterizing these hyperbranched, grafted surfaces, we also show that these surfaces are suitable for further covalent chemical modification with dyes and fluorinated amines. Finally, the polyelectrolyte grafts produced by these procedures are shown to be an effective interface for subsequent ionic self-assembly of cationic polyelectrolytes onto a polyethylene film.

Many different procedures have been used previously to modify the surface of polyethylene.[9] Our group has described simple functionalization of polyethylene by entrapment functionalization.[10] Oxidation of polyethylene by solution-phase or gas-phase oxidants is also well established.[9,11−13] However, when such surfaces are studied in contact with a condensed phase, the inherent ambiguities associated with polymer surfaces that are more interfaces than surfaces complicate further chemistry and characterization.[14,15] These ambiguities include the extent of surface coverage, the stability of the modified surfaces, and the reactivity of the groups at the surface in different milieu—issues that are addressed by various spectroscopic, physical, and chemical assay procedures.

Modifying polyethylene surfaces by grafting a second monomer onto the surface is well-known. Radical graft modification of polyethylene is most common.[3,16−18] We have also studied anionic grafting and direct incorporation of diblock copolymers into polyethylene.[19,20] In these cases, the presence of more functional groups from grafting simplifies the analytical problems. However, these procedures still suffer from the ambiguities arising from incomplete reaction, incomplete surface selectivity, or premature termination of the grafting reaction.

Ionic assembly of polyelectrolytes onto various surfaces has been recently developed.[21] Inorganic substrates are most commonly used. Nonetheless, there are numerous examples where functionalized organic polymers can be successfully coated with alternating cationic and anionic polyelectrolytes, and this chemistry too has been used to surface modify polyolefins.[22−24]

Here we show that modification of an oxidized polyethylene surface by covalent attachment of α,ω-diaminopoly(*tert*-butyl acrylate) is a viable alternative to this existing graft chemistry. These derivatized films have been investigated using X-ray photoelectron spectroscopy (XPS), contact angle analysis, and attenuated total reflectance-IR (ATR-IR) spectroscopy. These spectroscopic studies and further chemical studies in which polyelectrolytes assemble into a deprotonated poly(sodium acrylate) graft layer show that this hyperbranching chemistry is an efficient route to functionalized polyethylene surfaces.

Results and Discussion

Oxidized polyethylene films used in this chemistry were prepared by oxidation with $CrO_3-H_2SO_4$.[12,25] The oxidized film so prepared had a carbonyl peak at 1710 cm^{-1} in its ATR-IR spectrum. Most of the carbonyl signal intensity in this IR spectrum disappeared on treatment with base, and a new broad carboxylate peak appeared at 1560 cm^{-1}. The unoxidized film is hydrophobic ($\Theta_a = 105°$), but the hydrophilic oxidized film has a contact angle of $\Theta_a = 65°$. The base-treated film has a contact angle $\Theta_a = 24°$. These data are comparable to those reported previously.[26,27]

Scheme 1 illustrates the general graft chemistry used to amplify the carboxylic acid groups of oxidized polyethylene through hyperbranched grafting. This chemistry essentially parallels that used previously for hyperbranched grafting on Au-coated silicon wafers.[7]

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* Corresponding author. E-mail Bergbreiter@tamu.edu.

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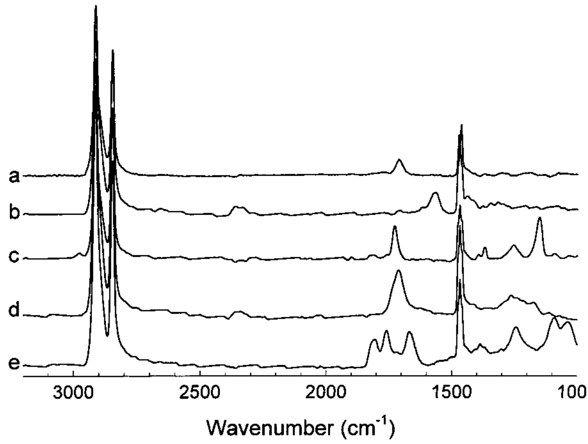
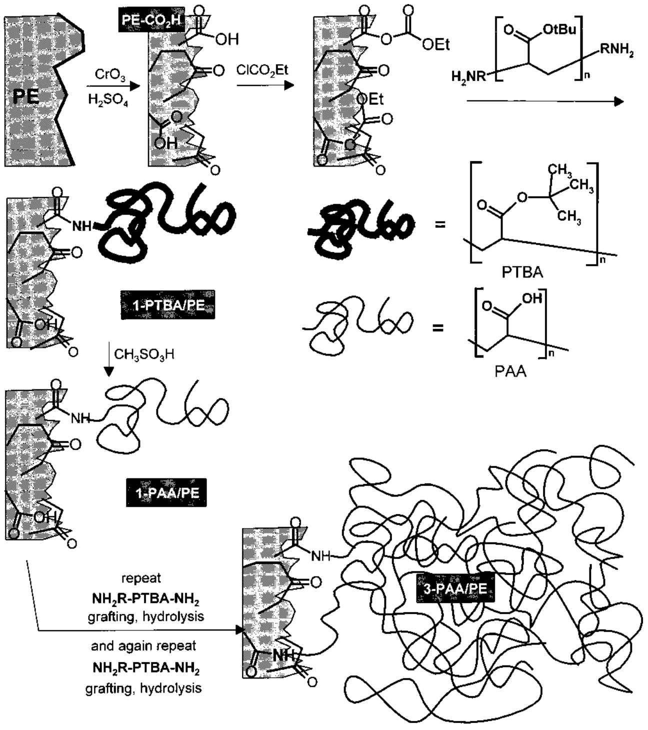


Figure 1. (a) Oxidized polyethylene (PE$-$CO$_2$H) with peaks due to carbonyl groups at 1710 cm^{-1}. (b) Deprotonated oxidized polyethylene (PE$-$CO$_2$$^-Na^+$) showing disappearance of the acid carbonyl peak and appearance of a carboxylate peak at 1560 cm^{-1}. (c) A 1-PTBA/PE film showing an ester peak at 1728 cm^{-1} and a C$-$O peak at 1152 cm^{-1}. (d) A 1-PAA/PE film showing the grafted poly(acrylic acid) carbonyl peak at 1710 cm^{-1} and the disappearance of the ester C$-$O peak at 1152 cm^{-1}. (e) An activated oxidized polyethylene film showing mixed anhydride peaks in the carbonyl region (1650$-$1820 cm^{-1}).

Scheme 1. Multistage Synthesis of 3-PAA/PE Using Hyperbranched Grafting with α,*ω*-Diaminopoly(*tert*-butyl acrylate)



The chemistry in this case was slightly modified by using a milder hydrolysis step (CH$_3$SO$_3$H at 25 °C for 25 min vs *p*-TsOH at 55 °C for 90 min) to generate the poly(acrylic acid) from the poly(*tert*-butyl acrylate).

As shown by the ATR-IR spectra in Figure 1, grafted carbonyl groups are present even at the 1-PTBA/PE or 1-PAA/PE stage. The intermediate mixed anhydride on the surface is also readily detected in these spectra (Figure 1e). The ATR-IR spectrum of the hydrolyzed 1-PAA/PE film was distinctly different from the 1-PTBA/PE film with a broadened and shifted carbonyl peak and loss of the C$-$O$-$C stretch at 1152 cm^{-1} (Figure 1). Control experiments showed that an oxidized polyethylene surface that was allowed to react with α,*ω*-diaminopoly(*tert*-butyl acrylate) without activation of the polyethylene carboxylic acid groups had no detectable poly(*tert*-butyl acrylate) on the polyethylene after extraction.

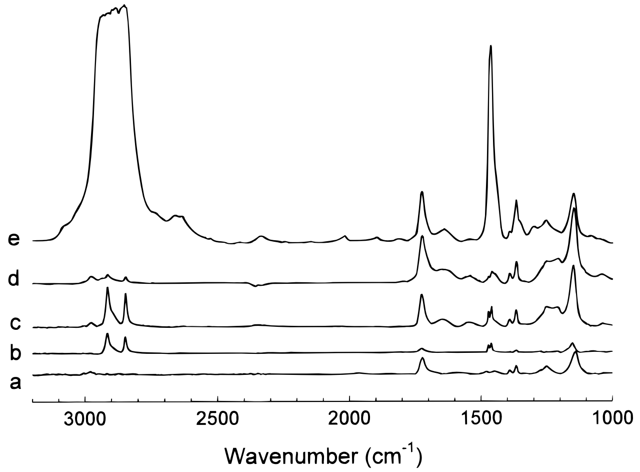


Figure 2. IR spectra of PTBA and PTBA/PE derivatives: (a) ATR-IR spectrum of PTBA powder; (b) ATR-IR spectrum of a 1-PTBA/PE film; (c) ATR-IR spectrum of a 3-PTBA/PE film; (d) ATR-IR spectrum of a 5-PTBA/PE film; and (e) transmission FT-IR spectrum of a 5-PTBA/PE film.

Several additional experiments demonstrate some of the features of these hyperbranched covalent grafts on oxidized polyethylene. First, just as deprotonation/protonation of the oxidized/hydrolyzed film leads to the disappearance and reappearance of the acid carbonyl at 1710 cm^{-1} and a change in contact angle for oxidized polyethylene, a protonated and deprotonated 1- or 3-PAA grafts have similar reversible spectral changes. In the case of the 3-PAA graft, the contact angles of the protonated and deprotonated films were $\Theta_a = 48°$ and 15°, respectively. The extent of growth of the grafts is also notable. A comparison of the ATR-IR spectra for 1-, 3-, and 5-PTBA/PE surfaces in Figure 2 shows significant growth in the intensity of the carbonyl peaks vs the C$-$H peak intensity. In the case of the 5-PTBA/PE film, even transmission IR spectra can be used to detect the carbonyl peak of the poly(*tert*-butyl acrylate) graft (Figure 2a). Several other characteristic peaks are also seen in these spectra. As is true for PTBA grafts on gold, a strong C$-$O peak appears at 1152 cm^{-1}. A broad carbonyl peak due to the carboxamide groups that are formed during the hyperbranch graft synthesis is also seen at 1650 cm^{-1} in the 3-PTBA/PE and 5-PTBA/PE spectra.

XPS spectroscopic analysis of the grafted surfaces confirms the ATR-IR spectroscopy results. These data are listed in Table 1 and show that the 3-PTBA/PE surface has essentially the same atomic composition as 5-PTBA/PE and that the hyperbranched graft surface is significantly different in atomic composition from the underlying oxidized polyethylene.

A second set of experiments was used to probe the extent of coverage by the hyperbranched grafts. In this chemistry, the oxidized polyethylene was first activated and then fluorinated by reaction with NH$_2$CH$_2$(CF$_2$)$_7$-CF$_3$. The fluoramidated film was then allowed to react with NH$_2-$R$-$PTBA$-$R$-$NH$_2$. At this point the film had a contact angle of 142° and an initial fluorine concentra-

Table 1. XPS Spectroscopic Analysis of the Surface Atomic Composition (in at. %) of Hyperbranched Grafted Polyethylene Films[a]

film[b]	C	O	N	F	Cs
polyethylene	98.9	1.1			
oxidized polyethylene ($PE-CO_2H$)	95.8	4.1			
1-PTBA/PE	81.1	17.5	1.4		
1-PAA/PE	79.9	18.9	1.1		
2-PTBA/PE	75.1	23.8	1.1		
2-PAA/PE	70.9	27.9	1.2		
3-PTBA/PE	75.6	23.7	0.7		
3-PAA/PE	67.2	31.3	1.5		
4-PTBA/PE	76.0	23.1	0.9		
5-PTBA/PE	74.5	24.8	0.6		
5-PAA/PE	63.4	34.9	1.7		
3-PAA−F/PE	42.9	8.9	2.1	45.9	
3-PAA−Cs/PE	68.3	23.6	1.7		6.3
1-PTBA/fluoramidated $PE-CO_2H$	61.2	10.6	0.6	27.6	
2-PTBA/fluoramidated $PE-CO_2H$	72.7	22.8	0.7	3.7	
3-PTBA/fluoramidated $PE-CO_2H$	77.3	20.8	1.4	0.4	
PTBA	77.8	22.2			
PAA	60.0	40.0			

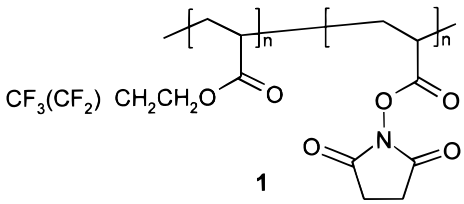
[a] Both medium- and high-density polyethylene films were used. Hyperbranched films generally had comparable atom compositions regardless of which polyethylene was used as starting material. Comparison of the atom percent values for multiple samples showed that the standard deviation of these atom percent values was consistently <±5% and typically <±3%. [b] Films were all extracted in a jacketed Soxhlet for 15 h and then dried before analysis.

tion of 28% as measured by XPS spectroscopy. ATR-IR spectra show that this fluoramidated film contains absorption peaks due to C−F groups (1240 and 1205 cm^{-1}). Earlier work with PAA grafts on Au films had shown that fluoramidation consumed approximately 47% of the carboxylic acid groups on a film. Thus, we expected that fluoramidation of a $PE-CO_2H$ film would also not be complete but that enough unreacted carboxylic acid groups would remain to serve as a platform for addition of the first PTBA layer. Indeed, when fluoramidation of $PE-CO_2H$ was carried out before the first PTBA graft, the extent of PTBA graft was roughly 50% less as determined by comparing the intensities, in the ATR-IR spectrum, of the ester carbonyls for a 1-PTBA/PE film and a 1-PTBA/fluoramidated $PE-CO_2H$ film. Successful further hyperbranched grafting of two additional PTBA layers to the first PTBA layer was then carried out using only $NH_2-R-PTBA-R-NH_2$. After these experiments, the product 3-PTBA/fluoramidated $PE-CO_2H$ film was analyzed to determine the extent to which the initial fluorine labels were covered by PTBA grafting. XPS spectroscopy of these PTBA surfaces as a function of the amount of additional PTBA grafting (Table 1) showed rapid decrease in the atom percent fluorine consistent with coverage of the underlying fluorinated amide by PTBA grafts. Spectra of grafts on both high-density and medium-density polyethylene films in these cases were very comparable with the concentration of fluorine decreasing from 28 at. % to <1%. The XPS data in Table 1 also show that the atom percent for carbon, oxygen, and nitrogen in the XPS analysis of the 3-PTBA/fluoramidated oxidized polyethylene film was similar to that of a 3-PTBA/PE film. The essential complete disappearance of the F_{1s} signal on subsequent grafting of PTBA is consistent with results reported in our earlier studies where subsequent hyperbranched grafting of PAA covered an initially formed hyperbranched fluoramidated ultrathin films on gold.[28]

We have also been able to successfully derivatize hyperbranched PAA grafts on PE using atomic labels as XPS probes. For example, 3-PAA/PE films were successfully activated and then derivatized with 1*H*,1*H*-pentadecafluorooctylamine to yield a very hydrophobic surface. Different experiments where 3-PAA-F/PE films were prepared starting with 3-PAA grafts on either an oxidized high-density polymer or an oxidized medium-density polymer film produced films containing 50.6 and 47.1 at. % fluorine, respectively. A typical fluoramidated 3-PAA film had Θ_a value of 135° as compared to the Θ_a of 48° for the starting 3-PAA film. Treatment of 3-PAA/PE films with CsOH in ethanol similarly produced a cesium-labeled film that had 6.3 at. % Cs. Both of these examples show that significant amounts of atomic labels can be incorporated into these films.

The experiments with XPS labels were qualitatively confirmed by experiments using colorimetric labels or fluorescent dyes. In this case, *N*-6-(aminohexyl)-1-pyrenebutanamide, an ethylenediamine derivative of dansyl chloride, and primary amine-terminated *p*-methyl red (MR) were all used. Visual examination and examination with a light microscope showed that the films labeled with the colorimetric or fluorescent dyes had uniform color or fluorescence intensity across the entirety of the film. In the case of the MR-labeled films, the film's color changed in response to changes in pH. Immersion of a 3-PAA/*p*-MR film in acidic ethanol produced a red film while immersion of the same film in ethanol containing NaOH produced a yellow film. Reflectance UV−vis spectra show a slightly higher absorption at 548 nm for the 3-PAA/*p*-MR film as compared to the 2-PAA/*p*-MR and 1-PAA/*p*-MR films, which was consistent with the slightly more intense red color for the acidic form of the 3-PAA/*p*-MR film vs the 2-PAA/*p*-MR film vs the 1-PAA/*p*-MR film. Extensive fluorescence studies of the pyrene-labeled or dansyl-labeled films were not carried out. However, extensive excimer formation (λ_{max}(excimer) of 485 nm) was noted for the former film, and quenching of the dansyl fluorescence ($\lambda_{max} = 495$ nm) on exposure to acid was noted for the latter film. These experiments are all consistent with the premise that hyperbranched grafting produces a surface grafted film that is densely functionalized and reactive.

Preliminary experiments show that the reactivity of PAA grafts on polyethylene can be modified by polymeric reagents that are both PE- and PAA-incompatible. For example, activation of the $-CO_2H$ groups of 1-PAA/PE and 3-PAA/PE with $ClCO_2Et$ followed by treatment with either excess 1,6-hexanediamine or an α,*ω*-diaminopoly(ethylene glycol) derivative produces an amine-rich surface that readily reacts with electrophilic fluoroacrylates such as the fluorous copolymer TAN-*c*-NASI (**1**).[29] The chemistry in these cases could be followed by



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ATR-IR spectroscopy and by dramatic changes in the contact angle of the product fluorinated film. The ATR-IR spectra of the aminated films prepared with either 1,6-hexanediamine or $NH_2-PEG_{2000}-NH_2$ showed that amidation had occurred on the basis of an increase in the amide I and II bands as well as the appearance of a C−O stretch in the case of the $NH_2-PEG_{2000}-NH_2$ modified film. Subsequent derivatization of the film with the fluorous copolymer TAN-c-NASI was confirmed by the appearance of C−F peaks in the ATR-IR spectrum at 1240 and 1200 cm^{-1} and an increase in the contact angle of this film to $\Theta_a = 145°$. ATR-IR spectra of the product fluorinated films suggested that the PEG-derivatized film was modified to a greater extent. Control experiments where 6-aminohexanol was first attached to the 1-PAA and 3-PAA films and the resulting films were allowed to react with the TAN-c-NASI polymer under the same conditions as were used for the diamine-modified hyperbranched grafted films produced no fluorination. There were no C−F peaks in the ATR-IR spectra after reaction, and the film did not become hydrophobic, showing that simple physisorption of the TAN on PE did not occur.

The change in hydrophilicity of hyperbranched PAA grafts on PE as a function of pH was noted above and is attributed to the change in the $-CO_2H$ groups of the PAA graft to $-CO_2^-Na^+$ groups. In the case of the gold films, in-situ ellipsometry showed that hyperbranced PAA grafts are highly solvated with thickness changing 5-fold as the film's environment is changed from the dry $-CO_2H$ form to a wet $-CO_2^-Na^+$ form.[30] These anionic polyelectrolyte thin films also reversibly complex cationic polyelectrolytes. We were unable to use ellipsometry with PAA grafts on PE. Nonetheless, we were able to show that hyperbranched grafts on PE do function as good substrates for ionic assembly like their hyperbranched PAA/Au counterparts.

Entrapment of cationic polyelectrolytes in a hyperbranched poly(acrylic acid) matrix on a gold surface has been attributed to polyvalent ionic interactions. Such entrapment has been demonstrated for cationic polyelectrolytes such as poly(allylamine), poly-D-lysine, and amine-terminated PAMAM dendrimers at pH 7. We reasoned that a hyperbranched poly(acrylic acid) graft on polyethylene too would undergo significant swelling on deprotonation in water and that it too would ionically incorporate cationic polyelectrolytes. Indeed, exchange of significant amounts of a cationic polyelectrolyte into the poly(acrylic acid) on polyethylene graft does occur at pH 7. This is illustrated by the ATR-IR spectra in Figure 3. As shown here, essentially all of the carboxylic acid groups of the hyperbranched 3-PAA/PE graft are deprotonated after immersion in a pH 7 buffer on the basis of the decrease in intensity of the carboxyl carbonyl peak at 1710 cm^{-1} and the increase in intensity of the $-CO_2^-Na^+$ peak at 1560 cm^{-1}. Thus, when a 3-PAA/PE film is put in a pH 7 buffer, it forms poly(sodium acrylate). If this pH 7 solution contains a fourth-generation Starburst amine-terminated PAMAM dendrimer or poly-D-lysine, changes in the films ATR-IR spectrum show that the cationic dendrimer or peptide polyelectrolyte is incorporated into the hyperbranched PAA graft. In both the dendrimer and poly-D-lysine cases, amide C=O and N−H bands appear. The incorporation of the ammonium salts into the film is also supported by the detection of a significant increase in the atomic percent nitrogen as measured by XPS spectroscopy. In the case of the dendrimer, the N_{1s} atom percent increases from 1.5 to 15.9 at. %. In the case of the poly-D-lysine, the N_{1s} atom percent increases from 1.5 to 10.6% (12.0%). Unlike similar intercalation in PAA/Au, incorporation of the dendrimer and the poly-D-lysine in 3-PAA/PE is tenacious. These cationic polyelectrolytes remain in the film even after all the carboxylate groups are reprotonated, possibly because the milieu is too hydrophobic for solvent to penetrate and dissolve the dendrimer or because of polyvalent hydrogen bonding the $PAA(CO_2H)/PE$−dendrimer composite graft. Attempted removal of these cationic polyelectrolytes from acidified 3-PAA/PE grafts used several different conditions. These treatments included 30 min, 2 h, 24 h, and 48 h treatments with ethanolic HCl, Soxhlet extraction with 95% ethanol for up to 4 days, 2−3 alternating acid (ethanolic HCl) and base treatments (NaOH, EtOH), and simple soaking of the films in 2-propanol or THF for up to 3 h with sonication or for 24 h without sonication. In each case, ATR-IR spectroscopy was used to verify that the carboxylic acid groups of the PAA grafts were protonated and that the dendrimer or the poly-D-lysine remained in the film. Comparisons of ionic assembly on a hyperbranched grafted surface with similar chemistry on an oxidized polyethylene film show that ionic assembly on the former is more facile and less reversible. Adsorption of a polycationic electrolyte such as poly(allylamine) on a surface-functionalized polyolefin has been reported.[22] Similarly, we have found that alternating layers of poly(allylamine) and sodium poly(styrenesulfonate) can be deposited on an oxidized polyethylene. However, all of our attempts to deposit a fourth-generation, amine-terminated PAMAM dendrimer on oxidized polyethylene were unsuccessful. In each case, the dendrimer washed off readily. This was true for both chromic acid etched polyethylene and sulfonated polyethylene. Separate experiments also show that the acidic form of 3-PAA/PE does not chemisorb the amine-containing dendrimer from methanol solutions. Together these experiments suggest that hyperbranched grafts may have advantages in ionic assembly, especially when ionic assembly occurs on a nonpolar surface-functionalized polymer.

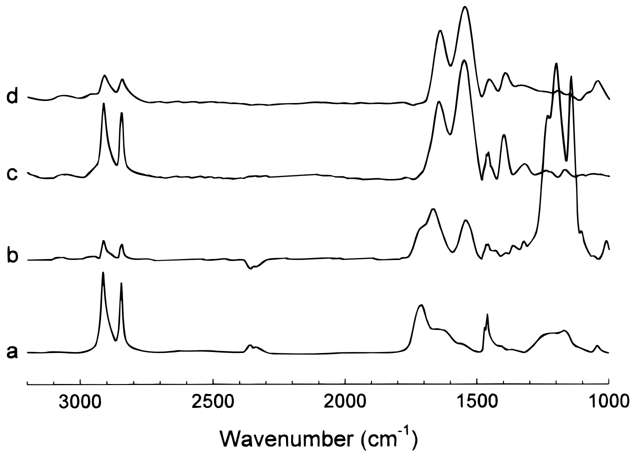
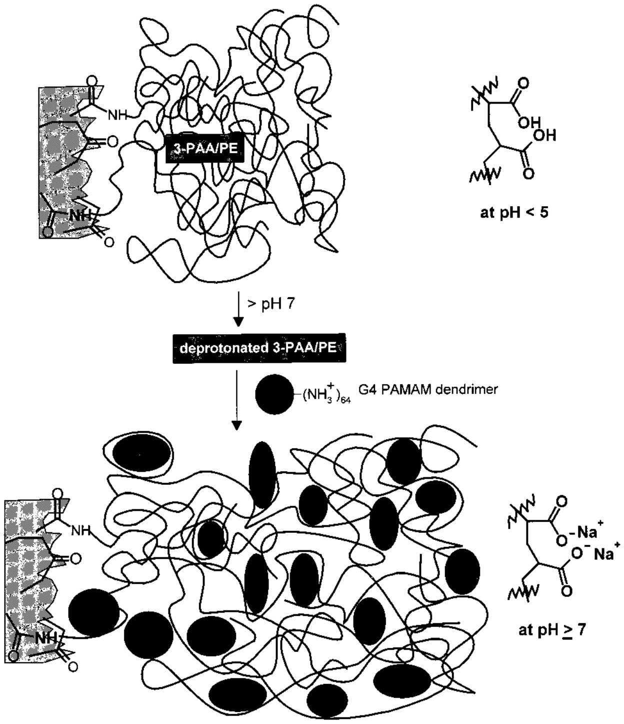


Figure 3. IR spectra of covalent and ionic derivatives of hyperbranched 3-PAA/PE: (a) 3-PAA/PE; (b) fluorinated 3-PAA/PE; (c) D-lysine entrapped in 3-PAA/PE film from a pH 7 solution; and (d) PAMAM dendrimer $(-NH_2)_{64}$ entrapped in a 3-PAA/PE film from a pH 7 solution.

Conclusion

Hyperbranched grafting using α,ω-diaminopoly(*tert*-butyl acrylate) can be utilized to build robust thin films

Scheme 2. Ionic Intercalation of Cationic Polyelectrolytes Such as an Amine-Terminated PAMAM Dendrimer into a Deprotonated Hyperbranched 3-PAA/PE Graft Surface



on an oxidized polyethylene surface. The hyperbranched film can be derivatized in a number of ways. Once derivatization occurs with amine-terminated molecules, predictable changes were seen in the contact angle, the ATR-IR spectrum, and the film's XPS spectrum. The completeness of the graft coverage has been investigated, and it appears that that grafting procedure covers the polyethylene surface completely. Finally, the polyelectrolyte character of the poly(acrylic acid) hyperbranched grafts on these surfaces facilitates ionic functionalization of polyethylene by both dendridic and linear cationic polyelectrolytes. The irreversible intercalation of dendrimers from a pH 7 solution into the hyperbranched PE grafts differs from the reversible intercalation of similar dendrimers in 3-PAA/Au surfaces. This suggests that polyethylene surfaces modified with a dense poly(acrylic acid) graft may be generally useful as substrates in the synthesis of ionic nanocomposites on the surface of an underlying otherwise unmodified nonpolar polymer.

Experimental Section

Materials. *tert*-Butyl acrylate (Aldrich, 98%) was distilled before use. Amine-terminated, G-4 Starburst PAMAM dendrimers (Dendritech, Inc., Midland, MI), 1,6-hexanediamine (Aldrich, 98%), 6-aminohexanol (Aldrich, 99%), ethylenediamine (Aldrich, 99%), 1,1′-carbonyldiimidazole (CDI, Aldrich), 4,4′-azobis(4-cyanovaleric acid) (Aldrich, 75+%), *p*-dioxane (EM Industries, Inc., NJ), chromium(VI) oxide (J. T. Baker, Inc., NJ), sulfuric acid (EM Industries, Inc., NJ), 1*H*,1*H*-pentadecafluorooctylamine (PCR, 97%), poly-D-lysine hydrobromide (Aldrich, Mv: 4000−15 000), and 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate (Zonal TAN, Dupont) were used as received. *O*,*O*′-Bis(2-aminoethyl)poly(ethylene glycol) (M_n ca. 2000) was synthesized from poly(ethylene glycol) (Aldrich, M_n ca. 2000) analogous to a literature procedure.[31] *N*-Acryloxysuccinimide (NASI), *N*-6-(aminohexyl)-1-pyrenebutanamide, and 1-(dimethylamino)-5-naphthalenesulfonylethylenediamine (dansylamine) were synthesized following literature procedures.[7,32,33]

Characterization. X-ray photoelectron spectroscopy (XPS) spectra were acquired using a Perkin-Elmer (PHI) model 5500 spectrometer using a Mg Kα source and a take-off angle of 45°. Attenuated total reflectance infrared (ATR-IR) spectroscopy measurements were made using a Mattson Galaxy 4021 spectrometer with a Wilks model 10 ATR accessory at an angle of 45° with a KRS-5 crystal. The spectra were recorded at 1 cm^{-1} resolution between 4000 and 400 cm^{-1} and were the sum of 256 individual scans.

α,*ω*-Diaminopoly(*tert*-butyl acrylate) Synthesis. The α,*ω*-diaminopoly(*tert*-butyl acrylate) ($NH_2-R-PTBA-R-NH_2$) polymer was synthesized by radical polymerization of 15 mL of distilled *tert*-butyl acrylate using 0.380 g of the initiator 4,4′-azobis(4-cyanovaleric acid) in 60 mL of 1,4-dioxane under a nitrogen atmosphere for 15 h at 120 °C. The polymer was recovered by precipitation into a methanol:water 1:1 mixture. The acid-terminated polymer was purified by two precipitations in methanol:water 1:1 and was then characterized using ^{1}H NMR spectroscopy, FT-IR spectroscopy, and gel permeation chromatography (GPC). In selected cases, the diacid polymer was also characterized by titration. Such titrations used 0.01 N NaOH and provided an M_n value of 15 450 (assuming difunctionality). The M_n determined by titration compared favorably with an M_n of 16 250 measured by GPC. The dispersity of the polymer as measured by GPC was 1.8. The ^{1}H NMR spectrum was not very informative, showing broad peaks in the expected regions, but the ^{1}H NMR spectrum did show that no monomer was present. The dominant peak was the ester peak at 1730 cm^{-1}. The acid-terminated polymer was then converted to a nucleophilic amine by allowing 5 g of the acid-terminated polymer to first react with 0.324 g of 1,1′-carbonyldiimidazole (CDI) for 5 h in 30 mL of CH_2Cl_2 and then with 0.2 mL of ethylenediamine for 15 h. The reaction mixture was washed with water and saturated brine (3 × 50 mL), and the organic layer was then dried over $MgSO_4$, and the CH_2Cl_2 solvent was removed at reduced pressure using a rotary evaporator. In cases where the acid-containing polymer had been analyzed by titration, the amine-containing polymer was also characterized by titration. The M_n increased slightly to 18 460, suggesting some dimerization in the reaction of the polymer with ethylenediamine. The amine-containing polymer was also characterized using ^{1}H NMR and FT-IR spectroscopy. The FT-IR spectrum indicated amidation of the diacid polymer had occurred on the basis of the introduction of an amide I peak at 1650 cm^{-1}.

Polyethylene Film Oxidation. Both high- and medium-density polyethylene films were used in this chemistry. The medium-density polyethylene film (Fortiflex J36-25-142) was provided by Soltex in the form of a blown film (density of 0.936 g/mL). The high-density polyethylene film was also provided by Soltex (Fortiflex J60-110-195, density 0.961 g/mL). These polyethylene films were cut into 5 × 5 cm square pieces which were extracted using CH_2Cl_2 in a jacketed Soxhlet apparatus for 15 h. The films were dried under vacuum (1 Torr) for 15 min. The films were then oxidized in a mixture of $CrO_3/H_2O/H_2SO_4$ for 5 min at 90 °C to form an oxidized film.[26,27] After the films were removed from the oxidizing solution, they were washed with water and then acetone. The films were allowed to air-dry. The oxidized films were extracted using CH_2Cl_2 in a jacketed Soxhlet apparatus for 15 h and finally dried under vacuum for 15 min (1 Torr). ATR-IR spectroscopy was used to confirm oxidation of the surface with a new carbonyl peak appearing at 1710 cm^{-1}. Grafting of the amine-terminated polymer onto this oxidized polyethylene film substrate then takes place through a sequence of activation, substitution, and hydrolysis. The starting acid end group of the oxidized film surface was activated using ethyl chloroformate (0.1 mL) and *N*-methylmorpholine (0.1 mL) in 7 mL of DMF for 15 min. The surface was then washed with ethyl acetate and dried with a stream of nitrogen. The activated film was then put into a solution of 0.25 g of $NH_2-R-PTBA-R-NH_2$ in 6 mL of DMF for 1 h. After 1 h the film was washed with ethanol and dried with a stream of nitrogen, and then the film was extracted for 15 h using CH_2Cl_2 in a jacketed Soxhlet apparatus. The film was then dried under vacuum for 15 min (1 Torr). The film was then hydrolyzed using 0.5 mL of $MeSO_3H$ in 15 mL of CH_2Cl_2 at room temperature for 25 min. The product 1-PAA/PE film was washed with ethanol and dried with a stream of nitrogen and then dried under vacuum for 1 h (1 Torr). The activation, grafting, and hydrolysis steps were repeated to construct the 2- to 5-PAA/PE films. Control experiments were conducted by activating an unoxidized PE film and putting the "activated" film into a grafting solution and by taking an oxidized PE film and putting the unactivated film into a grafting solution; no grafting took place in either case as indicated by no change in the ATR-IR spectra.

Primary Amine-Terminated *p*-Methyl Red. {2-[4-(Dimethylamino)phenylazo]benzoic acid} (3.866 g, 14.36 mmol) and 100 mL of CH_2Cl_2 were added to an oven-dried flask, and the apparatus was flushed with N_2. Then CDI (2.404 g, 14.38 mmol) in 36 mL of CH_2Cl_2 was added via syringe, and the mixture was stirred vigorously under N_2. After stirring for 7 h, the solution was transferred by forced siphon into a N_2-flushed flask containing 1,6-hexanediamine (8.475 g, 71.5 mmol) in 85 mL of CH_2Cl_2. The mixture was stirred under a slow N_2 flow overnight. The dark red solution was washed with water (3 × 150 mL) and dried over $MgSO_4$; the solvent was removed under reduced pressure, and the residue was dried in vacuo to yield 3.77 g (71% yield) of an orange solid: mp 175.5−176.4 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.36 (m, 6H), 1.65 (m, 4H), 2.62 (t, 2H), 3.12 (s, 6H), 3.52 (q, 2H), 6.20 (t, 1H), 6.76 (d, 2H), 7.90 (s, 4H), 7.95 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.07, 154.95, 152.76, 143.58, 134.78, 127.69, 125.36, 122.20, 111.43, 42.04, 40.28, 40.03, 33.56, 29.64, 26.79, 26.51. HRMS (*m*/*e*): Calcd for $C_{21}H_{29}N_5O$: 367.2372. Found: 367.2368.

Labeling of Oxidized or PAA-Grafted Polyethylene. The oxidized films and the PAA grafts (1-PAA, 2-PAA, 3-PAA) were derivatized using fluorous labels, fluorophores, and dyes. During this sequence, the carboxylic acid-containing films were activated with ethyl chloroformate as described above and then allowed to react with DMF solutions of 1*H*,1*H*-pentadecafluorooctylamine ($NH_2CH_2(CF_2)_6CF_3$) (0.1 mM), dansylamine (15 mg/6 mL), *N*-6-(aminohexyl)-1-pyrenebutanamide (15 mg/6 mL), or modified, primary amine-terminated, *p*-methyl red (15 mg/6 mL). In each case, after the film was removed from each derivatization solution, it was washed with ethanol and dried with a stream of nitrogen and then extracted for 15 h using CH_2Cl_2 in a jacketed Soxhlet apparatus. The films were dried under vacuum for 15 min (1 Torr).

Fluorination of Hyperbranched Films with Reactive Fluoroacrylate Copolymers. Derivatization of the 1-PAA/PE or 3-PAA/PE films with the fluorous polyacrylate copolymer consisting of 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate and *N*-acryloxysuccinimide (TAN-c-NASI) (**1**)[29] was accomplished by first allowing an activated 1PAA/PE or a 3-PAA/PE film to react with an excess of a diamine such as 1,6-hexanediamine or α,ω-diaminopoly(ethylene glycol) ($NH_2-PEG_{2000}-NH_2$). The aminated surfaces were allowed to then react with the copolymer in a solution of α,α,α-trifluorotoluene at 70° for 5 h. The films were sonicated for 15 min in 1,1,2-trichlorotrifluoroethane, following the reaction, to remove physisorbed TAN-c-NASI. A control experiment was done using 6-aminohexanol in place of the diamines; no graft of the TAN-c-NASI occurred.

Deprotonation of Carboxylic Acid-Containing PE Films ($PE-CO_2H$ or PAA/PE). Deprotonation of the oxidized or hydrolyzed films was accomplished stirring the film in NaOH/EtOH for 1 h. The film was then washed with ethanol and dried with a stream of nitrogen and then dried under vacuum. The films were successfully reprotonated using HCl/EtOH.

Ionic Assembly of Cationic Polyelectrolytes into 3-PAA/PE. Solutions of poly-D-lysine and 4-poly(amidoamine) (PAMAM) dendrimer in pH 7.0−7.2 buffer were made. When the 3-PAA/PE films were allowed to stand in the solutions for 30 min, removed, washed with ethanol, and dried with a stream of nitrogen, the entrapment of polycationic salts in the films was accomplished.

Hyperbranched Grafting onto Fluorinated Films. Fluorine labels were first attached to an oxidized polyethylene by activating the $PE-CO_2H$ with ethyl chloroformate and then treating this film with a DMF solution of 1*H*,1*H*-pentadecafluorooctylamine (0.1 M) for 15 min. Then the film was allowed to react with a DMF solution of $NH_2-R-PTBA-R-NH_2$ (250 mg/6 mL) for 1 h. After this treatment, a normal hyperbranched grafting process was followed with successive hydrolysis, activation, and grafting leading to a 2-PTBA overlayer. The piece of film was cut into three sections for XPS spectroscopic analysis.

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