New Routes to Hyperbranched Poly(acrylic acid) Surface Grafts on Polyethylene Films and Powders

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ABSTRACT: Hyperbranched grafting is a useful method for surface modification of both inorganic and organic polymer surfaces but is synthetically cumbersome as it requires synthesis of functional polymers as reagents. This paper describes an alternative approach using acrylic acid and Ce(IV) graft-on-a-graft chemistry. The substrates, polyethylene films and powders, were prepared for grafting by oxidation and incorporation of a low loading of a polyhydroxylated oligomer. In subsequent steps, the hydroxyl groups of this surface are successively grafted with Ce(IV) and acrylic acid. The resulting carboxylic acid groups were converted into yet more hydroxyl groups. Repetition of this process yields a hyperbranched graft. Copolymer grafts too can be prepared using appropriate mixtures of monomers.

Introduction

Grafting from inorganic and polymer surfaces to prepare functional interfaces is a well-established procedure.[1−3] Recent work using controlled radical polymerization chemistry and layer-by-layer ionic and hydrogen-bond-based grafting have expanded opportunities to prepare structurally tuned interfaces.[4−6] Radical,[1,7] anionic,[8] cationic,[9] and transition-metal mediated[10] grafting chemistry typically produce linear grafts on surfaces. Layer-by-layer self-assembly procedures produce structurally more complicated grafts.[3]

While the linear grafts prepared in normal grafting-from chemistry are useful, recent years have seen increased attention to routes to hyperbranched polymer grafts on surfaces.[11−16] Such grafts can be prepared using hyperbranched polymers as precursors or by hyperbranched grafting from a surface. An example of this latter approach is the graft-on-a-graft route to irregularly hyperbranched poly(acrylic acid) grafts developed by the Bergbreiter and Crooks groups that uses amine-functionalized poly(*tert*-butyl acrylate) ($H_2N-PTBA-NH_2$) as a reagent.[17] This chemistry has proven to be a general route to functional surfaces on diverse supports. Such surfaces have uses in catalysis,[18,19] corrosion inhibition,[20−23] enzyme immobilization,[24] adhesion promotion,[25] and the synthesis of biocompatible materials.[26,27] The $-CO_2H$ groups of such grafts can be modified by a variety of chemistry to produce amides, alcohols, esters, and other carboxylic acid derivatives.[27] These grafts are lightly cross-linked by virtue of the syntheses used. Polymerization using these grafts as starting materials is also feasible.[28] Substrates as diverse as polyethylene, polypropylene, gold, and glass are suitable for this grafting chemistry.

This paper describes an alternative simpler route to hyperbranched poly(acrylic acid) grafts that only requires a preformed polymeric reagent in the first step. This new route is more efficient as judged by the amount of $-CO_2H$ groups added in each grafting stage. This new scheme uses Ce(IV) grafting of aqueous solutions of acrylic acid onto a polyhydroxylated polyethylene surface. Contact angle analyses, elemental analyses using XPS spectroscopy, ATR-IR spectroscopy of polyethylene film and powder substrates, and titrimetric analysis of grafts on polyethylene powder substrates show that grafting using Ce(IV) and acrylic acid successfully forms poly(acrylic acid) grafts. While the Ce(IV) and $NH_2-PTABA-NH_2$ procedures produce comparable hyperbranched graft densities of $-CO_2H$ groups, the Ce(IV) route is actually more effective than the previously described PTBA-based chemistry. This Ce(IV) grafting chemistry is also suitable for formation of copolymer grafts.

Results and Discussion

Ceric ion grafting of water-soluble monomers onto hydroxylated materials has been used as a mild way to modify polyhydroxylated water-swellable macromolecular substrates.[29−32] This chemistry has, for example, been used to graft polyacrylamide, polyacrylonitrile, and poly(acrylic acid) onto starch. Water is used as a solvent—an advantage in a Green Chemistry sense.[33] The only requirement is that hydroxyl groups must be present on the substrate.

In the case of polyethylene, hydroxyl groups need to be introduced if Ce(IV) grafting is to be carried out. Simple oxidation and reduction can introduce some hydroxyl groups onto a polyethylene surface.[34] However, the loading of hydroxyl groups from such a process is relatively low, and the resulting surface is not very hydrophilic. We reasoned that the aqueous solutions used in Ce(IV) grafting would be more effectively used if we first treated an oxidized polyethylene surface with $ClCO_2Et$ and then $H_2N-PTBA-NH_2$. Acidolysis of these *tert*-butyl esters then produced covalently bound oligomers of poly(acrylic acid) (1-PAA/PE) that were reduced[28] to form a polyhydroxylated poly(allyl alcohol) surface (a 1-PAA-OH/PE film). Exposure of this 1-PAA-OH/PE film to an aqueous solution of acrylic acid and $(NH_4)_2Ce(NO_3)_6$ produced surface alkoxy radicals that graft acrylic acid to the surface to produce a 2-PAA/PE poly(acrylic acid) graft. Subsequent reduction of these new $-CO_2H$ groups to $-CH_2OH$ groups produced a 2-PAA-OH/PE film. Repetition of the Ce(IV) grafting produced a hyperbranched graft. This overall process is shown in Figure 1. The product grafted surfaces produced in this chemistry were extensively rinsed first

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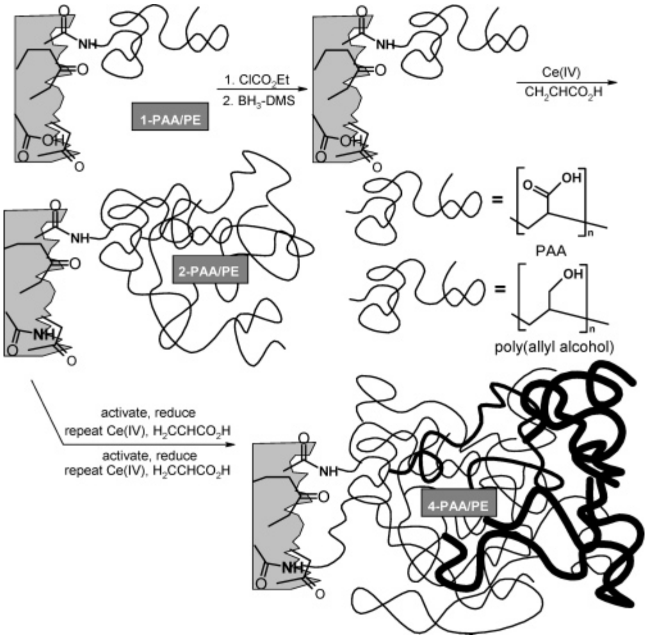

Figure 1. Multistage synthesis of 3-PAA/PE using hyperbranched grafting using $(NH_4)_2Ce(NO_3)_6$ and oxygen-free aqueous solutions of acrylic acid. The 3-PAA/PE notation refers to an initial 1-PAA/PE film that had been grafted with two subsequent stages of acrylic acid (AA) to form a 3-PAA graft.

with dilute NaOH and then with EtOH until no further physisorbed polymer was removed based on the lack of change in the ATR-IR spectra of the product film. This precaution was taken because chain transfer could lead to some solution-based polymer formation. Our prior work had shown that poly(acrylic acid) in solution can form hydrogen-bond-based grafts to a hydrogen-bond donor or acceptor rich surface.[35]

There are differences between the formation of hyperbranched surface grafts of poly(acrylic acid) by this Ce(IV) method and the previously used graft-on-a-graft chemistry that employed $H_2N-PTBA-NH_2$ as the grafting agent. The first of these differences is that the Ce(IV) method selectively modifies the surface of the substrate polyethylene because of the solvent used in grafting.[36] The water-soluble monomer, the PE-incompatible ceric ion, and the swelling of the product grafts in water ensure surface selectivity in grafting using aqueous solutions.[37] In the PTBA hyperbranched grafting method, surface selectivity presumably was the result of the size of the poly(*tert*-butyl acrylate) grafting agent. The second difference between these routes to hyperbranched polyethylene grafted surfaces is the reagent used. In the ceric ion method, commercially available monomer(s) are used after the first step. In the PTBA hyperbranched grafting method, much more of the polymeric reagent must be prepared.[20] This preparation is time-consuming. This is an advantage for the ceric ion hyperbranched grafting method since PTBA is only used in the first step. A third difference is the speed and facility with which the ceric ion grafting occurs. This was seen by ATR-IR spectroscopy when the relative integrated intensities of the peaks for the C−H's in the underlying bulk polymer were compared to the intensities for peaks for the C=O's in the carboxylic acid groups for films grafted with the Ce(IV) route vs films grafted using the $H_2N-PTBA-NH_2$ method. In these comparisons, the integrated intensity of the $\nu_{C=O}$ absorption from 1710 to 1715 cm^{-1} vs the integrated intensity of the ν_{C-H} absorption at 2800−3000 cm^{-1} were compared. The integrated values of the $\nu_{C=O}/\nu_{C-H}$ absorptions were ca. 1:1 for the Ce(IV) grafted 2-PAA film while they were only ca. 1:4 for the 2-PAA/PE film prepared using the $H_2N-PTBA-NH_2$ graft chemistry.

Table 1. Comparison of XPS Spectroscopic Data for Hyperbranched Grafted Polyethylene Films Grown via the PTBA Route and the Ce(IV) Routes[a]

film[b]	C (atom %)	O (atom %)	N (atom %)
polyethylene	99.3	0.3	0.4
oxidized polyethylene	96.2	3.7	0.1
1-PTBA/PE	86.8	12.7	0.6
1-PAA/PE	80.0	18.8	1.2
2-PTBA/PE	82.9	16.5	0.6
2-PAA/PE via PTBA	77.9	20.6	1.5
2-PAA/PE via Ce(IV)	75.9	23.2	0.9
2-PAA/1-PDMAM/PE[c]	75.4	21.5	3.1
3-PAA/2-PDMAM/PE[d]	71.4	24.2	4.4
4-PAA/3-PDMAM/PE[e]	66.1	28.3	5.6

[a] The polyethylene films were all extracted with EtOH in a jacketed Soxhlet for 15 h and then dried before analysis. [b] Either medium- or high-density polyethylene films were used in the initial oxidation. Hyperbranched films generally had comparable atom compositions regardless of which type of polyethylene was used as starting material. [c] This notation refers to a PE film with one copolymerization stage after the initial 1-PAA step (one Ce(IV)-mediated copolymerization step using a mixture of acrylic acid (AA) and *N*,*N*-dimethylacrylamide (DMAM)) to form a graft with poly(acrylic acid) (PAA) and poly(*N*,*N*-dimethylacrylamide) (PDMAM). [d] This notation refers to the product of two Ce(IV)-mediated copolymerization steps leading to a copolymer graft with poly(acrylic acid) (PAA) and poly(*N*,*N*-dimethylacrylamide) (PDMAM). [e] This notation refers to the product of three Ce(IV)-mediated copolymerization steps leading to a copolymer graft with poly(acrylic acid) (PAA) and poly(*N*,*N*-dimethylacrylamide) (PDMAM).

XPS spectroscopic analyses confirmed the rapid growth of the poly(acrylic acid) groups on polyethylene surfaces grown via the ceric ion method. These data are listed in Table 1 and show that a 2-PAA/PE film grown via the ceric ion method has a lower C atom % and a higher O atom % than a 2-PAA/PE counterpart grown using $H_2N-PTBA-NH_2$ graft chemistry. This is consistent with the idea that there are more carboxylic acid groups masking the underlying polyethylene layer in the grafts prepared using the ceric ion initiator than in the grafts produced through the $H_2N-PTBA-NH_2$ graft chemistry.

Titrimetric quantification of the $-CO_2H$ groups on powders grafted using the ceric ion method support the premise that poly(acrylic acid) hyperbranched grafts grow faster via the ceric ion method than via the $H_2N-PTBA-NH_2$ graft chemistry (Figure 2).[18] The titrimetric data show that at the same grafting stage the ceric ion method of grafting produced a denser loading of carboxylic acid groups per gram of polyethylene powder than the PTBA route.

Comparing the growth of the grafts prepared by the PTBA method and the ceric ion method is complicated because of the different chemistry of these methods. In both routes, a thin layer of poly(*tert*-butyl acrylate) is grafted to the surface in the first step. While acidolysis of these *tert*-butyl esters using CH_3SO_3H is very efficient, the next steps in PTBA grafting are activation of the $-CO_2H$ groups with $ClCO_2Et$ and amidation of the resulting mixed anhydride with $H_2N-PTBA-NH_2$. Amidation of the activated carboxylic acid groups with this oligomeric amine is incomplete so only a fraction of the surface-bound carboxylic acids are converted to PTBA-containing amide groups. After acidolysis of the *tert*-butyl esters, the total number of $-CO_2H$ groups

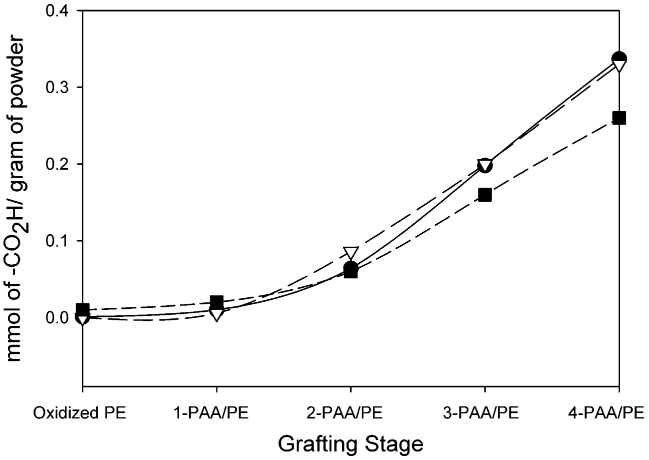

Figure 2. Titration data for hyperbranched poly(acrylic acid) grafts grown via the PTBA and ceric ion methods. The ■ symbol represents various stages of hyperbranched poly(acrylic acid) on polyethylene powders grown via the PTBA method. The ● and ∇ symbols represent various stages of two separately grown polyethylene powders covered with hyperbranched poly(acrylic acid) surface grafts.

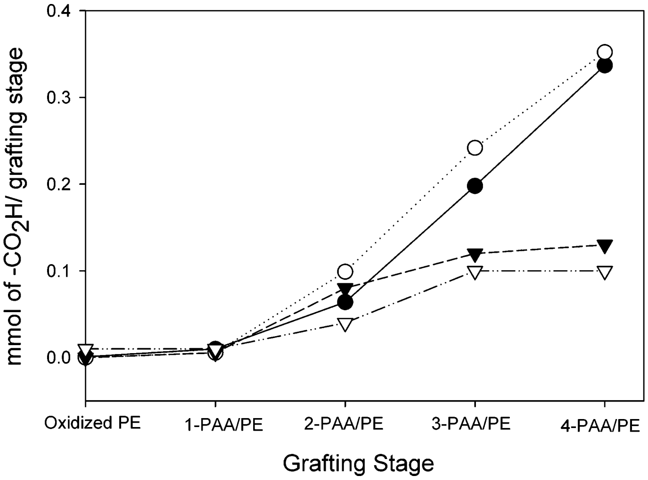

Figure 3. Amount of $-CO_2H$ groups grafted to polyethylene powder at each stage through various grafting stages in duplicate hyperbranched experiments using either the ceric ion method (closed and open circles) or the PTBA method (closed and open triangles).

measured in titration with 0.01 M NaOH is the number of carboxylic acid groups present at each grafting stage, and the titration assay includes both "new" and "old" carboxylic acids.

The ceric ion method works in a different way. In the ceric ion route, the "starter oligomer" containing $-CO_2H$ groups and all $-CO_2H$ groups of subsequent stages are quantitatively converted into poly(allyl alcohol) $-CH_2OH$ groups. This was confirmed by ATR-IR spectroscopy. Thus, when a grafting layer is attached, all the titratable $-CO_2H$ groups are "new". For example, after reduction of the 2-PAA/PE stage to the 2-PAA-OH/PE stage, there are no titratable $-CO_2H$ groups from the earlier stage left. Thus, the 0.34 mmol of $-CO_2H$/g of PE powder in 3-PAA/PE is due to this last stage of grafting.

The differences in chemistry of these routes make a precise comparison of the efficiency of the ceric ion route to the $H_2N-PTBA-NH_2$ graft chemistry problematic. However, it is possible to qualitatively estimate the difference in these procedures if we assume a particular efficiency for amidation of the $-CO_2H$ groups in $H_2N-PTBA-NH_2$ graft chemistry. For example, assuming ca. 25% conversion of the $-CO_2H$ groups to amides, we can estimate the number of $-CO_2H$ groups introduced at each stage in $H_2N-PTBA-NH_2$ graft chemistry and compare these values to the known amount of $-CO_2H$ groups introduced at each grafting stage in the Ce(IV) method. These numbers were calculated for two separate grafting experiments using either the Ce(IV) or the $H_2N-PTBA-NH_2$ graft chemistry, and the data for these duplicate experiments are plotted in Figure 3. This comparison again shows greater efficiency in terms of the mmol of $-CO_2H$ groups introduced per graft stage with the Ce(IV) method.

Control experiments established that the presence of hydroxyl groups on the surfaces was necessary for the ceric ion graft chemistry. Specifically, if 1-PTBA/PE grafts were used instead of their reduced counterparts, no grafting of acrylic acid was detectable by ATR-IR spectroscopy. In the second control experiment, a 1-PTBA/PE film was exposed to an aqueous solution of poly(vinyl alcohol), Ce(IV), and acrylic acid. In this case, grafting of acrylic acid to the soluble poly(vinyl alcohol) did occur. However, after extraction, the recovered 1-PTBA/PE film had no trace of grafting as shown by ATR-IR spectroscopy or contact angle analysis.

Contact angle analyses of the $-CO_2H$-rich surfaces were in accord with the chemistry in Figure 1. While the starting PE had an advancing water contact angle of $\theta_a = 104°$, the more polar hyperbranched poly(acrylic acid) grafted films were more hydrophilic. The 1-PAA/PE film had a θ_a of 80°, which changed to values of 55°, 46°, and 44° after Ce(IV)-mediated formation of the 2-PAA/PE, 3-PAA/PE, or 4-PAA/PE film in the acid form. These data are comparable to those previously reported for PTBA-based hyperbranched grafting.[18,36]

The same general graft chemistry used in Figure 1 can also be used to prepare hyperbranched copolymer grafts on polyethylene surfaces. In this case, the ceric ion initiator's role is the same as before. The Ce(IV) ions produce surface alkoxy radicals from surface hydroxyl groups, and these radicals in turn react with one or the other water-soluble monomer, acrylic acid (AA) or *N,N*-dimethylacrylamide (DMAM) (Figure 4).

ATR-IR spectroscopy was used initially to follow the graft copolymerization. However, the peaks due to the two different types of carbonyls present in this graft, carboxylic acid and amide carbonyls, overlap. The product film consists of a broadened peak at 1710 cm^{-1} with an amide shoulder at 1650 cm^{-1}. ATR-IR spectroscopy was capable of detecting both sorts of carbonyls once the film was treated with base. After base treatment, the film contained separated amide carbonyl (1650 cm^{-1}) and carboxylate carbonyl (1550 cm^{-1}) peaks.

Various ratios of monomers were used in this graft copolymerization reaction. When equimolar amounts of monomers were used, ATR-IR spectra of the product films showed that poly(*N,N*-dimethylacrylamide) was the major constituent of the graft on the polyethylene surface. When a solution with a ratio of 6.25:1 (mol:mol) of acrylic acid to *N,N*-dimethylacrylamide was used, ATR-IR spectroscopy showed approximately equal amounts of grafted acid and amide were present. When a 27.5:1 ratio (mol:mol) of acrylic acid to *N,N*-dimethylacrylamide was used, the principal species on the surface were $-CO_2H$ groups. The relatively nonpolar environment at the surface (versus an aqueous solution) may be partly responsible for a preference for *N,N*-

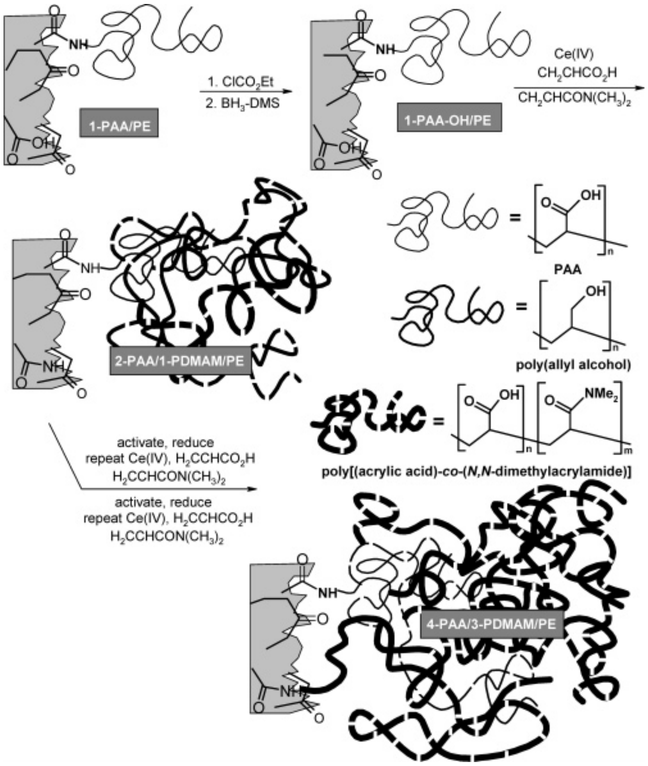

Figure 4. Multistage synthesis of 4-PAA/3-PDMAM/PE hyperbranched copolymer grafts using acrylic acid and *N,N*-dimethylacrylamide monomers. At each stage, the $-CO_2H$ groups of the acrylic acid comonomer are reduced to form intermediate $-CH_2OH$ groups that with Ce(IV) ion provide sites for a subsequent stage of graft chemistry. The result is a randomly assembled copolymer graft with poly(allyl alcohol), poly(acrylic acid), and poly(*N,N*-dimethylacrylamide) on a polyethylene surface. The notation in this figure, 2-PAA/1-PDMAM/PE or 4-PAA/3-PDMAM/PE, refers to an original 1-PAA/PE graft that was treated with a second cografting stage with both poly(acrylic acid) (PAA) and poly(*N,N*-dimethylacrylamide) PDMAM) or three additional cografting stages with both poly(acrylic acid) (PAA) and poly(*N,N*-dimethylacrylamide) PDMAM).

dimethylacrylamide incorporation. The reactivity ratio in these copolymerizations cannot be readily calculated quantitatively, but these results are in any case not too qualitatively different from what would be expected given the roughly equal reactivity ratios for these same monomers in solution-state radical polymerizations.[38]

XPS spectroscopic analysis of the atom % composition of the grafted PAA−PDMAM surfaces confirmed graft copolymerization occurred. These data are listed in Table 1 and show that the hyperbranched graft surface is significantly different in atomic composition than either the underlying bulk oxidized polyethylene or hyperbranched poly(acrylic acid) hyperbranched grafts. These data were obtained for surfaces through four graft cycles. They show that the copolymerization did indeed produce hyperbranched poly[(acrylic acid)-*co*-(*N,N*-dimethylacrylamide)]. At the 4-PAA/3-PDMAM/PE stage, the XPS atom % values are in accord with a graft that completely covers the underlying PE with an equimolar amount of acrylic acid and *N,N*-dimethylacrylamide.

Hyperbranched copolymerization experiments were carried out on polyethylene powders in addition to the films. The powders were analyzed in the same fashions as the films. Additionally, the $-CO_2H$ loading on these powders was quantitatively measured by titration using 0.01 M NaOH. The titrimetric analyses shown in Figure 5 interestingly show that grafting of copolymers is as efficient as grafting as acrylic acid alone.

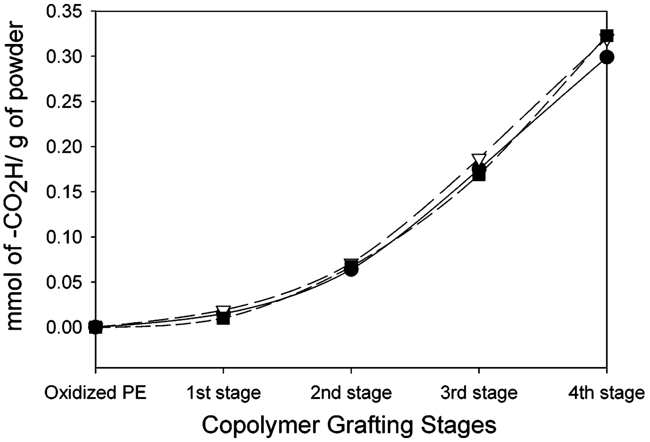

Figure 5. Titrimetric analyses of the $-CO_2H$ groups present in poly[(acrylic acid)-*co*-(*N,N*-dimethylacrylamide)] hyperbranched grafts on polyethylene surfaces: (●, ■, ▽) represent three independent copolymer hyperbranched grafting experiments. The first stage is 1-PAA/PE, the second stage is 2-PAA/1-PDMAM/PE, the third stage is 3-PAA/2-PDMAM/PE, and the fourth stage is 4-PAA/3-PDMAM/PE. A ratio of 6.25:1 (mol:mol) of acrylic acid to *N,N*-dimethylacrylamide was used in the copolymerization grafting.

Conclusion

Hyperbranched grafting using Ce(IV) grafting of hydroxymethyl starter groups on PE films and powders has been investigated by ATR-IR, contact angle measurements, XPS, and titrimetric analyses. The Ce(IV) method appears to produce more dense coverage of the films at a quicker pace than previous chemistry using condensation graft-on-a-graft chemistry using α,ω-diaminopoly(*tert*-butyl acrylate) polymers. The necessary starter hydroxyl groups were introduced onto the surface by reduction of the $-CO_2H$ groups of a previous acrylic acid graft. Extensions of this aqueous-based hyperbranched grafting using acrylic acid, *N,N*-dimethylacrylamide, and a ceric ion initiator can be used to build robust thin copolymer films on oxidized polyethylene surfaces. The surface coverage of these multifunctional films has been investigated by ATR-IR spectroscopy, XPS spectroscopy, and titrimetric analysis.

Experimental Section

General Procedures. Toluene and THF were distilled under N_2 from a sodium−benzophenone mixture before use. Ethyl acetate, ethanol, and methylene chloride were dried over 3 Å sieves before use. *tert*-Butyl acrylate (Aldrich, 98%) and acrylic acid (Aldrich, 99%) were distilled before use. Acrylic acid was additionally degassed using a freeze−pump−thaw method prior to use. X-ray photoelectron spectra were obtained on a Kratos Axis Ultra XPS (Manchester, UK) using a monochromatic Al Kα source (400 W) in a UHV environment (ca. 5×10^{-9} Torr). During acquisition, surfaces were kept from charging by the application of low-energy electrons. Surface elemental composition was determined by normalized integration of the resulting peaks using Kratos software. ^1H and ^{13}C NMR spectroscopy experiments were carried out using Mercury 300, Unity 300, or Unity 500 spectrometers. Contact angle measurements were obtained using a FTÅ model 200 goniometer using doubly distilled water. The contact angle values reported are the average of four measurements obtained at different spots on the same film. The estimated error is ±3°. ATR-IR spectra were obtained with a Mattson Galaxy 4021 series FT-IR with a Wilks model 10 ATR accessory at an angle of 45° using a KRS-5 crystal.

Ceric Ammonium Nitrate Solution. The ceric ammonium nitrate initiator solution was prepared using 0.02 M $(NH_4)_2Ce(NO_3)_6$ and 0.40 M HNO_3.

Preparation of 1-PAA/PE Films and Powders. The starting poly(acrylic acid) oligomer modified films and powders were synthesized from polyethylene film or powder following a reported procedure.[36]

Hyperbranched Grafting onto PE Films or Powders Using α,ω-Diaminopoly(*tert*-butyl acrylate) ($NH_2-PTBA-NH_2$). This chemistry followed the reported procedure[18,36] beginning with a 1-PAA/PE graft.

Hyperbranched Grafting via the Ceric Ion Route. Grafting onto the polyethylene films and powders used similar procedures. Grafting of acrylic acid onto an oxidized polyethylene substrate[18,36] then was carried out using a sequence of activation, reduction, and polymerization steps. This sequence of steps begins after the initial "starter group" is attached to the surface. The initial substrate was 6 cm^2 of a 1-PAA/PE film or 1 g of a 1-PAA/PE powder that had been washed with ethanol and dried with a stream of nitrogen and then dried under vacuum for 1 h (1 Torr) before use. The $-CO_2H$ groups of the substrate were first activated using 0.1 mL of ethyl chloroformate (1.0 mL for the powder) and 0.1 mL of *N*-methylmorpholine (1.0 mL for the powder) in 7 mL of DMF (60 mL for the powder) for 15 min (1 h for the powder). The substrate was washed with ethyl acetate and dried with a stream of nitrogen. Then a solution of dry THF (50 mL) and 2 M borane−methyl sulfide (10 mL) was added to the substrate, and the mixture was allowed to reflux under nitrogen for 12 h. After the 12 h, the substrate was removed and rinsed with successively for 10 min with water, hydrochloric acid (1 M), and ethanol. After drying the product film or powder under vacuum, ATR-IR spectroscopy was used to confirm that reduction was complete based on the absence of a carbonyl peak at 1710 cm^{-1}.

The reduced surfaces were then allowed to react with 75 mL of an aqueous solution that contained 6 mL of acrylic acid and 3 mL of the $(NH_4)_2Ce(NO_3)_6$ solution described above. Oxygen was excluded from this reaction by bubbling nitrogen through the water for 45 min prior to beginning the grafting experiment. This grafting was carried out at room temperature 6 h or less, after which point the substrates were removed and washed with water and then ethanol. In these studies, a reaction time of 6 h was used for convenience. While a few experiments suggested shorter reaction times lead to less grafting, we did not carry out extensive studies to optimize this time. Extraction for 15 h with ethanol in a jacketed Soxhlet apparatus ensured complete removal of any noncovalent graft poly(acrylic acid). This 2-PAA/PE graft was then subjected to additional activation, reduction, and grafting steps 1 to 2 more times to produce 3-PAA/PE and 4-PAA/PE surfaces, respectively. After each grafting stage the surfaces were analyzed by ATR-IR spectroscopy, contact angle measurement, and (for powders) titrimetric analysis. The ATR-IR spectra confirmed growth on the surfaces if the integrated intensity of the carbonyl peak (1710−1715 cm^{-1}) increased in intensity in comparison to the intensity of the underlying bulk polymer C−H peaks (2800−3000 cm^{-1}). The average contact angle measurement for 1-PAA/PE, 2-PAA/PE, 3-PAA/PE, and 4-PAA/PE films was 78°, 55°, 46°, and 44°, respectively. Titration using NaOH of powders showed that the mmol of carboxylic acid per gram of polyethylene powder for 1-PAA/PE, 2-PAA/PE, 3-PAA/PE, and 4-PAA/PE was 1.00×10^{-3}, 0.01, 0.0640, 0.1980, and 0.3370 mmol/g, respectively.

Control Experiments for Ceric Ion Route. Control experiments were conducted to show that hydroxyl groups on the surfaces were indeed necessary for the acrylic acid to form a hyperbranched graft. In the first experiment, a 1-PTBA/PE film was used instead of its reduced hydroxyl-containing counterpart. After exposing this 1-PTBA/PE films to the aforementioned aqueous solution of acrylic acid ceric ammonium nitrate for 12 h, the film was removed, washed with ethanol, and dried with a stream of nitrogen. It was then extracted with EtOH in a jacketed Soxhlet apparatus for 15 h. There was no change in the ATR-IR spectrum, the XPS spectrum, or contact angle analysis for the "product" film from the initial 1-PTBA/PE film. For example, XPS spectroscopic data showed that there was 86.7 atom % C and 12.7 atom % O in the initial 1-PTBA/PE film. The "product" film had 85.3 atom % C and 13.0 atom % O. A second control experiment also used a 1-PTBA/PE film but included 4 mL of poly(vinyl alcohol) in the grafting solution. After the 6 h, the PE film substrate was removed from the viscous solution, and the film was rinsed with EtOH. Extraction in a jacketed Soxhlet apparatus for 15 h removed any soluble polymer. Again, the spectroscopic evidence (ATR-IR, contact angle, and XPS) showed no significant change in the initial 1-PTBA/PE film. The ATR-IR spectra for this product only showed an ester peak at 1730 cm^{-1} with no acid carbonyl peak at 1710 cm^{-1}. XPS spectroscopic data showed that there was 86.7 atom % C and 12.7 atom % O in the initial 1-PTBA/PE film and 86.0 atom % C and 13.1 atom % O in the product film.

Copolymerization of Acrylic Acid and *N,N*-Dimethylacrylamide on Polyethylene Films or Powders. Graft copolymerization of acrylic acid and *N,N*-dimethylacrylamide onto a 1-PAA/PE substrate was carried out using the same sequence of activation, reduction, and polymerization described above. The only difference was that reduced films were grafted using a 75 mL aqueous solution that contained a predetermined mixture of acrylic acid and *N,N*-dimethylacrylamide along with 5 mL of the aforementioned $(NH_4)_2Ce(NO_3)_6$ solution. The ratio of the acrylic acid and *N,N*-dimethylacrylamide was varied as discussed in the Discussion section.

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