Surface Functionalized Polypropylene: Synthesis, Characterization, and Adhesion Properties

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ABSTRACT: Modification of polypropylene by hyperbranched grafting with a poly(acrylic acid) graft was carried out using techniques previously used with gold, aluminum, silicon, and polyethylene surfaces. An initial etching oxidation produced a modified polypropylene that was presumed to contain carboxylic acid functional groups (though none were detected by IR spectroscopy). Then, a series of repetitive grafting experiments using an α,ω-diamine derivative of poly(*tert*-butyl acrylate) were used to produce surfaces containing significant amounts of poly(acrylic acid). The resulting surfaces were characterized by ATR-IR spectroscopy, contact angle measurements, and XPS spectroscopy. Treatment of the surfaces with alkali produced a more hydrophilic carboxylate surface. Treatment of these surfaces first with ethyl chloroformate followed by pentadecylfluorooctylamine produced a hydrophobic fluorinated surface. Mechanical tests show that such surface modification not only serves as a route to modify polypropylene's hydrophilicity/hydrophobicity—such modification substantially affects the adhesive strength between this modified polypropylene and an epoxy adhesive. Double cantilever beam tests show that adhesion increases from 2 J/m^2 for unmodified polypropylene to up to 29 J/m^2 with the modified polypropylene.

Polypropylene (PP), like polyethylene and other polyolefins, has become an increasingly important material. The ability to tailor the bulk properties of polyolefins through catalyst design makes these already important polymers derived from relatively inexpensive feedstocks even more important. However, these materials' surface chemistry is not always ideal. Polyolefins are generally hydrophobic materials. In many practical instances, improved adhesion, wettability, printability, or biocompatibility is desired, and such properties can only be imparted to these surfaces by a postpolymerization surface modification step. As a result, there is continuing and widespread interest in new chemistry capable of modifying these polymers' surfaces.[1−3] Here we describe chemistry that produces highly functional thin film grafts in a forgiving manner on polypropylene surfaces. The studies below show that the recently described hyperbranched graft chemistry we have described for polyethylene[4] and other solids[5−8] is applicable to polypropylene, and we also show that the products have enhanced properties as measured by adhesion tests.

Polypropylene (PP) has excellent balanced physical and mechanical properties. Polypropylene-based materials are inexpensive and can be easily recycled, thus making them attractive for many engineering applications. However, while the bulk materials properties of polypropylene are attractive and potentially variable through synthesis, the surface properties of polypropylene are not as easily controlled.[1] This has undesirable consequences. For example, adhesion of polypropylene to other polar materials is generally low because of polypropylene's low surface free energy. This has significantly limited polypropylene's engineering applications. An approach to improve bondability of polypropylene is chemical modification of polypropylene's surface. Such surface modification and the consequences of surface modification of polypropylene bondability are the focus of this study.

Polypropylene surface functionalization has been the subject of a variety of prior studies. Both gas-phase and solution-phase chemistry have been used. Several groups have described solution-state oxidative etching chemistry.[9] Various gas-phase treatments or plasma oxidations also yield polypropylene with surface groups.[10−12] We also have reported procedures leading to surface-modified polypropylene using a blending technique.[13] Finally, various grafting chemistries have been successfully used on polypropylene.[3,14−18]

While surface functionalization of polypropylene can be effected by plasma treatments, wet oxidative etching, physical blending chemistry, or grafting, these techniques are generally less effective than similar chemistry on polyethylene.[19] The ineffectiveness of such chemistry reflects both the more reactive nature of the polypropylene surface and the chemistry that leads to ablative etching.[20] Moreover, even when successfully modified, polypropylene surfaces like other polyolefin surfaces generally have a tendency to reorganize or reconstruct.[21] The relative ineffectiveness of many surface modification procedures can be compensated for by using grafting chemistry wherein the introduced surface groups are polyfunctional polymer or oligomer chains. Such chemistry multiplies the quantity and effect of whatever functional groups are introduced at the polypropylene surface. Much of the existing chemistry for grafting onto polypropylene is based on chemistry of solutions or melts of polypropylene and is not surface specific.[22] However, surface grafting including photoinitiated grafting,[14] living radical grafting,[15] ceric ion-induced grafting,[16] layer-by-layer ionic grafting,[17] and plasma polymerizations[18] have all been described as being effective for introduction of polyfunctional grafts onto polypropylene surfaces. Condensation po-

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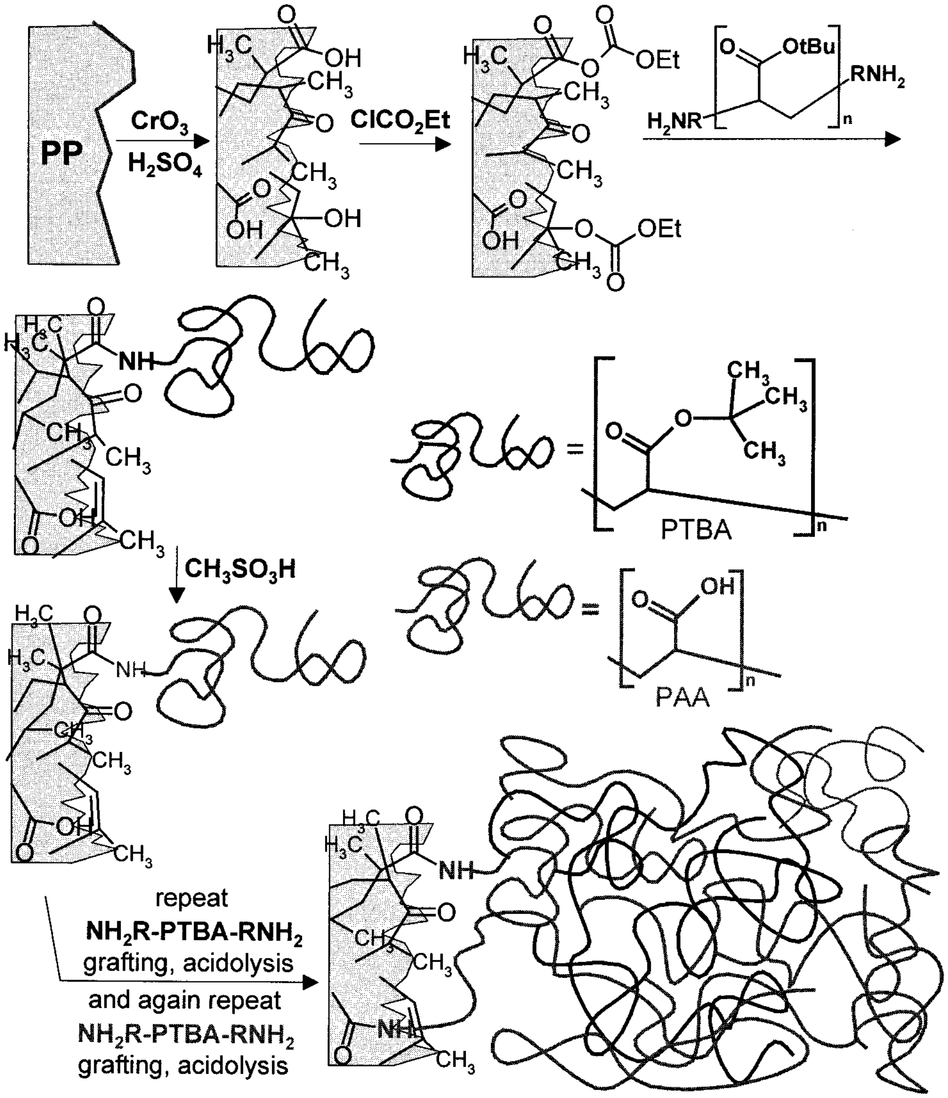
Scheme 1. The "Forgiving" Graft-on-a-Graft Strategy Used To Prepare Irregular Hyperbranched Poly(acrylic acid) (PAA) Grafts on Polypropylene (PP) Using Amine-Terminated Poly(*tert*-butyl acrylate) (PTBA) as a Synthetic Reagent



lymerization has, however, not been used effectively. Here we describe how the "forgiving" nature of the hyperbranched polymerization process we recently developed[5] effectively allows one to use condensation reactions and a graft-on-a-graft strategy to produce heavily functionalized polypropylene films. We further show that such surface functionalized films have significantly increased wettabilities and that such wettability can be modified by further synthesis. Finally, we show that these grafts have measurable consequences in adhesion between polypropylene and an epoxy resin when the bonding strengths of a neat polypropylene and a surface-modified polypropylene to an epoxy-based adhesive are compared using a double cantilever beam (DCB) test.

Results and Discussion

Our efforts to surface graft onto polypropylene were based on our earlier successes in grafting hyperbranched grafts onto gold, aluminum, glass, silicon, and polyethylene surfaces.[4−8,23] The chemistry used here for polypropylene is illustrated in Scheme 1. It is based on the approach used in these earlier cases and is a graft-on-a-graft strategy that was conceived to be a "forgiving" synthetic approach. The general idea was that a repetitive process of grafting an amine containing polymer to a carboxylic acid-containing surface by condensation chemistry, converting the grafted polyvalent polymer's pendant groups to more carboxylic acids and repeating this process several times would produce an irregular hyperbranched graft. The polyvalent nature of the surface means that even an originally inefficient introduction of starting sites or of more polyvalent sites onto the surface would be acceptable as a way to achieve high levels of functionality since this repetitive "forgiving" process eventually produces a heavily functionalized surface.

The ATR-IR spectra of polypropylene subjected to the chemistry in Scheme 1 aptly illustrates the importance of this repetitive process. As can be seen in the IR spectrum in Figure 1b, there is no detectable carbonyl group introduced onto polypropylene by chromic acid etching.

Indeed, even after one cycle of α,ω-diaminopoly(*tert*-butyl acrylate)/methanesulfonic acid treatment, the intensity of the carbonyl peak in the ATR-IR spectrum (Figure 1c) of the presumed poly(acrylic acid) graft (1-PAA/PP) is essentially nil. However, a low-intensity

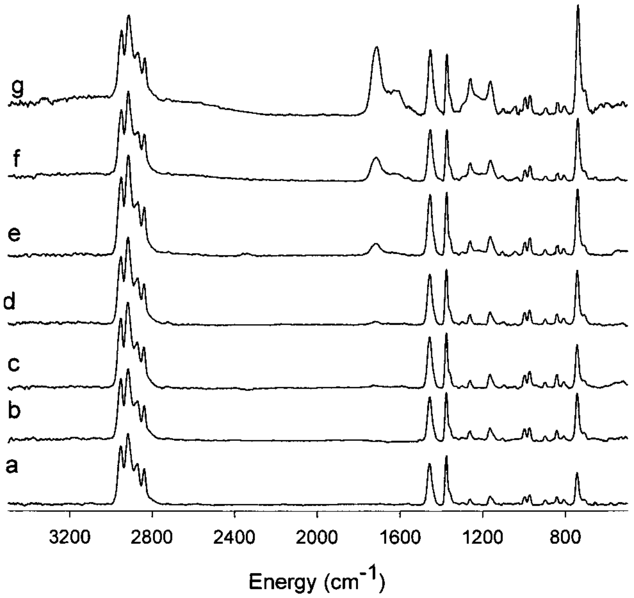


Figure 1. ATR-IR spectra of polypropylene (PP) films illustrating the low intensity of the initial carbonyl peaks and the subsequent growth in carbonyl peak intensity as hyperbranched grafting of poly(acrylic acid) (PAA) proceeds from oxidized polypropylene through 5-PAA/PP (the number of stages of hyperbranched grafting "*n*" is defined by "*n*"-PAA): (a) starting polypropylene; (b) oxidized polypropylene prepared by chromic acid etching; (c) 1-PAA/PP; (d) 2-PAA/PP (a faint $\nu_{C=O}$ is seen in this spectrum at 1710 cm^{-1}); (e) 3-PAA/PP; (f) 4-PAA/PP; and (g) 5-PAA/PP.

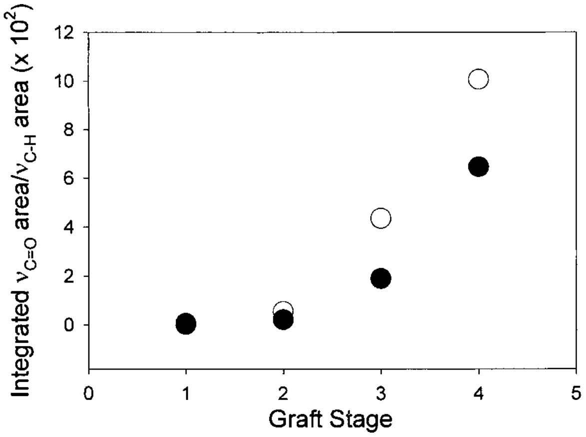


Figure 2. (a) Plot of the ratio of the integrated peak intensity of the C═O peaks (1670−1715 cm^{-1}) in the ATR-IR spectrum of a poly(acrylic acid) (PAA) graft relative to the integrated peak intensity of the C−H peaks (2800−3050 cm^{-1}) (●). (b) Plot of the ratio of the integrated peak intensity of the C═O peaks (1670−1740 cm^{-1}) of a poly(*tert*-butyl acrylate) graft relative to the integrated peak intensity of the C−H peaks (2800−3050 cm^{-1}) (○) vs the grafting stage for hyperbranched grafting on polypropylene.

peak attributed to $-CO_2H$ carbonyl groups does appear after two cycles (2-PAA/PP) (Figure 1d). After several more cycles, the carbonyl peak intensity increases significantly and is one of the major peaks in the ATR-IR spectrum after five cycles (5-PAA/PP) (Figure 1g).

A graph of the integrated intensity of the $\nu_{C=O}/\nu_{C-H}$ peaks in the 1670−1740 and 2800−3050 cm^{-1} regions of the ATR-IR spectra vs cycle number for both the poly(*tert*-butyl acrylate) and poly(acrylic acid) grafts on polypropylene (Figure 2) shows that the increase in graft density in each grafting stage reaches a constant value by stage 3 or 4. However, the interface analyzed by ATR-IR spectroscopy is still predominantly polypropylene since the integrated $\nu_{C=O}/\nu_{C-H}$ peak intensity is still only a fraction of the integrated $\nu_{C=O}/\nu_{C-H}$ peak intensity for a pure poly(*tert*-butyl acrylate) or poly(acrylic acid) sample. In the case of the poly(acrylic acid) graft, the $\nu_{C=O}/\nu_{C-H}$ peak intensity at the 4-PAA stage is only about 7% of the value for pure poly(acrylic acid). In the case of the poly(*tert*-butyl acrylate graft), the $\nu_{C=O}/\nu_{C-H}$ peak intensity at the 4-PTBA stage is ca. 10% of the value for the $\nu_{C=O}/\nu_{C-H}$ peak intensity for pure poly(*tert*-butyl acrylate). This is not surprising since ATR-IR spectroscopy analyzes a relatively thick interface (on the order of 1−10 μm depending on the IR wavelength).[24]

XPS spectroscopic studies of these modified polypropylene surfaces confirm the IR results shown in Figures 1 and 2. These results are listed in Table 1 below and show that the polypropylene surfaces after five stages of hyperbranched grafting have an elemental composition like that of poly(acrylic acid). Similar results were seen in XPS spectroscopic analyses of hyperbranched poly(acrylic acid) grafts on polyethylene and gold surfaces.[4,5] Polypropylene films containing the cesium salt of poly(acrylic acid) and the pentadecylfluoramidated derivative of a poly(acrylic acid) hyperbranched graft were also analyzed by XPS spectroscopy. These results listed below show that the product surfaces largely correspond to predicted elemental analysis though the 5-PAA-Cs/PP surface had significantly less Cs than expected.

Contact angle analysis data (Θ_a, advancing water contact angle) for grafting show that the surface hydrophilicity changes more rapidly. Some of these results are listed in Table 2. These results show that a polypropylene wafer that was first mechanically polished and then subjected to the derivatization chemistry shown in Scheme 1 becomes quite hydrophilic. In this case, the penultimate contact angle for the $-CO_2H$-containing surface was ca. 21°, a value very similar to that of hyperbranched poly(acrylic acid) grafts prepared on smooth Au films.[5] A plot of contact angle vs reaction stage shown in Figure 3 shows that significant hydrophilicity is seen even before there is a significant C═O peak in the ATR-IR spectrum. This is a reasonable result given the relative depth sensitivity of contact angle measurements vs ATR-IR spectroscopy.[25] These data along with contact angle data for other polypropylene substrates are also listed in Table 2. The data shown in Table 2 include results from our previous work and show that Θ_a values depend on both the chemistry of the surface and surface physical morphology. Smoother surfaces with similar chemistry have lower Θ_a values. The idea that the physical roughness of the starting substrate affects the penultimate hydrophobicity of the substrate as measured by contact angle analysis is precedented.[26] In our results, a hyperbranched poly(acrylic acid) graft prepared on the rough polypropylene wafer was more hydrophobic. In this case, the Θ_a value for the 3-, 4-, and 5-PAA/PP surfaces were ca. 63°, a value somewhat higher than the ca. 43° value we reported for similar grafts on polyethylene films[5] and much higher than the 21° value for similar grafts on a polished polypropylene wafer or than the 30° value for similar grafts on a smooth gold.[5]

The measured water contact angles for derivatives of the hyperbranched graft changed as expected. Conver-

Table 1. XPS Spectroscopic Data for Analyses of Hyperbranched Polypropylene Surfaces after Various Grafting Stages (e.g., Five Grafting Cycles in a 5-PAA Sample) or Various Chemical Treatments and Expected atom % Values for Surfaces Containing No Functional Groups (e.g., the Starting Polypropylene)[a] or the Functionality Shown in Brackets for a Modified Polypropylene

	element (%)				
substrate polypropylene film	C	O	N	Cs	F
polypropylene (PP) at. %	70	30			
expected at. %	100				
5-PAA (CH_2CHCO_2H)[b]/PP at. %	60	40	1		
expected at. %	71	28			
base-treated 5-PAA (CH_2CHCO_2Cs)[c]/PP at. %	59	37	1	4	
expected at. %	47	36		16	
fluoramidated 5-PAA ($CH_2CHCONHCH_2(CF_2)_6CF_3$)[d]/PP at. %	44	12	4		40
expected at. %	39	4	4		53

[a] The starting polypropylene was not extensively purified and contained significant levels of oxygenated impurities as noted by the XPS results. [b] A polypropylene (PP) sample after five stages of hyperbranched grafting containing a poly(acrylic acid) (PAA) graft. [c] A 5-PAA/PP film that was treated with CsOMe in methanol to for the cesium salt of poly(acrylic acid). [d] A 5-PAA/PP film that was treated first with $ClCO_2Et$ and then with $NH_2CH_2(CF_2)_6CF_3$ to form a fluoramidated polypropylene.

Table 2. Advancing Contact Angles (deg) for Grafts of Poly(acrylic acid) (PAA) or Poly(*tert*-butyl acrylate) (PTBA) and Their Derivatives on Polypropylene

substrate	advancing water contact angle
polypropylene (PP)	105
1-PTBA/PP[a]	100
1-PAA/PP[a]	40
2-PTBA/PP[a]	105
2-PAA/PP[a]	20
3-PTBA/PP[a]	98
3-PAA/PP[a]	20
4-PTBA/PP[a]	95
4-PAA/PP[a]	23
5-PAA/PP[a]	21
5-PAA ($-CO_2Na$)/PP[a]	0
3-PAA/Au[b]	30
3-PAA ($-CO_2Na$)/Au[b]	0
3-PAA ($-CONHCH_2(CF_2)_6CF_3$/Au[b]	107
3-PAA/PE[c]	48
3-PAA ($-CO_2Na$)/PE[c]	15
3-PAA ($-CONHCH_2(CF_2)_6CF_3$/PE[c]	135
5-PAA/roughened PP	61
5-PAA ($-CO_2Na$)/roughened PP	27
5-PAA ($-CONHCH_2(CF_2)_6CF_3$/roughened PP	124

[a] The polypropylene wafer was mechanically polished before beginning the grafting experiments. [b] Data taken from ref 5. [c] Data taken from ref 4.

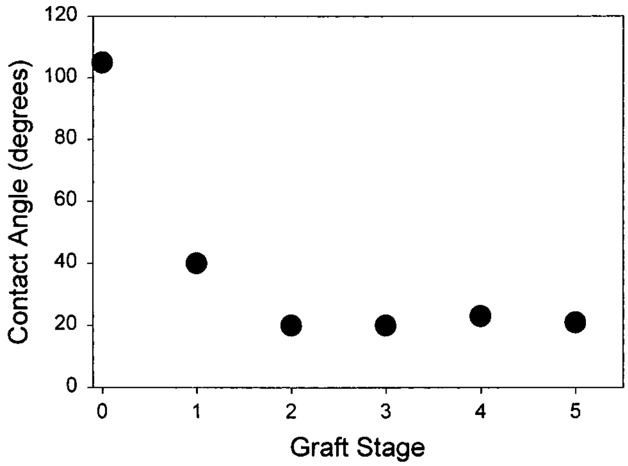


Figure 3. Plot of advancing water contact angle (Θ_a) vs graft stage for hyperbranched grafting of PAA onto a polished polypropylene wafer.

sion of the $-CO_2H$ groups of a PAA graft into a carboxylate salt on treatment with alkali makes the surface hydrophilic. A 5-PAA/PP graft with a starting contact angle of 61° had a contact angle of 27° after the carboxylate salt had formed. Conversion of the PAA hyperbranched graft into a fluorinated amide using the chemistry shown in Scheme 2 produced a more hydrophobic surface with a Θ_a value of 124°. The increased hydrophilicity or hydrophobicity seen for these derivatives of hyperbranched poly(acrylic acid) grafts on polypropylene in these experiments mirrored similar changes for hyperbranched poly(acrylic acid) grafts on gold (3-PAA to 3-PAA ($-CO_2Na$), 30° to ca. 0°; 3-PAA to 3-PAA ($-CONHCH_2(CF_2)_6CF_3$), 30° to 107°) and polyethylene (3-PAA to 3-PAA ($-CO_2Na$), 48° to 15°; 3-PAA to 3-PAA ($-CONHCH_2(CF_2)_6CF_3$), 48° to 135°).[5,6]

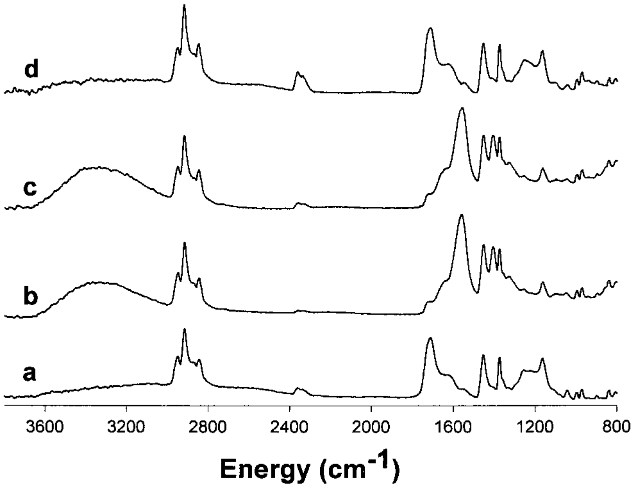
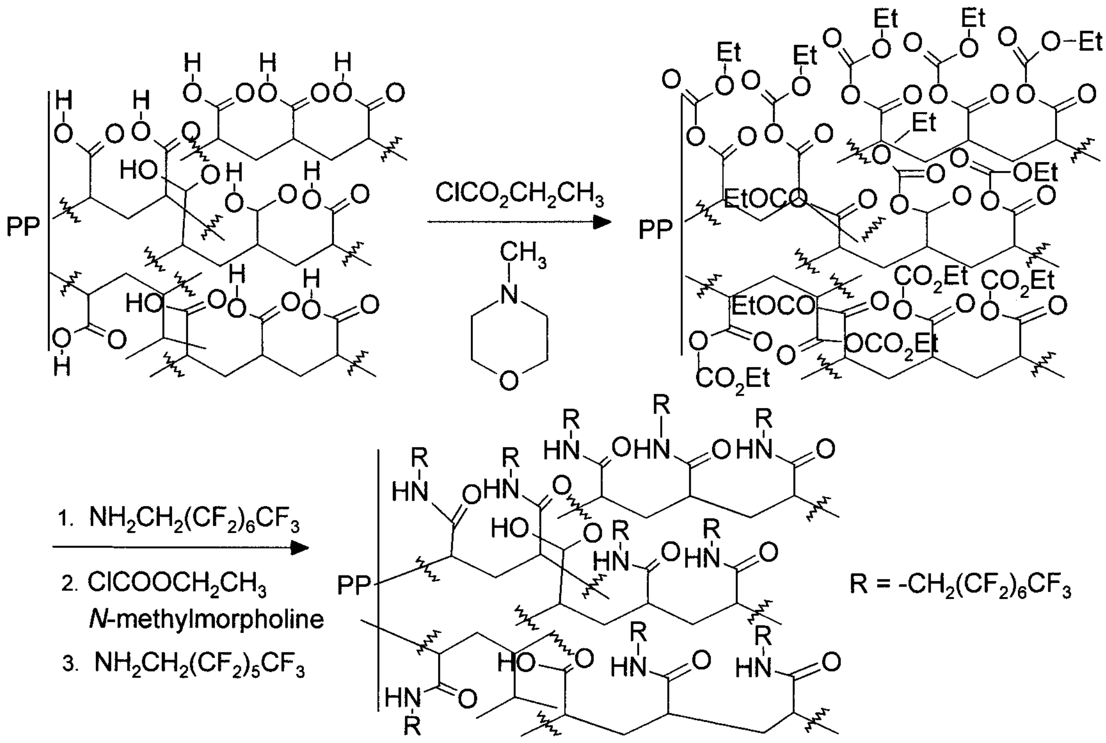


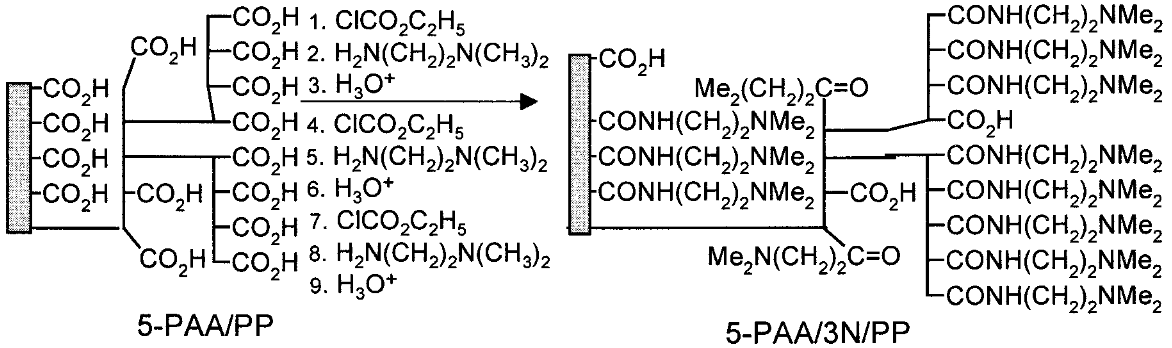
Figure 4. ATR-IR spectra of 6-PAA/PP films (a) initially, (b) after an initial treatment with 0.1 N NaOH in aqueous EtOH, (c) after four successive treatments first with 0.1 N NaOH in aqueous EtOH, then with 0.1 N HCl in aqueous EtOH, and finally with a fifth treatment with 0.1 N NaOH; and (c) after final acidification with 0.1 N HCl in aqueous EtOH.

We have also briefly examined the stability of these hyperbranched grafts. Stability both to extraction and to repeated aqueous base/acid treatments was studied. Extraction in a Soxhlet apparatus with CH_2Cl_2 for 1 day led to no detectable changes in these films. This is expected on the basis of our earlier results. More importantly, these films were stable to repeated treatments with strong aqueous base and strong aqueous acid. This is illustrated both by the IR spectra shown in Figure 4 and by contact angle analyses. In the contact angle studies, a 5-PAA/PP film was acidified and then treated with 0.1 N NaOH in aqueous EtOH and finally with 0.1 N HCl in aqueous EtOH through five cycles

Scheme 2



Scheme 3



with no change in contact angle for the $-CO_2H$-containing film after five such acid/base treatments.

We also recently reported that the thin highly functionalized interfaces derived from hyperbranched grafting are useful substrates in reversible surface modification by ionic self-assembly and hydrogen bonding.[4,27] The polypropylene interfaces described here behave similarly.[27,28] We illustrated this by first converting a 5-PAA/PP hyperbranched interface containing poly(acrylic acid) into an amine derivative (Scheme 3).[28] When this basic film was immersed in an aqueous pH 7 solution containing poly(acrylic acid) that had been labeled with pyrene, a pyrene-labeled film was formed. This fluorescently labeled film presumably contained ammonium groups in the hyperbranched interface that ionically bind the carboxylate groups of the soluble pyrene-labeled poly(acrylic acid) and immobilize this fluorescently labeled polyelectrolyte in the hyperbranched graft. The product of this process is in effect an ionically grafted interface.[17,29,30] Since our studies described above show that PAA grafts on polypropylene are stable to base and acid and since this ionic grafting is pH sensitive, we can reverse this ionic grafting process. This reversible grafting can occur because the graft is formed by ionic bonds. Treatment of the interface with base leads to loss of the pyrene-labeled polyacrylate since exposure of the interface to higher pH would form amines from the ammonium salts. As shown in Figure 5, reversible loading of the pyrene-labeled poly(acrylic acid) into the amine-containing interface was successful. Similar experiments using poly(sodium *p*-styrenesulfonate) (PSSS) were also successful. In this case, a 6-PAA/3N/PP surface was allowed to react with an aqueous pH 3 solution of PSSS. Intercalation of PSSS into the cationic hyperbranched interface was confirmed by ATR-IR spectroscopy by the appearance of new peaks at 1124, 1181, and 1212 cm^{-1}. These peaks, which are due to PSSS, disappear after base treatment.

Given the changes in wettability and the IR and XPS evidence for introduction of significant amounts of poly(acrylic acid) onto these polypropylene films, some changes in surface oriented physical properties should accrue to these modified polypropylene films. It is also clear from the fluorescence studies that other polymers can interpenetrate into these interfaces. Thus, we expected these hyperbranched poly(acrylic acid) modified polypropylene substrates to exhibit different physical properties in mechanical adhesion tests.[31] To test this, we secured some thick polypropylene blocks, modi-

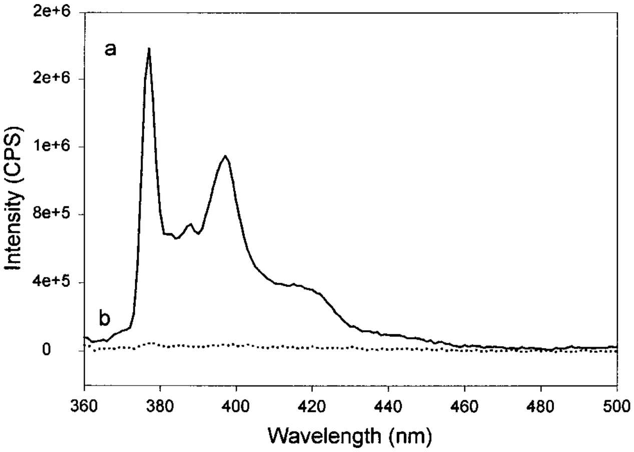


Figure 5. Fluorescence spectra of 5-PAA/3N/PP films (5-PAA/PP films that were treated three separate times with $ClCO_2Et$ and $NH_2CH_2CH_2N(CH_3)_2$ to form an amine-containing graft) and (a) after treatment with a solution of pyrene-labeled poly(acrylic acid); (b) after treatment of the fluorescent-labeled film first with base and second with HCl showing that the fluorescent labeling is reversible.

fied them with the same chemistry described above, and tested them using a double cantilever beam (DCB) test with a commercially available epoxy adhesive.

The purpose of the DCB test in this study is to compare the bonding strengths of different PP substrates with a commercially available epoxy adhesive. The bonding strength between the substrate and the adhesive is evaluated on the basis of the critical strain energy release rate (G_{1C}) concept.[32] The strain energy released from stored elastic or potential energy of the loading system can be calculated and used as a measure of the energy required to extend a crack over a unit area. G_{1C} was calculated using eq 1

$$G_{1C} = (4P^2_{(max)}/E_s db^2)[1 + (3a_c^{\ 2}/d^2)] \qquad (1)$$

where E_s is Young modulus of the substrate (E_s is 1.6 GPa for the PP substrate used), $P_{(max)}$ is the maximum load, d is the thickness of the substrate, b is the width of the substrate, and a_c is the crack length.

Energies involved in breaking secondary and/or primary bonds on the fracture surface and the localized viscoelastic and/or viscoplastic energy dissipative processes in the crack tip region are the two main sources of mechanisms contributing to crack resistance. There are generally three types of adhesive failure modes: (i) cohesive failure of the adhesive, (ii) adhesive failure at the interface between the substrate and the adhesive, and (iii) substrate failure where the skin portion of the substrate is pulled off upon adhesive fracture. In practice, an adhesive failure may involve a combination of all of the above failure modes.

By examining the failed DCB specimens, it is found that obvious adhesive failure has occurred for both neat PP and surface-modified PP substrates, indicating the low bonding strength between the adhesive and the substrate. However, the surface modification on PP makes a big difference in G_{IC} values. The maximum loads during the DCB tests and the calculated G_{1C} values are listed in Table 3. The maximum load required to cause crack propagation for the surface-modified PP substrate is much higher than that for the unmodified PP substrate during the DCB tests. Since G_{1C} is proportional to the square of the maximum load, the bonding strength between the epoxy adhesive and the surface-modified PP is much higher than that with the unmodified PP. Therefore, we conclude that the grafting of polar groups on PP surface is effective in greatly increasing adhesive strength between epoxy adhesive and PP substrate.

Table 3. Summary of DCB Tests.

test	substrate	P_{max} (N)	a_c (mm)	G_{1c} (J/m^2)
1	modified[a] PP	124	14.9	29.6
2	modified[a] PP	111	13.7	20.4
3	modified[a] PP	120	13.3	25.0
4	neat PP	40	13.1	2.0

[a] The modified PP was a 5-PAA/PP sample that had been modified with five stages of hyperbranched grafting.

Conclusions

Hyperbranched grafting is an effective way to modify polypropylene surfaces. Significant amounts of functionality can be introduced in this way using condensation chemistry with a graft-on-a-graft approach. The resulting interfaces can be modified by treatment with base or by covalent modification to be more hydrophilic or more hydrophobic. These hyperbranched grafts are stable to repeated treatments with strong aqueous acid or base. They can also be modified ionically by other polymers. Finally, these surfaces exhibit enhanced mechanical properties with a greater than 10-fold increase in adhesion to a commercially available epoxy resin.

Experimental Procedures

Materials and General Procedures. A 1/2 in. thick plate of polypropylene (ACHIEVE 3854) was obtained from Exxon-Mobil Chemical Company. The epoxy adhesive used was a two-component adhesive system obtained from Dow Automotive. The epoxy resin was Betamate 73312, and the hardener was Betamate 73313. The resin/hardener ratio used for curing was 2. Reagents for the hyperbranched graft chemistry were obtained commercially from Aldrich, prepared as described in previous reports or prepared as described below. *tert*-Butyl acrylate (Aldrich, 98%) was distilled before use. Other reagents including poly(acrylic acid) and poly(sodium *p*-styrenesulfonate) used were obtained from Aldrich and Sigma and were used as received. All the solvents are HPLC grade. Toluene and THF were distilled over sodium metal and stored under nitrogen. Ethyl acetate and DMF were dried with 4 Å molecular sieve overnight. Attenuated total reflectance (ATR) spectra were obtained using a Mattson Galaxy 4201 spectrometer with a Wilks model 10 ATR accessory at an angle of 45° using a KRS-5 crystal. Spectra were recorded at 4 cm^{-1} resolution between 4000 and 400 cm^{-1} and were the sum of 256 individual scans. Fluorescence spectra were recorded with a Fluorolog-3 spectrofluorometer. When working with pyrene-labeled samples, the spectra were obtained with an excitation wavelength of 343 nm. Contact angles were measured with a FTÅ 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 in contact angle measurements is ±3°.

Preparation of α,ω-Diaminopoly(*tert*-butyl acrylate) (H_2NR-PTBA-RNH_2). 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 (0.1 mol) using 0.380 g of the initiator 4,4′-azobis(4-cyanovaleric acid) (1.3 mmol) 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 12 g (ca. 90%) of acid-terminated polymer so obtained was purified by two additional precipitations in 1:1 methanol:water and was characterized using ^{1}H NMR spectroscopy, FT-IR spectroscopy, and titration. 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 in the IR spectrum was the ester peak at 1730 cm^{-1}. The dispersity of this polymer as measured by GPC was 1.8. The acid-terminated polymer so formed was then converted to a nucleophilic amine-containing polymer by allowing 5 g of the acid-terminated polymer to first react with 0.324 g of 1,1′-carbonyldiimidazole (CDI) (2 mmol) for 5 h in 30 mL of CH_2Cl_2 and then with 0.2 mL of ethylenediamine (3 mmol) for 15 h. The reaction mixture was washed with water and saturated brine (3 × 50 mL), the organic layer was then dried over $MgSO_4$, and the CH_2Cl_2 solvent was removed at reduced pressure using a rotary evaporator. This procedure led to 4.5 g of this amine-containing polymer. The isolated amine-containing polymer was analyzed by titration and had an M_n value of 20 000. 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 a small amide I peak at 1650 cm^{-1}.

Polypropylene Oxidation. Polypropylene (PP) film or wafer samples were first extracted with CH_2Cl_2 in a Soxhlet apparatus for 24 h. After they were dried under vacuum, they were treated at 70 °C for 5 min with an oxidizing solution containing a 1/1/2 (by weight) mixture of H_2SO_4, CrO_3, and water. After this period, the samples were washed first with water and then with acetone and finally allowed to air-dry before being extracted overnight in a Soxhlet with CH_2Cl_2.

Preparation of a 5-PAA/PP Hyperbranched Graft. A polypropylene film (e.g., a 4 cm^2 film) or a wafer (10 × 1.25 cm) that had first been oxidized was used as a substrate for a condensation grafting reaction with α,ω-diamino-poly(*tert*-butyl acrylate). The $-CO_2H$ groups that were presumed to be present on the oxidized polypropylene were first activated using ethyl chloroformate (0.1 mL, 1 mmol) and *N*-methylmorpholine (0.1 mL, 0.91 mmol) in 10 mL of dry DMF for 15 min. The activated sample was then washed with ethyl acetate and dried with a stream of N_2 and allowed to react with a solution of 0.2 g of α,ω-diamino-poly(*tert*-butyl acrylate) (ca. 1.5 mequiv of $-CH_2CH(CO_2CMe_3-$ groups) in 6 mL of DMF for 1 h. After this grafting, the polypropylene substrate was washed with ethanol and dried with a stream of N_2. Acidolysis was accomplished using 0.5 mL of $MeSO_3H$ (7.7 mmol) in 15 mL of CH_2Cl_2 at room temperature for 15 min. At this point, the film or wafer was physically removed from the reaction solution, washed with EtOH, and dried. Up to this point, there was essentially no detectable carbonyl group in the ATR-IR spectrum. Nonetheless, the grafting was continued after these 1-PAA/PP substrates were washed with first with water and then with ethanol and finally dried with a stream of N_2. These activation, grafting, and hydrolysis steps were repeated a total of five times, eventually yielding a hyperbranched 5-PAA/PP product that was characterized by contact angle analysis, XPS spectroscopy, and ATR-IR spectroscopy.

Coupling of *N*,*N*-Dimethylethylenediamine to a 5-PAA/PP Graft. A 5-PAA/PP wafer or film was first activated with ethyl chloroformate (see above procedure). The activated surface was then immersed in 10 mL of 1.0 M *N*,*N*-dimethylethylenediamine solution in DMF at room temperature for 1 h. After reaction, the sample was washed with ethanol and then acidified with 0.1 M HCl (in ethanol) for 15 min, washed with ethanol, and dried with a stream of N_2. The above procedure was then repeated twice more to obtain a 5-PAA/3N/PP wafer or film.

Deprotonation of Hyperbranched Poly(acrylic acid)/PP Grafts. Grafted polypropylene film was allowed to react with 0.1 N NaOH in aqueous EtOH for 1 h. ATR-IR spectroscopy showed that all the $-CO_2H$ groups of the starting film were converted to $-CO_2Na$ groups. Introduction of Cs ions was accomplished using cesium methoxide in methanol.

Fluoramidation of Hyperbranched Poly(acrylic acid)/PP Grafts. Hydrophobic surfaces were prepared by fluoramidation. In this chemistry, the initial 5-PAA on polypropylene (5-PAA/PP) wafer was first treated with $ClCO_2Et$ as described above. Then 10 mL of a 1 M solution of $NH_2CH_2(CF_2)_6CF_3$ in DMF was added. The amidation was allowed to continue for 1 h at room temperature. The extent of amidation was then analyzed by ATR-IR after any carboxylate groups were converted back into $-CO_2H$ groups by acidification with HCl. A relatively high conversion of the $-CO_2H$ groups into fluorinated amides was seen by ATR-IR spectroscopy (Figure 6b). A second treatment of this 5-PAA ($-CONHCH_2(CF_2)_6CF_3$)/PP wafer with ethyl chloroformate and the fluorinated amine led to a fluoramidated product, a 5-PAA ($-CONHCH_2(CF_2)_6CF_3$)/PP wafer that had virtually no unreacted $-CO_2H$ groups based on ATR-IR spectroscopy (Figure 6c).

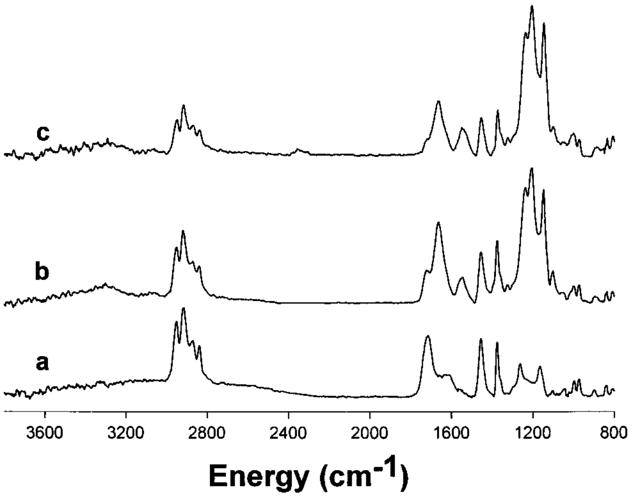


Figure 6. Extent of amidation of a 5-PAA/PP wafer after treatment of 5-PAA/PP as measured by ATR-IR spectroscopy: (a) the initial 5-PAA/PP sample; (b) the product of treatment of the 5-PAA/PP first with $ClCO_2Et$, then with $NH_2CH_2(CF_2)_6CF_3$, and finally with acid (to acidify any ammonium salts); and (c) the product of a second treatment of the 5-PAA/PP first with $ClCO_2Et$, then with $NH_2CH_2(CF_2)_6CF_3$, and finally with acid (to acidify any ammonium salts).

Dansyl-Labeled Poly(acrylic acid). Poly(acrylic acid) (2.16 g, 450 000 M_W, Aldrich, 30 mequiv of $-CO_2H$ groups) was dissolved in 80 mL of water, cooled to 0 °C, and allowed to react with 100 mg of EDC (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride) (0.5 mmol) and 60 mg of *N*-hydroxysuccinimide (0.5 mmol) for 30 min. Then 60 mg of *N*-2-(aminoethyl)-1-pyrenebutanamide (0.2 mmol) (prepared from pyrenebutyric acid, carbonyldiimidazole, and excess ethylenediamine)[5] in 20 mL of CH_2Cl_2 was added, and the resulting mixture was stirred for 15 h. The mixture was washed with CH_2Cl_2, and the aqueous solution was evaporated to dryness at reduced pressure to yield 2.2 g of the labeled poly(acrylic acid). Fluorescence spectroscopy of this polymer showed peaks expected for pyrene.

Ionic Assemble/Disassembly. An amidated 6-PAA/3N/PP wafer was immersed in a solution of 0.05 g of PAA (or pyrene-labeled PAA) in 10 mL of pH 7 buffer and allowed to sit for 5 h. The wafer was removed from the solution, treated with buffer for an additional 2 h, washed with buffer and ethanol, and dried under reduced pressure. Wafers that had been modified by PAA using ionic assembly were disassembled by treatment with 0.1 N NaOH for 2 h. Exposure to 0.1 N HCl for an additional 2 h followed by washing with EtOH and drying regenerated the starting cationic thin film (based on ATR-IR analysis).

Similar experiments were used for PSSS ionic assembly. In this case, the 6-PAA/3N/PP wafer was immersed in 20 mL of a pH 3 solution containing 200 mg of PSSS for 2 h. Rinsing with dilute HCl, water, and ethanol and drying led to a product wafer that contained PSSS by ATR-IR spectroscopic analysis. Removal of the PSSS could be accomplished using the same procedure used for dansyl-labeled PAA.

Adhesion Experiments. A polypropylene plate was cut into DCB substrates with dimensions of 10 × 1.25 cm. Two

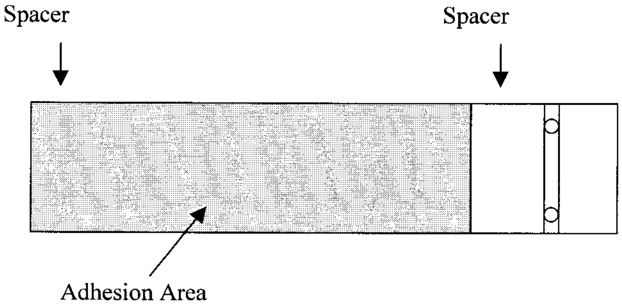


Figure 7. Schematic of the substrate setup for the DCB (double cantilever beam) test.

types of polypropylene substrates were studied in adhesion tests. One type of substrate had a surface that was first treated with sandpaper with a constant flow of water to lubricate and cool the substrate. The substrate was subsequently dried using compressed air. The second type of substrate had a surface that had been modified by hyperbranched grafting. A groove and two holes were introduced at about half an inch away from one end of the substrate for holding gripping wires (Figure 7). The gripping wire employed is a 20 gauge steel wire (0.03 in. diameter). After the substrate was prepared, an adequate amount of adhesive was applied on the PP surfaces and spread on the designated adhesive bonding area. Then, two substrates were joined and held together with a clamp. Metal spacers with a thickness of 0.2 mm were placed between the substrates to ensure uniform adhesive bond thickness throughout the DCB specimens. Any excessive adhesive squeezed out of the substrates was removed. The adhesive was cured at room temperature overnight. The DCB tests were performed on a SINTECH mechanical tester at a constant crosshead speed of 0.1 in./min.

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References and Notes

(1) *Polymer Surface Modification and Characterization*; Chan, C. M., Ed.; Hanser/Gardner Publications: Cincinnati, OH, 1994.
(2) Dhamodharan, R.; Nisha, A.; Pushkala, K.; McCarthy, T. J. *Langmuir* **2001**, *17*, 3368−3374.
(3) Singh, R. P. *Prog. Polym. Sci.* **1992**, *17*, 251−281.
(4) Bergbreiter, D. E.; Franchina, J. G.; Kabza, K. *Macromolecules* **1999**, *32*, 4993−4998.
(5) Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1997**, *13*, 770−778.
(6) Zhou, Y.; Bruening, M. L.; Liu, Y.; Crooks, R. M.; Bergbreiter, D. E. *Langmuir* **1996**, *12*, 5519−5521.
(7) Zhao, M.; Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1997**, *13*, 1388−1391.
(8) Zhao, M.; Liu, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 923−930.
(9) Lee, K. W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 309−313. Sheng, E.; Sutherland, I.; Brewis, D. M. Heath, R. J. *J. Adhes. Sci. Technol.* **1995**, *9*, 47−60. Novak, I.; Pollak, V. *Angew. Makromol. Chem.* **1994**, *220*, 189−197.
(10) Johnsen, K.; Kirkhorn, S.; Olafsen, K.; Redford, K.; Stori, A. *J. Appl. Polym. Sci.* **1996**, *59*, 1651−1657 and references therein.
(11) Strobel, M.; Walzak, M. J.; Hill, J. M.; Lin, A.; Karbashewski, E.; Lyons, C. S. *J. Adhes. Sci. Technol.* **1995**, *9*, 365−383.
(12) Brun, C.; Chambaudet, A.; Mavon, C.; Berger, F.; Fromm, M.; Jaffiol, F. *Appl. Surf. Sci.* **2000**, *157*, 85−91.
(13) Bergbreiter, D. E.; Walchuk, B.; Holtzman, B. Gray, H. N. *Macromolecules* **1998**, *31*, 3417−3423.
(14) Zhang, P. Y.; Rånby, B. *J. Appl. Polym. Sci.* **1991**, *43*, 621−636. Li, Y.; Desimone, J. M.; Poon, C. D.; Samulski, E. T. *J. Appl. Polym. Sci.* **1997**, *64*, 883−889. Ruckert, D.; Geuskens, G. *Eur. Polym. J.* **1996**, *32*, 201−208. Decker, C.; Zahouily, K. *Macromol. Symp.* **1998**, *129*, 99−108. Piletsky, S. A.; Matuschewski, H.; Schedler, U.; Wilpert, A.; Piletska, E. V.; Thiele, T. A.; Ulbricht, M. *Macromolecules* **2000**, *33*, 3902−3908. Chun, H. J.; Cho, S. M.; Lee, Y. M.; Le, H. K.; Suh, T. S.; Shinn, K. S. *J. Appl. Polym. Sci.* **1999**, *72*, 251−256.
(15) Living Ma, H.; Davis, R. H.; Bowman, C. N. *Macromolecules* **2000**, *33*, 331−335.
(16) Bamford, C. H.; Al-Lamee, K. G. *Polymer* **1994**, *35*, 2844−2849.
(17) Rieser, T.; Lunkwitz, K.; Berwald, S.; Meier-Haack, J.; Muller, M.; Cassel, F.; Dioszeghy, Z.; Simon, F. *ACS Symp. Ser.* **2000**, *744*, 189−204.
(18) Dogue, I. L. J.; Forch, R.; Mermilliod, N. *J. Adhes. Sci. Technol.* **1995**, *9*, 1531−1545.
(19) Bergbreiter, D. E. *Prog. Polym. Sci.* **1994,** *19*, 529−560.
(20) France, R. M.; Short, R. D. *Langmuir* **1998**, *14*, 4827−4835.
(21) Carey, D. H.; Grunzinger, S. J.; Ferguson, G. S. *Macromolecules* **2000**, *33*, 8802−8812. Rouse, J. H.; Twaddle, P. L.; Ferguson, G. S. *Macromolecules* **1999**, *32*, 1665−1671. McCarthy, T. J. *Chimia* **1990**, *44*, 316−318. Holmes-Farley, S. R.; Reamey, R. H.; Nuzzo, R.; McCarthy, T. J.; Whitesides, G. M. *Langmuir* **1987**, *3*, 799−815.
(22) Borsig, E. *J. Macromol. Sci., Pure Appl. Chem.* **1999**, *A36*, 1699−1715. Lu, H. L.; Chung, T. C. *J. Polym. Sci., Part A.: Polym. Chem.* **1999**, *37*, 4176−4183. Xu, G.; Lin, S. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34*, 555−606.
(23) Bergbreiter, D. E.; Tao, G.; Kippenberger, A. M. *Org. Lett.* **2000**, *2*, 2853−2855.
(24) Bergbreiter, D. E.; Srinivas, B. *Macromolecules* **1992**, *25*, 636−643.
(25) Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897−5898.
(26) Youngblood, J. P.; McCarthy, T. J. *Macromolecules* **1999**, *32*, 6800−6806.
(27) Bergbreiter, D. E.; Tao, G.; Franchina, J. G.; Sussman, L. *Macromolecules* **2001**, *34*, 3018−3023.
(28) Bergbreiter, D. E.; Tao, G. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3944−3953.
(29) Decher, G. *Science* **1997**, *277*, 1232−1237.
(30) Ionic exchange of simple (nonpolymeric) cations into polyelectrolyte PAA grafts on polypropylene is precedented. Cf.: Lin, W.; Hsieh, Y.-L. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 631−642.
(31) Dogue, I. L. J.; Mermilliod, N.; Boiron, G.; Staveris, S. *Int. J. Adhes.* **1995**, *15*, 205−210. Brewis, D. M.; Briggs, D. *Polymer* **1981**, *22*, 7−16.
(32) Kinloch, A. J. *Adhesion and Adhesives: Science and Technology*; Chapman and Hall: London, 1987.

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