Heterogeneous Grafting Chemistry Using Residual Unsaturation as a Graft Site Precursor

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ABSTRACT: Hydroboration of residual carbon–carbon double bonds in preformed polyethylene and poly(vinyl chloride) films has been shown to be an effective and mild way to initiate grafting chemistry. This chemistry presumably produces carbon–boron intermediates that can, in turn, be used with vinyl monomers and oxygen to carry out radical graft polymerizations. Suitable vinyl monomers examined include methyl methacrylate, acrylamide, *N,N*-dimethylacrylamide, acrylic acid, hydroxyethyl methacrylate, isobutyl methacrylate, *tert*-butyl acrylate, and methacrylonitrile. The products of these grafting reactions have been studied gravimetrically, by transmission and ATR-IR spectroscopy and by XPS spectroscopy. These spectroscopic studies as well as physical and mechanical studies show that this procedure produces a covalently modified substrate polymer in which bulk grafting and significant modification of the substrate polymer's bulk and surface properties have occurred.

Many polymers contain residual unsaturation. For example, polyethylene contains residual unsaturation from disproportionation in a radical polymerization or as a result of β-hydride elimination in a coordination polymerization process.[1] Similarly, other vinyl addition polymers often contain some residual alkene groups because of disproportionation or atom transfer during the polymerization process.[2] Poly(vinyl chloride) is an example of the latter sort of polymer commercially prepared by radical polymerization that contains small amounts of residual carbon–carbon unsaturation in the main chain and some terminal vinyl groups.[3] In many cases, such residual unsaturation sites are reactive sites and are thought to affect the thermal or oxidative stability of the product polymer. This is the case in polyethylene. It is also the case in poly(vinyl chloride). While such sites are often detrimental to the thermal or oxidative stability of polymers, it is also possible that such sites can serve as handles in polymer functionalization. Indeed, residual unsaturation or unsaturated sites deliberately introduced into or on polyethylene are likely important in oxidative etching chemistry used to functionalize polyethylene.[4] This paper describes our initial studies of new ways in which we exploit the chemical reactivity of such sites in insoluble polymers in heterogeneous graft polymerization chemistry.

Hydroboration of carbon–carbon double bonds is an important reaction in organic chemistry that is broadly applicable and compatible with many sorts of functional groups.[5] While the alkylborane products in such chemistry are typically not isolated, it has been known for almost 40 years even before the development of alkene hydroboration that trialkylboranes can initiate polymerizations.[6,7] Recently, Chung's group has developed some very innovative chemistry using this combination of hydroboration chemistry, the stability of alkylboranes to conventional Ziegler–Natta catalysts, and the reactivity of alkylboranes to oxygen to prepare some very interesting and potentially useful graft copolymers.[8-10] We report here that this same combination of chemistry—hydroboration and oxygen-induced radical polymerization— is an attractive method for graft polymerization onto solid polymers like poly(vinyl chloride) and polyethylene using only the residual unsaturation present in each of these commercial materials. Such chemistry avoids high-energy plasma treatments and harsh reactions that can lead to chain scission and etching. The borane chemistry and subsequent treatment with oxygen and vinyl monomer described below represent an especially mild method for graft initiation.

In the discussions below, we have exclusively used the term graft copolymerization. However, the modified polymers produced by these procedures are likely not all graft copolymers. A true graft copolymer may be formed in cases where polymers contain more than one residual unsaturation site in each chain. In other cases, such as polyethylene, the residual unsaturation is likely at the chain ends and the product polymer chains would be more properly described as block copolymer chains. However, we have chosen to not make this distinction in the discussion below for several reasons. First, we emphasize the similarity of the chemistry described. Second, we are in all cases using solid films and attaching to them many pendant chains, a process that is best described by the consistent use of graft copolymerization.

Our strategy for grafting is illustrated by the reaction depicted in eq 1. In this chemistry, a convenient source of BH_3 like borane–dimethyl sulfide was first added to a solid polymer film suspended in a solvent. In the two examples discussed below, solvents were chosen such that they did not dissolve the polymer during the hydroboration step. However, the solvents chosen for polyethylene (THF) and poly(vinyl chloride) (diethyl ether) both likely swell the polymer and presumably facilitate hydroboration of residual unsaturation at sites significantly below the polymer surface. Thus, potential grafting sites include unsaturated groups near the surface and sites in the bulk polymer. Subsequent additions of a vinyl monomer either with deliberate or adventitious introduction of oxygen to the intermediate polymeric alkylborane produce grafting. After this work had begun, Chung's group reported on the accessibility of alkylborane sites in polypropylene solids to aqueous solutions of oxidants like alkaline hydrogen peroxide. Their observations provide additional reason to expect success in and generality for the chemistry of eq 1.[10]

Results and Discussion

Our initial work first tested the accessibility of the residual carbon–carbon double bonds of polyethylene (PE) and poly(vinyl chloride) (PVC) films to the hydroboration–oxidation chemistry sequence. These studies used ATR-

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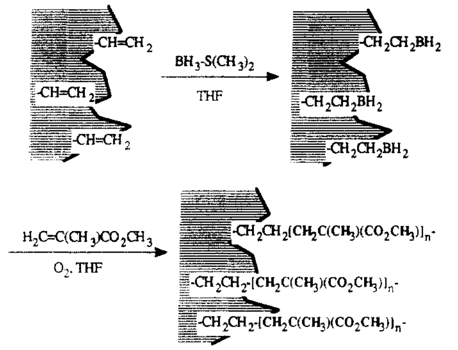
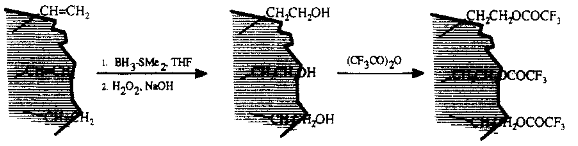


(1)

IR spectroscopy of films before and after hydroboration and further functionalization to demonstrate the accessibility of the double bonds and the intermediate alkylboranes to soluble reagents. XPS spectroscopy results provided further confirmation of these IR results. The specific sequence of reactions used is shown in eq 2 for



(2)

polyethylene. ATR-IR spectroscopic studies of films subjected to this sequence showed complete disappearance of the carbon–carbon double bond peak in the IR spectrum at 908 cm^{-1}. In addition, after alkaline hydrogen peroxide oxidation and trifluoroacetylation with trifluoroacetic anhydride, we observed a new carbonyl peak in the IR spectrum of the product film at 1780 cm^{-1}. This peak was present in both ATR-IR spectra and transmission spectra. Finally, XPS spectroscopy showed that the final trifluoroacetylated film contained both fluorine and oxygen peaks that were not present in the starting polyethylene film (F, 2%; O, 4%). Similar studies were also performed using poly(vinyl chloride) films containing carbon–carbon double bonds introduced by base treatment. As was true for PE, the double bonds in the modified PVC films disappeared during hydroboration and the product oxidized film contained hydroxyl groups that could be tagged with trifluoroacetate groups. These studies show that surface functionalization occurred. The results described below suggest that the chemistry seen occurred both at the polymer films' surface and in the polymers' bulk.

Since the simple functionalization studies showed that the carbon–carbon double bonds in the ATR-IR interface of PE and PVC were accessible to reagents like BH$_3$·S(CH$_3$)$_2$, we proceeded to explore the grafting chemistry depicted in eq 1. As predicted, grafting using the chemistry shown in eq 1 was successful. Figure 1 shows the ATR-IR spectra of PE films grafted with methyl methacrylate (PE-*g*-PMMA) (Figure 1a), *N,N*-dimethylacrylamide (PE-*g*-PDMMA) (Figure 1b), and methacrylonitrile (PE-*g*-PMAN) (Figure 1c). It can be seen that the absorbance band at 908 cm^{-1} (–CH=CH$_2$) on the pure PE (Figure 1d) disappeared after the grafting copolymerization. PE-*g*-PMMA showed strong absorbance bands at 1730 cm^{-1} ($\nu_{C=O}$) and 1150 cm^{-1} (ν_{COC}). PE-*g*-PDMMA showed a strong band at 1610 cm^{-1} ($\nu_{C=O}$). On the spectrum of PE-*g*-PMAN, there was a weak peak at 2235 cm^{-1} (ν_{CN}). XPS studies of grafting also showed that there was significant grafting at the surface of these polymers. Figures 2 and 3 illustrate this. XPS spectra (Figure 2) of grafted film samples of PE-*g*-PMMA (Figure 2a) showed an O_{1s} peak (C:O = 77:23) which did not appear in the spectrum of the pure PE starting material (Figure 2b). The spectrum of PE-*g*-PDMMA (Figure 2c) showed N_{1s} and O_{1s} peaks with an N:O:C atomic ratio of 2:3:95. High-resolution spectra of C_{1s} of PE-*g*-PMMA (Figure 3a) also gave a C_{1s} peak at higher binding energy that did not appear on the pure PE spectrum (Figure 3b). This high binding energy C_{1s} peak is from carbonyl carbons on the modified surface.

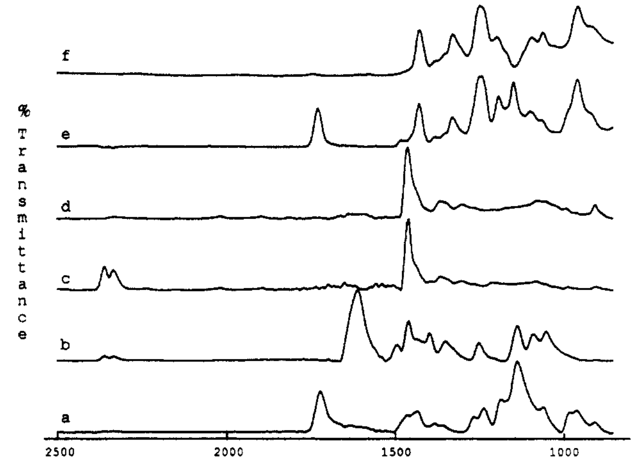


Figure 1. ATR-IR spectra of (a) PE-*g*-PMMA, (b) PE-*g*-PDMMA, (c) PE-*g*-PMAN, (d) PE, (e) PVC-*g*-PMMA, and (f) PVC.

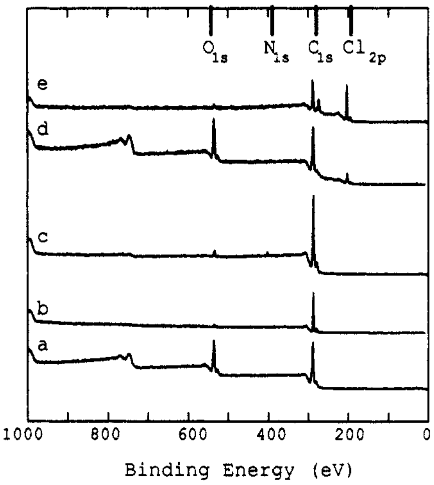


Figure 2. XPS spectra of (a) PE-*g*-PMMA, (b) PE, (c) PE-*g*-PDMMA, (d) PVC-*g*-PMMA, and (e) PVC.

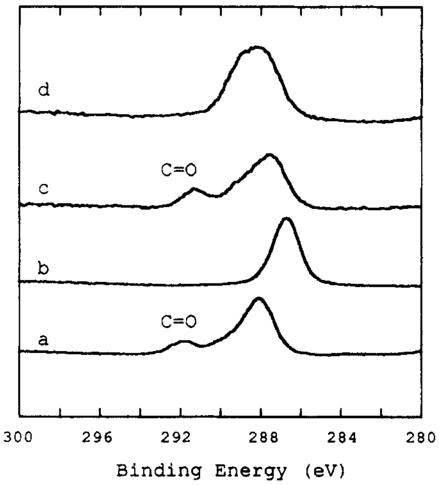


Figure 3. High-resolution spectra of the C_{1s} region of (a) PE-*g*-PMMA, (b) PE, (c) PVC-*g*-PMMA, and (d) PVC.

The extension of this grafting chemistry to polymeric materials that contain C=C bonds other than polyethylene was also successful. This was illustrated using poly(vinyl

Table 1. Grafting of PVC and PE Films with Methyl Methacrylate (MMA) or *N,N*-Dimethylmethacrylamide (DMMA) after Hydroboration of Residual Unsaturation[a]

film[b]	hydroboration time (h)	grafting time (h)	increase in film wt (%)[c]	increase in film thickness (%)[d]
PVC-*g*-PMMA	1	1	5	15
PVC-*g*-PMMA	1	12	9	20
PVC-*g*-PMMA	12	1	6	12
PVC-*g*-PMMA	12	12	5	12
PE-*g*-PMMA	1	1	4	0
PE-*g*-PMMA	1	12	12	0
PE-*g*-PMMA	12	1	20	3
PE-*g*-PMMA	12	12	61	9
PE-*g*-PMAA	24	24	230	70
PE-*g*-PDMMA	12	12	118	100

[a] Reactions were run at 25 °C in a solvent with either 1 mL of added air (PVC) or no added air (PE) during the addition of the vinyl monomer. [b] The starting films were cast from additive-free PVC or were obtained commercially as a blown film (PE; Fortiflex, $d = 0.936$ g/cm^3, MI = 0.25 g/10 min). Before reaction, the PE film was first extracted with THF and then hexanes for 24 h each. [c] The product films were washed either with acetone (MMA, 24 h) or THF (DMMA, 12 h) using a Soxhlet apparatus in the case of polyethylene films. PVC films were washed at room temperature as noted in the text. [d] The films' thickness and lateral dimensions increased during grafting. The starting thickness of the commercial film was 0.025 mm.

chloride) as a substrate. Since it is known that PVC contains some residual C=C bonds,[3] graft polymerization onto films of this polymer can be used to introduce additional C=C unsaturation onto PVC.

In a typical procedure, we prepared a PVC-*g*-PMMA graft copolymer using either virgin PVC or base-treated PVC following a hydroboration–grafting protocol like that used above the PE modification. However, because of the solubility of PVC in solvents like THF, we used diethyl ether for the hydroboration reaction and heptane for the grafting reaction. The reaction work-up conditions were similar to those used in the preparation of PE-*g*-PMMA. The product PVC-*g*-PMMA film was washed by a chloroform/ethanol (5:5, v/v) mixture (a good solvent for PMMA homopolymer). After being washed 10 times for 1 h each with shaking, the PVC-*g*-PMMA was dried under vacuum for 24 h. The ATR-IR spectrum of the PVC-*g*-PMMA film (Figure 1e) showed strong IR absorbance bands at 1725 cm^{-1} ($\nu_{C=O}$) and 1150 cm^{-1} (ν_{COC}) which did not appear on the pure PVC film (Figure 1f). An XPS spectrum (Figure 2d) of the grafted film also showed an O_{1s} peak (O:Cl:C = 24:4:72). High-resolution spectra of the C_{1s} of PVC grafted films (Figure 3c) also showed evidence for C=O carbons like that shown for PE-*g*-PMMA in Figure 3a.

In addition to the spectroscopic studies shown above, gravimetric and NMR studies were used to quantify the amount of grafting which occurred. The results listed in Table 1 show that graft formation on both polyethylene and poly(vinyl chloride) films could be quite extensive. While the extent of grafting appeared to vary with different acrylate monomers, we believe the variation reflects slight differences in graft initiation by adventitious oxygen. However, when longer reaction times were used in either the hydroboration step or the grafting step in the case of polyethylene, the amount of grafting increased. In some cases, the film's total mass more than doubled for PE-*g*-PMMA. However, this did not represent a drastic change in the density of the polymer. In cases where large amounts of grafting occurred, the film thickness measurably increased. There were also small measured changes in the lateral physical dimensions for some of these films on grafting. These changes, which were usually not as large as the observed thickness increase, together with the measured film thickness changes suggest extensive grafting both at the surface and in the bulk of the substrate film samples. However, there were clear changes in surface chemistry for these films. For example, advancing water contact angles changed for polyethylene from 104° to 97° for PE-*g*-PMMA (230% PMMA) and changed from 90° to 79° for PVC (containing 6% PMMA).

The gravimetric data in Table 1 represent averages of at least two separate grafting runs. However, the dual role of oxygen as an initiator and as a chain terminator for these radical reactions led to significant variations in the weight increases observed from run to run, especially in cases where large amounts of grafting occurred. There also appeared to be a small effect due to substrate film thickness. Thinner films generally had slightly higher amounts of grafting under similar reaction conditions. More consistent gravimetric results were obtained when larger amounts of oxygen were deliberately added. However, the extent of grafting was lower when more oxygen was present. A qualitative study wherein progressively larger excess amounts of oxygen were added to a methyl methacrylate grafting reaction illustrated this effect. In this study, grafting continued to occur even with additions of up to 4 mL of air. However, comparison of the carbonyl peak intensities with the intensity of the polyethylene absorbance peaks indicated lower amounts of grafting occurred with increasing amounts of oxygen. In practice, the use of nondegassed monomers and/or nondegassed solvents seemed to be the simplest method of introducing the necessary oxygen initiator.

While the gravimetric results varied somewhat from run to run, the gravimetric results for individual runs agreed well with separate analyses of the degree of graft polymerization. Comparison of gravimetric results for a PE-*g*-PMMA sample (12 h of hydroboration, 12 h of grafting) or of a PE-*g*-PMMA sample (24 h of hydroboration, 24 h of grafting) with solution-state NMR analysis of the same film showed mole ratios of PMMA/PE of 0.25 versus 0.28 and 0.65 versus 0.84, respectively.

The graft polymerization chemistry described above also worked in gas-phase reactions. In this chemistry, a poly(vinyl chloride) film was suspended above neat $BH_3 \cdot S(CH_3)_2$ for 24 h. Then the $BH_3 \cdot S(CH_3)_2$ was replaced with neat methyl methacrylate. The film was again suspended over the monomer for 24 h. After reaction, the film was washed and analyzed by ATR-IR and XPS spectroscopy. XPS spectroscopy showed 27% oxygen at the surface of the product film, and there was an obvious carbonyl peak in the ATR-IR spectrum at 1725 cm^{-1}. This ester carbonyl was approximately half as large as the carbonyl peak in PVC-*g*-PMMA in Figure 1e based on a comparison with the CH peak at 1450 cm^{-1}.

Transmission IR studies were also carried out to supplement the ATR-IR studies shown above in Figure 1. Typical spectra shown in Figure 4 for polyethylene-*g*-poly(methyl methacrylate) and poly(vinyl chloride)-*g*-poly(isobutyl methacrylate) show differences between an ATR-IR and a transmission IR spectrum. These differences arise from the greater sampling depth of IR at lower wavenumbers in the ATR-IR and are expected. The more significant feature in the transmission spectra of both the polyethylene-*g*-poly(methyl methacrylate) and poly(vinyl chloride)-*g*-poly(isobutyl methacrylate) (parts a and c of Figure 4, respectively) is the presence of strong carbonyl peaks. If only functionalization in the ATR-IR interface had occurred, these peaks would be much less intense since

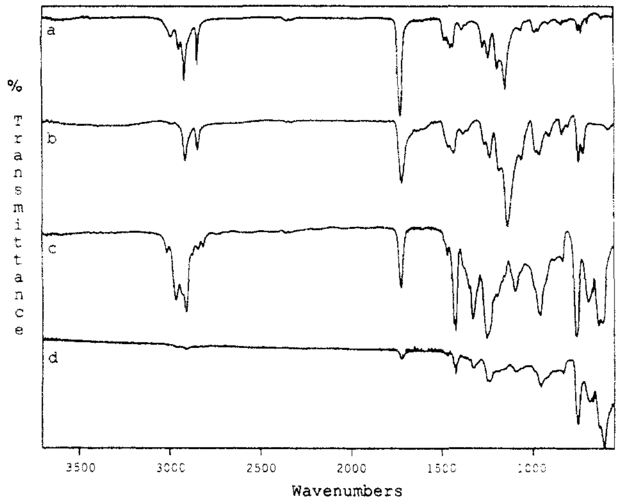


Figure 4. Comparison of transmission and ATR-IR spectra for polyethylene-*g*-poly(methyl methacrylate) (12 h of hydroboration and 12 h of grafting) (a and b, respectively) and poly(vinyl chloride)-*g*-(isobutyl methacrylate) (24 h of hydroboration, 24 h of grafting) (c (transmission IR) and d (ATR-IR), respectively).

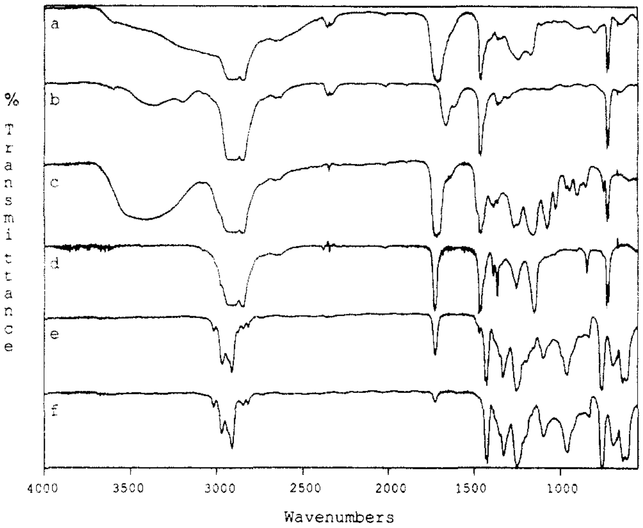


Figure 5. Transmission spectra of polyethylene and poly(vinyl chloride) films grafted with various monomers: (a) polyethylene-*graft*-poly(acrylic acid); (b) polyethylene-*graft*-polyacrylamide; (c) polyethylene-*graft*-poly(hydroxyethyl methacrylate); (d) polyethylene-*graft*-poly(*tert*-butyl acrylate); (e) poly(vinyl chloride)-*graft*-poly(isobutyl methacrylate); (f) poly(vinyl chloride)-*graft*-poly(*tert*-butyl acrylate).

the ATR-IR interface comprises but a small fraction of the total thickness of either film. This strongly supports our belief that this chemistry resulted in both surface and bulk modification of the polymer.

It appears that many other acrylic acid derivatives can be used in this chemistry. Experiments confirming this expectation were largely confined to grafts using PE substrates. IR spectra shown in Figure 5 show several examples of grafted films containing HEMA and acrylic acid as graft materials. Evidence that these materials contained covalently grafted materials includes the lack of room-temperature solubility of the product grafted film's poly(acrylic acid) derivative component in solvents that should have dissolved that hompolymer. More significantly, the retention of significant amounts of the graft polymer at both the ATR-IR and XPS interface, even after extraction for 24–48 h in a Soxhlet apparatus is not consistent with simple network polymer formation. Table 2 contains a survey of gravimetric data for grafted films prepared using other acrylic acid derivatives with both PE and PVC substrate films.

Table 2. Gravimetric Data for Grafting of Other Monomers onto Polyethylene and Poly(vinyl chloride)[a]

film sample	hydroboration time	grafting time (h)	wt increase (%)
PE-*g*-polyacrylamide	24	24	20
PE-*g*-poly(acrylic acid)	24	24	35
PE-*g*-poly(butyl acrylate)	24	24	5
PE-*g*-poly(hydroxyethyl acrylate)	24	24	45
PE-*g*-poly(butyl methacrylate)	24	24	150
PE-*g*-poly(*tert*-butyl acrylate)	24	24	20
PVC-*g*-poly(*tert*-butyl acrylate)	12	12[b]	10
PVC-*g*-poly(hydroxyethyl acrylate)	12	12[b]	9
PVC-*g*-poly(butyl acrylate)	12	12[b]	14
PVC-*g*-poly(isobutyl methacrylate)	12	12[b]	16

[a] Grafting experiments were carried out by hydroboration of solid films in neat borane–dimethyl sulfide for the indicated time at 25 °C followed by grafting with the neat monomer at 25 °C for the time indicated. The product PE films were in all cases extracted in a Soxhlet for 24 h. Grafted PVC films were washed at room temperature with a solvent known to readily dissolve the graft homopolymer.
[b] Adventitious oxygen was used to initiate the grafting copolymerization.

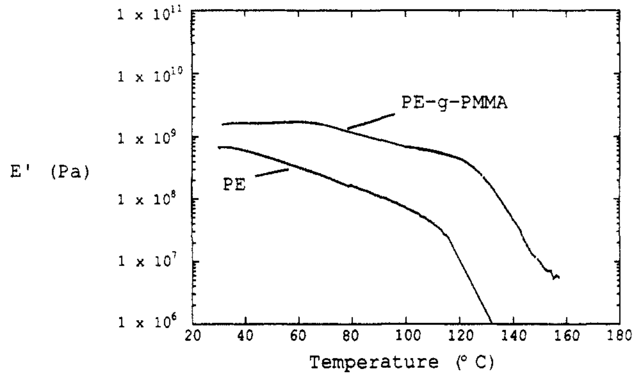


Figure 6. Dynamic mechanical spectra of PE-*g*-PMMA in the temperature range 25–160 °C.

Dynamic mechanical thermal analysis of the PE-*g*-PMMA material yielded the results shown in Figure 6. These results show that the product film has properties that differ significantly from a pure PE film. It is less flexible than the starting polyethylene and has a greater resemblance to a PMMA film than to a PE film. The storage modulus of PE-*g*-PMMA is higher than the E' of pure polyethylene, and this difference is exaggerated on heating.

The solubility of the graft polymer has not been extensively studied. However, qualitative solubility studies of a PE-*g*-PMMA sample containing 230% by weight PMMA proved interesting. A sample of this polymer (ca. 0.066 g) that was dissolved in 5 mL of toluene at 110 °C did not precipitate as a mixture of a toluene solution of poly(methyl methacrylate) and a polyethylene gel on cooling as did a similar mixture of 0.02 g of the starting polyethylene film and 0.046 g of a commercial poly(methyl methacrylate) in 5 mL of toluene. The PE-*g*-PMMA sample instead stayed in solution as a somewhat cloudy viscous oil. No solid could be separated on centrifugation. The simple admixture of polyethylene and poly(methyl methacrylate) was in contrast visually heterogeneous, and centrifugation did separate the polyethylene component as a swollen gel. Removal of the toluene and addition of THF to the PE-*g*-PMMA product produced a similar cloudy viscous oil in THF. Ethanol addition did precipitate the PE-*g*-PMMA. These qualitative solubility studies are consistent with the idea that the product is in large part a covalent graft rather than an intimate mixture of the two otherwise incompatible homopolymers. These

Table 3. Permeability Changes in Polyethylene Films Grafted with Methyl Methacrylate[a]

film sample	$P(N_2)$(×10^{11} cm^3 cm/ cm^2 s cmHg)	$P(O_2)$(×10^{11} cm^3 cm/ cm^2 s cmHg)	P(H_2O)(×10^{11} g cm/ cm^2 s cmHg)
starting PE[b]	8.1	22.9	0.25
LDPE[c]	9.7	29.3	0.73
HDPE[c]	1.5	4.0	0.10
PE-*g*-PMMA[d]	1.9	10.1	3.90
PE-*g*-PMMA[e]	1.0	4.9	
PMMA[f]	0.6	2.9	8.90
PMMA[g]		1.0	13.70
PMMA[c]		1.54	5.14

[a] Permeability measurements were made using the procedures detailed in the Experimental Section or are from the literature as noted. Where necessary, permeability data were corrected to STP. [b] The starting PE film was a commercial blown film. [c] These data are from ref 12. [d] This film contained a 0.9:1 weight ratio of PMMA/PE and was derived from a reaction using 12 h of hydroboration and graft copolymerization steps. [e] This film contained a 2.3/1 weight ratio of PMMA/PE and was derived from a reaction using 24 h of hydroboration and graft copolymerization steps. [f] The PMMA film was solution cast from chloroform. [g] These data are from ref 13.

data, however, do not exclude the presence of either homopolymer.

The physical difference in miscibility of the PE-*g*-PMMA material versus a simple mixture of homopolymers was also manifest in the solid state. Removal of the toluene solvent from a solution containing pure PE and pure PMMA produced a powdery film that appeared to be an immiscible mixture of PE and PMMA. In contrast, similar experiments using the PE-*g*-PMMA material produced a much more homogeneous film, a result very much like the compatibilization already described by Chung or by others using PP-*g*-PMMA or other graft copolymers as compatibilizers for polymer blends.[10,11]

Preliminary studies of permeability changes in a PE-*g*-PMMA film further support the bulk nature of the grafting chemistry described above. Table 3 shows the results of measurements of oxygen, nitrogen, and water permeability in PE films, PMMA films, and PE-*g*-PMMA films. As expected, the transport properties of PE-*g*-PMMA film were intermediate between those of PE and PMMA. There was a ca. 8-fold decrease in oxygen and nitrogen permeability relative to the starting PE film and a 15-fold increase in water permeability relative to the PE film.[12] The product film also has higher oxygen and nitrogen permeability than a pure PMMA film.[12,13]

Though we have not explored the issue, there is also evidence in the literature that plasma modification of polymer surfaces can introduce unsaturation. Specifically, plasma modification of low-density polyethylene films followed by hydroboration and deliberate or adventitious oxidation has been described by Nuzzo and Smolinsky.[14] Though those studies were principally aimed at studying the sorts of oxygen functionality that could be introduced onto polyethylene films through plasma and subsequent chemical treatments, some of the increased oxygen (hydroxyl) content of the products seen after hydroboration could be the result of hydroboration chemistry. This was indeed the case when hydroboration was followed by an oxidation step (using pyridine *N*-oxide). These workers also reported that boron–carbon bonds at a polyethylene surface were protonated by methanol. This is not the case in a homogeneous solution. This enhanced reactivity toward electrophilic protonation by carbon–boron bonds was not explained by Nuzzo and Smolinsky. Nonetheless, it may be relevant to the mechanism of the graft polymerization described here. Specifically, the possibility that carbon–borane bonds at a polyethylene surface react in significantly different ways than in a homogeneous solution suggests that other mechanistic explanations for the grafting described here should be considered. In any case, this prior work and the present study indicate that hydroboration of plasma-treated surfaces followed by exposure to vinyl monomers and oxygen could also be a useful method of surface grafting.

Summary and Conclusions

There are several advantages to the grafting chemistry described in this paper. First, it is a very mild method for copolymerization that our results suggest leads to covalent bond formation between the grafted copolymer chain and the polymer substrate. The grafted copolymer chains are not easily removed in solvents in which the grafted homopolymer would have been soluble. Second, the grafting conditions are especially mild. Room temperature is used in every step. Third, unlike many other procedures, an oxidative step that leads to chain scission is not necessary prior to grafting using this chemistry. Fourth, the chemistry produces product materials whose physical properties are usefully modified. Finally, since the chemistry relies on the presence of existing low levels of alkene groups already present in the substrate film, no separate functionalization step is required.

While the chemistry shown above is quite successful, there are some unresolved questions. First, the efficiency in grafting acrylic acid derived monomers such as acrylamide and acrylate esters was much higher than seen in preliminary work with other monomers. This is illustrated by comparison of the spectra for methacrylonitrile grafting with other grafting in Figure 1. Second, the effects of and the appropriate concentration of oxygen have not been maximized. Preliminary work suggests that continued decreases in the oxygen concentration lead to continually increased amounts of grafting. Third, we have only begun to explore the potentially interesting changes in solubility and permeability engendered by this grafting chemistry and we have not yet begun to explore the potential of changing reaction conditions or reagents to achieve surface selectivity. Finally, though the chemistry we have described to date does not exhibit surface selectivity, changes in the hydroboration step, a prior plasma treatment, or changes in the grafting step, all could provide ways to alter this chemistry to effect more surface selective chemistry.

We conclude that the residual double bonds (C=C) in some polymeric materials are accessible to the hydroboration. The alkylboranes so formed can serve as initiators for radical grafting chemistry. Clearly this method is a very mild and simple procedure that can be used to modify solid polymeric materials containing residual carbon–carbon double bonds. Furthermore, since introduction of carbon–carbon double bonds through reactions like allylation or acylation is synthetically simple and since other techniques like plasma treatment can also introduce unsaturation, this method should have broad applicability. The extent to which this chemistry can be controlled to modify bulk polymer or surfaces of polymers is still unknown, while the mechanism and scope of the polymerization for vinyl monomer substrates other than acrylic acid derivatives is still not fully clear. We hope to address these and other issues in ongoing work.

Experimental Section

General Methods. The starting polymers were obtained from commercial sources. The polyethylene used (Fortiflex J36-25-

142) was a linear low-density polymer provided by Soltex in the form of a blown film (density of 0.936 g/mL) (MI = 0.25 g/10 min). The starting films' thickness and the thickness of the grafted films were measured with a micrometer by folding the film repeatedly and measuring the thickness of the resulting multiply folded material. Dividing the measured thickness by the number of folds yielded the reported value for the film thickness in Table 1. The starting film has a thickness of 0.025 mm. The starting films also contained detectable amounts of residual unsaturation (IR spectroscopy) from the polymerization process. The starting poly(vinyl chloride) was obtained from Vista Chemicals as an additive-free resin. Poly(vinyl chloride) films were solution cast at 25 °C from a 15% (w/v) tetrahydrofuran solution. ^{1}H NMR spectra were recorded at 105 °C at 200 MHz using a Varian Gemini spectrometer. Contact angles were measured using doubly distilled water and a Ramè Hart goniometer. IR spectra were taken using a Mattson Galaxy spectrometer using an MCT detector and a hemispherical Zn–Se crystal and a Seagull ATR–IR apparatus from Harrick Scientific for ATR-IR studies. A DTGS detector was used for transmission IR spectra. Monomers were obtained commercially from Aldrich Chemical Co. Monomers were purified prior to use by distillation where noted.

Typical Procedure for Grafting with a Polyethylene Film Substrate. The starting polyethylene film used in this work was a medium-density resin (0.936 g/mL) that contained unsaturation from the polymerization conditions used as evidenced by C=C absorbances in the infrared spectrum at 908 cm^{-1}. This resin film was insoluble in all solvents studied at 25 °C and was extracted prior to use first with THF (24 h in a Soxhlet) and then with hexanes (24 h in a Soxhlet). The film was then placed in a flame-dried 100-mL round-bottomed flask equipped with a septum stopper under an argon atmosphere. After flushing the flask for an additional 10 min with argon, 30 mL of dry THF was added. Then 1 mL of $BH_3{\cdot}S(CH_3)_2$ was added and the resulting suspension stirred at room temperature for 1–24 h. The solvent was then removed, and a THF solution of methyl methacrylate (30 mL of a 1:1 (v/v) mixture of THF and methyl methacrylate) was added. Even if the THF used in this step was first distilled under nitrogen, sufficient adventitious oxygen was evidently present in the methacrylate monomer or was inadvertently added to initiate polymerization. Experiments where 1 mL of air was deliberately added proceeded similarly but usually with slightly lower extents of grafting. The polymerization was continued for various time periods. At the end of the polymerization step, the film was removed and washed first at room temperature in THF and then for 24 h in a Soxhlet apparatus. The extraction solvent varied depending on the graft monomer and was THF in the case of methyl methacrylate. After extraction the film was vacuum dried and then analyzed by IR spectroscopy, gravimetry, XPS spectroscopy, or contact angle analysis.

Typical Procedure for Grafting onto Poly(vinyl chloride). A piece of additive-free PVC film was placed under argon in a 50-mL round-bottomed flask equipped with a septum stopper. Then 20 mL of 5% borane–dimethyl sulfide (in ethyl ether) solution was transferred by forced siphon using a cannula. After 12 h of reaction, the solution phase was removed by forced siphon. Then 20 mL of a methyl methacrylate and heptane mixture (1:1, v/v) was intorudced to the flask containing the hydroborated PVC film. The grafting copolymerization was carried out for 12 h after the injection of 1 mL of air. The product grafted film samples prepared by this procedure were washed with a mixture of chloroform and ethanol (1:1, v/v) 10 times for 1 h each time. Separate experiments confirmed that this mixture was a good solvent for the PMMA homopolymer and that this solvent mixture could remove PMMA from a physical mixture of PVC and PMMA.

Dynamic Mechanical Spectroscopy. Dynamic mechanical spectra of PE and PE-*g*-PMMA were recorded on a Rheometrics solid analyzer (RSA-II) at a frequency of 10 Hz and a heating rate of 4 °C/min over a temperature range of 25–160 °C.

Permeability Studies. To measure permeability changes, a 5 × 5 cm film sample of PE-*g*-PMMA was prepared. Gas permeability measurements were performed by connecting a gas permeation cell like that described by Paul[15] that was placed in a thermostated oven at 30 °C to a Varian 3700 gas chromatograph equipped with a thermal conductivity detector. The upstream driving pressures were 35 psi for nitrogen and oxygen. For the water permeability measurement, a piece of polymer film was sealed on the top of a glass cup containing a certain amount of water. This sealed cup was kept in an anhydrous desiccator at 25 °C. The water permeability was calculated from the amount of water vapor (measured by an analytical balance) permeating through the film and the length of time the cup was placed in the desiccator. The upstream driving pressure of water vapor was 23.8 Torr (25 °C). This procedure was modeled after a previously reported method.[16,17] All the permeability measurements were continued until the measured permeability had reached a constant value.

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