Communications to the Editor

Synthesis of Maleic Anhydride Grafted Polypropylene with High Molecular Weight Using Borane/O$_2$ Radical Initiator and Commercial PP Polymers

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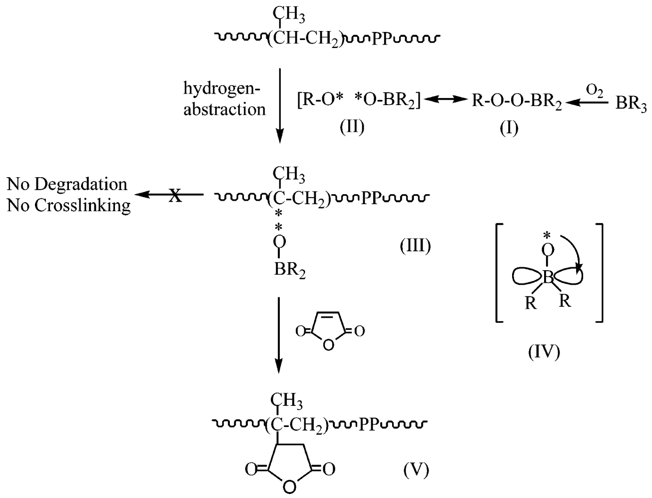
Introduction. Functionalization of polyolefins (PE, PP, EP, etc.) has been a long scientific challenge and an industrial important area,[1−5] which represents a route to expand polyolefin applications and to produce higher value products. It is particularly important in the PP case, with fast growing commercial uses due to its low cost, good mechanical properties, easy processing, and excellent recyclability. Unfortunately, isotactic PP (i-PP) is also one of the most challenging polymers in functionalization chemistry, which can only be prepared by early transition metal catalysts (Ziegler−Natta and metallocene) that are very sensitive to polar functional groups.

By far, maleic anhydride modified polypropylene[6] is the most important commercial functionalized polyolefin. Because of the unique combination of the low cost of maleic anhydride reagent (MAH), high activity of succinic anhydride moiety, and good processablity of maleic anhydride modified PP, it is the popular choice of material for improving the compatibility, adhesion, and paintability of polypropylene. They can be found in many important commercial products, such as glass fiber reinforced PP,[7] anticorrosive coating for metal pipes and containers,[8] metal−plastic laminates,[9] multilayer sheets of paper for chemical and food packaging,[10] and polymer blends such as PP/polyamide and PP/polyester,[11−14] as well as polymer/clay nanocomposites.[15−19]

Commercial MAH modified PP is normally prepared by the chemical modification of preformed PP using free radical chemistry.[20,21] It is generally accepted that the modification reaction involves an initiation step of abstracting tertiary hydrogen atoms from PP chain by free alkoxyl radicals that are in situ generated by the decomposition of a peroxide initiator at an elevated temperature (details shown in Supporting Information). The formed tertiary macroradical promotes rapid β-scission[22] that degrades the PP chain into two parts: a chain-end unsaturated PP and a radical-terminated PP macroradical. The terminal macroradical with good mobility then reacts with the MAH molecule to form MAH-terminated PP, having a terminal succinic anhydride group,[23,24] and PP molecular weight that is inversely proportional to the extent of MAH incorporation. In addition, three are some other side reactions, including oligomerization of MAH molecules to result in a complex color (yellowish to brownish) mixture. The darkness of the product is also proportional to the MAH incorporation. The combination of low molecular weight MAH modified PP and impurities has significantly reduced its ability as the interfacial agent in PP blends and composites. Overall, the MAH modified PP technology barely satisfies the current technological needs.

Scheme 1



A few years ago, we reported a new chemical approach[25] to address the reduction of PP molecular weight problem. The chemistry involved the preparation of “reactive” PP containing some borane units, using metallocene-mediated copolymerization process. The incorporated borane groups selectively and spontaneously oxidized by oxygen to form the polymeric radicals[26−30] that are associated with the in situ formed “stable” borinate radicals.[31] With the presence of MAH, the polymeric radical in situ reacts with maleic anhydride at an ambient temperature to produce MAH grafted PP polymer (PP-*g*-MAH), without altering the PP main chain structure. This method was also extended to the preparation of MAH-terminated PP polymers[32] with predeterminated PP molecular weight. One major drawback is the multiple reaction steps and the commercial unavailability of the “reactive” borane-containing PP polymers.

Results and Discussion. In this paper, a new synthetic route is discussed, which is aimed to use commercial PP and a simple (drop-in) postpolymerization process to prepare PP-*g*-MAH polymer with a high molecular weight and a desirable MAH concentration. In other words, the chemistry involves direct MAH modification of commercially available isotactic PP using our borane technology to prevent side reactions. Scheme 1 illustrates the ideal reaction mechanism.

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Table 1. Summary of Maleation Reaction of Several Polyolefins Using Borane/Oxygen Initiators[a]

	starting polymer					product	
entry	polymer[b]	M_v ($\times 10^3$)	initiator	solvent	temp (°C)	MAH (wt %)	M_v ($\times 10^3$)
control 1	a-PP	17	BBu_3/O_2	benzene	25	0.9	17
control 2	a-PP	17	$BEt_2(OMe)/O_2$	benzene	25	0	17
1	i-PP	270	BBu_3/O_2	benzene	25	0.4	270
2	i-PP	270	BBu_3/O_2	biphenyl	50	0.6	258
3	i-PP	270	BBu_3/O_2	biphenyl	100	1.0	150
4	i-PP	270	BPO	biphenyl	100	0.8	54
5	PP[c]	217	BBu_3/O_2	benzene	25	0.8	200
6	P(E-*co*-*p*-MS)[d]	217	BBu_3/O_2	biphenyl	100	1.3	217
7	s-PS	110	BBu_3/O_2	biphenyl	125	1.8	115

[a] Reaction condition: borane/O_2 mole ratio = 1/1. [b] a-PP: atactic PP; i-PP: isotactic PP; s-PS: syndiotactic polystyrene. [c] PP copolymer contains 0.3 mol % of ethylene units. [d] PE copolymer contains 1 mol % of *p*-MS.

Upon spontaneous monooxidation reaction of BR_3 with a controlled amount of oxygen, the formed $R-O-O-BR_2$ (I) decomposes into a reactive $R-O^*$ and a dormant $^*O-BR_2$ species (II), in which the boroxyl radical (IV) may be stabilized by back-donating of the radical to the empty p-orbital of the boron atom. The $R-O^*$ radical effectively carries out tertiary hydrogen abstraction from the PP chain, and the dormant $^*O-BR_2$ radical in situ caps with the formed polymeric radical to obtain a relatively "stable" polymeric radical (III), which prevents the undesirable side reactions (degradation, cross-linking, and oligomerization of MAH). However, in the presence of maleic anhydride reagent, the polymeric radical (III) reacts with maleic anhydride to produce maleic anhydride grafted PP (PP-*g*-MAH) (V) with a single MAH unit onto the linear polymer backbone. Ideally, this reaction should produce PP-*g*-MAH polymer with a desirable MAH content and high molecular weight comparable to that of the starting PP in a white power form (without oligomerization of MAH).

In a typical reaction, PP powder was suspended in a hydrocarbon solvent before adding the desirable amounts of maleic anhydride and trialkylborane reagents (the experimental details are shown in the Supporting Information). The graft reaction was initiated by slowly introducing a controlled amount of oxygen. The mixture was then stirred for few hours at certain reaction temperature before precipitating it into acetone. The resulting white PP-*g*-MAH powder was washed with acetone to remove the unreacted MAH and isolated by filtration.

Table 1 summarizes the experimental results of MAH modification of a commercial i-PP ($M_v = 250 \times 10^3$ g/mol) by different initiators, including tributylborane, diethylmethoxyborane, and a regular peroxide (BPO). Because of insolubility of the i-PP polymer in low-temperature range, a low molecular weight and room temperature soluble atactic polypropylene ($M_v = 17 \times 10^3$ g/mol) was also used in a control study to examine maleation reaction by borane initiators. The MAH contents were determined by FTIR by comparing with the commercial PP-*g*-MAH polymers with known MAH contents. The polymer molecular weight (M_v) was determined from the intrinsic viscosity of the polymer, which was measured in a dilute decalin solution at 135 °C with a Cannon-Ubbelohde viscometer. The melting point (T_m) of the polymer was determined by differential scanning calorimetry (DSC).

Comparing two control reactions 1 and 2, both were carried out at ambient temperature in ideal homogeneous solution. The BBu_3/O_2-mediated maleation reaction is very effective in incorporating MAH (0.9 wt %) to a-PP without changing polymer molecular weight. On the other hand, there was no detectable MAH incorporation in a-PP after Me-O-BEt_2/O_2-mediated maleation reaction. It is very curious to know the reactive borane oxidation adduct that is responsible for MAH grafting reaction. Figure 1 compares ^{11}B NMR spectra of BBu_3 and two oxidation adducts of BBu_3 and Me-O-BEt_2 with a stoichiometric amount of oxygen (the same oxidation conditions). The detail oxidation mechanisms are discussed in the Supporting Information. In the Bu_3B case (Figure 1b), the chemical shift at 86 ppm for BBu_3 almost disappears, and three new peaks include a major peak at 58 ppm, corresponding to monooxidized species (Bu-O-BBu_2) and two minor peaks at 35 and 33 ppm for two types double oxidized $(Bu-O)_2$-BBu and (Bu-O-O)(Bu-O)-BBu species,[33] respectively. In the Me-O-BEt_2 case (Figure 1c), the chemical shift at 58 ppm for Me-O-BEt_2 almost disappears, and only one oxidized species (Et-O-O)(Me-O)-BEt at 33 ppm is observed. Apparently, both double oxidized $(Bu-O)_2$-BBu and (Bu-O-O)(Bu-O)-BBu species are too stable to react with PP chain. The reactive species in the MAH graft reaction is only the monooxidized trialkylborane species (R-O-O-BR_2) (II), which reacts with BR_3 in the absence of the PP substrate to form stable R-O-BR_2 with a chemical shift at 58 ppm. In the presence of PP chain, the (R-O-O-BR_2) species induces proton extraction of PP chain to form a polymeric radical (III), as illustrated in eq 1.

Entries 1−3 compare the Bu_3B/O_2-mediated maleation reaction of i-PP, having high molecular weight ($M_v = 250 \times 10^3$ g/mol) and a high melting temperature (T_m = 162 °C), at several reaction temperatures that also control the homogeneity of reaction solution. The room temperature heterogeneous reaction produces lower MAH content (0.4 wt %). With the increase of the reaction temperature, the MAH content increased. The polymer solution became homogeneous at 100 °C in biphenyl, and about 1 wt % of MAH was incorporated in i-PP, which is slightly higher than that (0.8 wt %) mediated by a regular BPO initiator (entry 4) under similar reaction conditions. In addition, the molecular weights of PP-*g*-MAH polymers prepared by Bu_3B initiator are significantly higher than those prepared by regular peroxide initiators and commercially available MAH modified PP polymers. However, some change in the polymer molecular weight at high temperature (entry 3) may be associated with the fast reversible capping of polymeric radical with a dormant $^*O-BR_2$ radical, so that the tertiary radical may have some chance to degrade the PP chain. Figure 2 compares the FTIR spectra of the starting i-PP and two corresponding PP-*g*-MAH samples (entries 1 and 3). After the MAH graft-from reaction, two new absorption peaks were observed at 1860 and 1780 cm^{-1}, corresponding to two

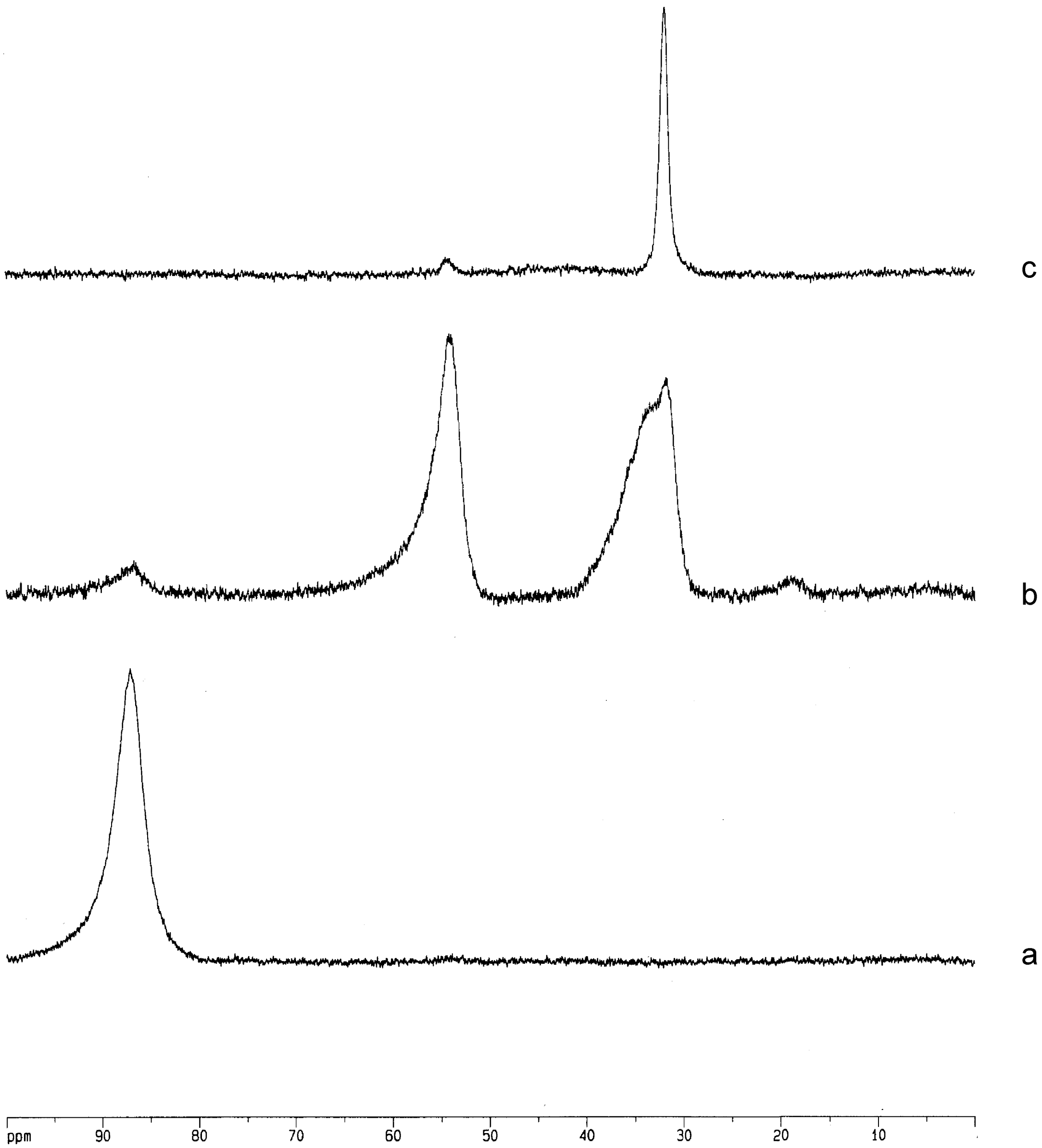


Figure 1. ^{11}B NMR spectra of (a) tributylborane and oxidation adducts of (b) BBu_3/O_2 (1/1) and (c) Me-O-BEt_2/O_2 (1/1 mole ratio).

$\upsilon_{C=O}$ vibrational stretching modes in succinic anhydride. The MAH content in PP-*g*-MAH was calculated by the following equation: MA wt % = $K(A_{1780}/d)$, where A_{1780} is the absorbance of the carbonyl group at 1780 cm^{-1}, d is the thickness (mm) of the film, and K is a constant (= 0.25) detected by calibration of the known MAH content of PP-*g*-MAH polymer. Figure 3 compares three DSC curves of the starting i-PP, PP-*g*-MAH (entry 3), and a commercially available MAH modified PP (Aldrich). An almost identical melting peak at 162 °C was observed for both starting i-PP (Figure 3a) and PP-*g*-MAH (Figure 3b) polymers. On the other hand, the commercial polymer (Figure 3c) shows a lower and broader melting peak, indicating inhomogeneous polymer structures that are associated with polymer chain degradation during the MAH modification.

Overall, the extent of degradation in PP polymer is remarkably alleviated in the system of using tributylborane as an initiator. This indicates that the in situ formed *OBR_2 radical does stabilize the tertiary carbon radical in the PP main chain and noticeably prevents the latter from participating in the degradation reaction of PP. Note that this chemistry of using trialkylborane/O_2 as an initiator for grafting reaction can be extended to other polyolefins, such as ethyl/propylene copolymer, poly(ethyl-*co*-*p*-methylstyrene), and syndiotactic polystyrene. Entries 5−7 in Table 1 show that the MA modified polymers have similar molecular weight as their corresponding starting materials. There is no detectable cross-linking or other noticeable side reaction in all polymers during the grafting reactions. This provides additional support that the in situ formed *O-BR_2 radical does stabilize the tertiary carbon radical in the PP and s-PS and the secondary carbon radical in the PE backbone.

The direct evidence to show PP-*g*-MAH polymer is to carry out a reactive blending reaction with a polyamide containing a terminal NH_2 group. The PP-*g*-MAH (entry 3 in Table 1, M_v = 150K) was used as a compatibilizer in the reactive PP/polyamide blend containing PP (M_n = 100 000 g/mol) and nylon-11 (M_n = 24 800 g/mol). The reaction was carried out in a *m*-cresol/1,1,2,2-tetrachlo-

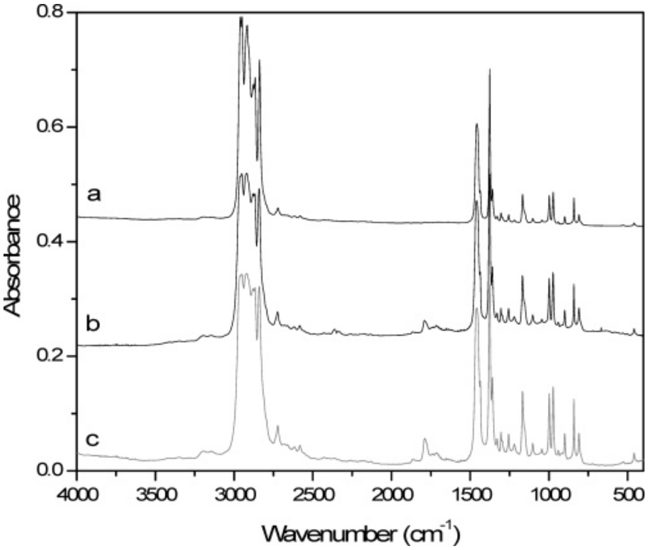


Figure 2. FTIR spectra of (a) the starting i-PP and two PP-*g*-MAH polymers with (b) 0.4 wt % MAH (entry 1) and (c) 1.0 wt % MAH (entry 3).

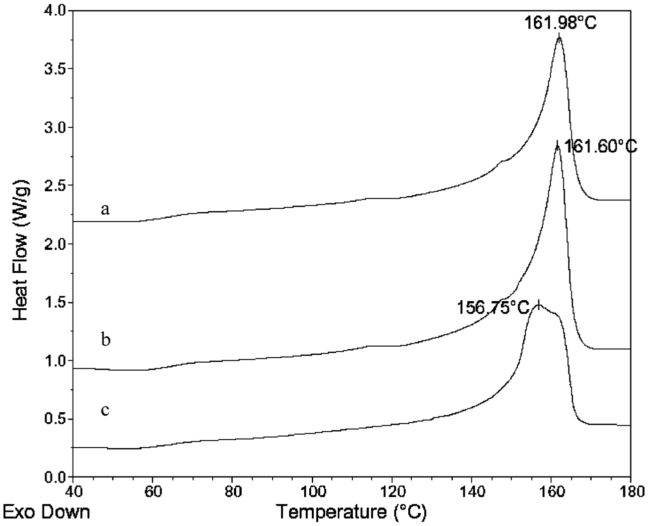
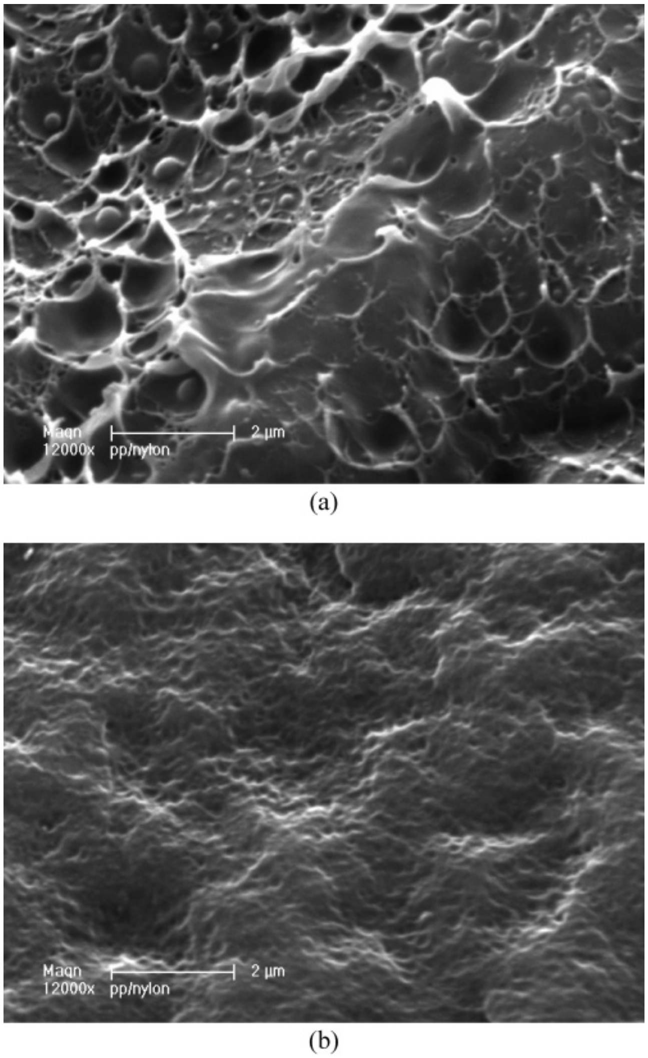


Figure 3. DSC curves of (a) the starting i-PP, (b) PP-*g*-MAH (entry 3), and (c) a commercial MAH modified PP (Aldrich).

roethane mixed solvent at 120 °C. Ideally, the PP-*g*-MAH would react with nylon-11 in situ right at the interfaces between PP and nylon-11 domains and produce a PP-*g*-nylon-11 graft copolymer that serves as the interfacial agent to promote the formation of uniform microphase-separated morphology. The morphology of the polymer blend was examined by an SEM micrograph, with the surface topography of cold fracture film edges representative of bulk morphology. Figure 4 shows SEM photographs of the polymer blend of PP and nylon-11 with and without PP-*g*-MAH in the ratio of 30/70 wt % of PP to nylon-11. In the simple homopolymer blend in Figure 4a, the minor PP components are grossly phase separated into poorly dispersed domains and voids at the fracture surface. This "ball-and-socket" topography is indicative of poor interfacial adhesion between PP and nylon-11 domains and represents minor component domain PP that is pulled out from the nylon-11 matrix. Such pullout indicates that no stress transfer takes place between phases during fracture. On the other hand, the introduction of 10 wt % of PP-*g*-MAH compatibilizer into the PP/nylon-11 blend in situ forms PP-*g*-nylon-11 graft copolymer at the interface which serves as a compatibilizer between PP and nylon-11. A completely different morphology of the fracture cross section of the polymer blend is observed in Figure 4b. There are no distinct globules in the fracture surface. Rather, a relatively flat mesalike fracture surface is shown, and the domain size of the disperse phase PP in this system is much smaller than that in the homopolymer PP/nylon-11 blend. Overall, the ternary blend PP/PP-*g*-MAH/nylon-11 exhibits a strong interface adhesive, and the cold fracture is mainly due to cohesive failure. The cocrystallization between PP-*g*-nylon-11 copolymer and PP homopolymer must take place, which overwhelms the tendency of PP-*g*-nylon-11 to form a discrete domain by itself. On the other hand, the surge of hydrogen bonding provides the interactions between PP-*g*-nylon-11 copolymer and nylon-11 homopolymer in the continuous matrix. Therefore, the high molecular PP-*g*-MAH can form strong interactions with both PP and nylon-11 phases which secure both PP and nylon-11 interfaces.



(a)

(b)

Figure 4. SEM micrographs of polymer blends, including (a) PP/nylon-11 = 30/70 wt % and (b) PP/PP-*g*-MAH/nylon-11 = 20/10/70 wt %.

Conclusion. We have shown a new chemical route to prepare MAH-modified polyolefins with high polymer molecular weight and desirable MAH content. The chemistry is centered on borane/O_2 initiator that can in situ form a monooxidized adduct ($R-O^{*}\ {}^{*}O-BR_2$) species, which then carries out a hydrogen abstraction of the PP chain at ambient temperature to form a stable tertiary polymeric radical associated with a dormant *O-BR_2 radical. Such a stable polymeric radical engages the subsequent MAH graft reaction without showing any significant side reactions. The resulting PP-*g*-MAH polymer exhibit high melting temperature and high molecular weight as the starting PP. In the polymer blending experiment, PP-*g*-MAH shows effective compatability in the PP/nylon-11 blend due to in situ formation of PP-*g*-nylon-11 copolymer located right at the interfaces between PP and nylon-11. The SEM micrograph of the fracture cross section of PP/PP-*g*-nylon-11/nylon-11 shows a relatively flat mesalike fracture surface and a smaller domain size of the disperse phase. In contrast, the simple PP/nylon-11 blend shows a "ball-and-socket" topography that is indicative of poor interfacial adhesion between PP and nylon-11 domains.

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Supporting Information Available: Experimental procedures and reaction mechanisms. This material is available free of charge via the Internet at http://pubs.acs.org.

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