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# Synthesis of Polypropylene-*graft*-poly(methyl methacrylate) Copolymers by the Borane Approach

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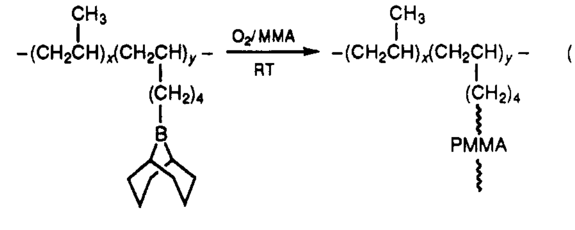
ABSTRACT: This paper describes new PP-*g*-PMMA copolymers which have an isotactic polypropylene (PP) backbone and several poly(methyl methacrylate) (PMMA) side chains. The chemistry involves a graft-from reaction using borane-containing polypropylene and oxygen. The oxidation reaction of the borane groups, such as alkyl-9-BBN, is selective and produces free radicals located at the ends of the side chains on polypropylene. These free radicals are effective initiators for the polymerization of methyl methacrylate. A broad range of PP-*g*-PMMA copolymers have been prepared without significant homopolymerization. The graft copolymers are useful compatibilizers in i-PP/PMMA polymer blends.

## Introduction

Polypropylene (PP) has inadequate compatibility with other polymers and virtually no adhesion to metals or glass. Its low surface energy is due to crystallinity and the lack of chemical functionalities. Accordingly, the chemical modification of polypropylene has been an area of intense interest as a route to improve this important commodity polymer. The uses of block and graft (A–B) copolymers as emusifiers[1–3] in A and B homopolymer blends have been an established technique to improve the compatibility.

Numerous methods have been employed in forming graft copolymers with polypropylene. Ionizing radiation (X-ray, $\gamma$-rays, and e-beams) in the presence of air, ozone, UV with accelerators, and free-radical initiators has been used to form polymeric peroxides[4,5] which can initiate graft polymerizations in the presence of monomers. Unfortunately, these high-energy reactions lead to severe chain degradation and loss of mechanical properties. In many cases, the structure and composition of copolymers are difficult to control.

In our previous paper, we discussed a new route[6] to prepare poly(1-octene) graft copolymers using borane intermediates. The reaction was carried out in a homogeneous solution under mild reaction conditions. Various compositions of poly(1-octene)-*g*-poly(methyl methacrylate) copolymers were obtained. It is certainly interesting to extend the chemistry to isotactic polypropylene (i-PP) which is a commercially important product. In addition, the heterogeneous reaction conditions in the i-PP case will be a severe test for this new graft reaction. The reaction involves borane-containing polypropylene (I) and a graft-from reaction which is initiated by the pendant borane groups with oxygen as shown in eq 1. The graft copolymers of PP-*g*-PMMA will be used as an example to demonstrate the chemistry. In addition, the use of the graft copolymer as the compatibilizer in polymer blends will also be discussed.



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## Results and Discussion

Borane-containing polypropylene copolymer (I) was prepared by direct polymerization, using a combination of Ziegler–Natta catalysis and propylene/borane monomer ($\alpha$-olefin–$\omega$-borane) as illustrated in eq 2. As previously demonstrated, Ziegler–Natta catalysts are stable in the presence of Lewis acid boron alkyls.[7,8] Therefore, borane monomer can copolymerize with propylene, unlike other functional monomers which poison the metal–alkyl catalyst. The $^{11}$B NMR of copolymer I showed a single peak at 87 ppm, the same as the shift for the unpolymerized monomer, indicating an unaltered trialkylborane.[9] In this study, a copolymer containing 0.5 mol % of borane monomers was synthesized with high molecular weight

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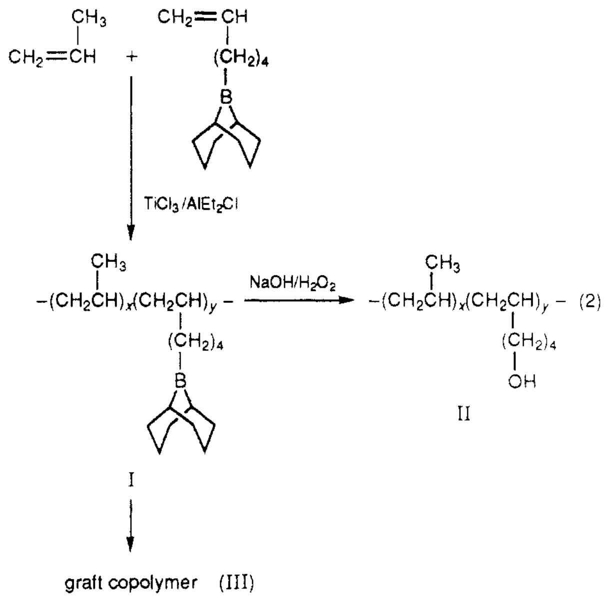
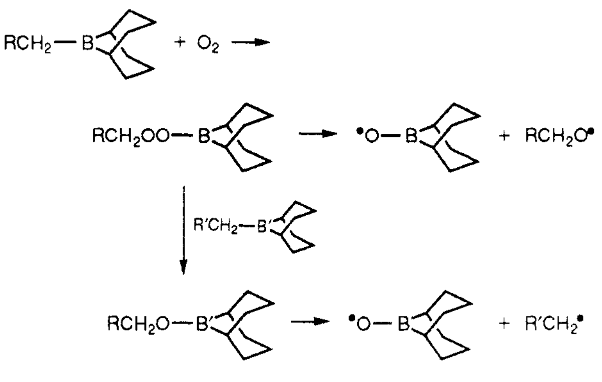


($M_v$ ~200 000). The molecular weight was determined by the intrinsic viscosity of the corresponding hydroxylated polypropylene (PP-OH) (II) which was obtained by oxidation[10] of borane-containing polypropylene (I) with $NaOH/H_2O_2$.

The borane-containing polypropylene is stable for long periods of time (6 months in a drybox) or at elevated temperatures (120 °C during NMR measurement) as long as $O_2$ is excluded. By contact with $O_2$, the autoxidation of boranes proceeds through a free-radical homolytic chain mechanism[11] as shown in eq 3. The driving force is the conversion of B–C bonds (107 kcal/mol) to the stronger B–O bonds (192 kcal/mol). Oxygen will oxidize boranes, producing boron peroxides which can react further with an alkylborane. The reduction of the peroxide by another trialkylborane yields a borinate B–O• radical and an alkyl radical. The boron peroxides will also homolytically cleave to generate an alkoxy radical and a B–O• radical. The radicals can then initiate the polymerization of MMA at room temperature.



(3)

In a typical example, a powder form of copolymer I containing 0.5 mol % of borane monomer was suspended in methyl methacrylate (MMA) monomer with or without solvent. Benzene and THF were used as reaction media for the graft reaction although the polymer does not dissolve. The reaction was initiated by injecting dry $O_2$ into the reaction flask at room temperature. Even though the final B:O ratio was 1:1, only less than 10% of the oxygen was added hourly. After 12 h the reaction was terminated by precipitation in MeOH. The polymer was isolated by filtration and washed with boiling MeOH. The white solid was extracted with acetone in a Soxhlet apparatus for 24 h. This process proved to effectively remove all PMMA homopolymer from the mixture of isotactic PP and PMMA. The acetone-soluble fraction usually was less than 5 wt %, which was PMMA homopolymer with a molecular weight of $M_n$ ~70 000 by GPC and a polystyrene calibration curve. It is interesting to note that a similar molecular weight of PMMA was obtained from a control reaction using octyl-9-BBN as initiator under similar reaction conditions. The acetone-insoluble fraction (>95%) was PP-*g*-PMMA graft copolymer and was completely soluble in xylene at elevated temperature. The dissolution temperature is dependent on the concentration of PMMA. The copolymer with PMMA/PP = 52/48 became a homogeneous solution in xylene above 100 °C.

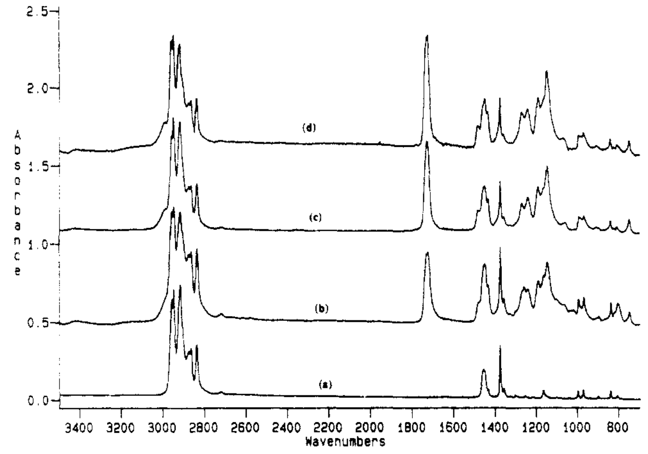


**Figure 1.** IR spectral comparison of (a) poly(propylene-*co*-hexenol) with 0.5 mol % hydroxy groups and PP-*g*-PMMA with various PMMA concentrations: (b) 18, (c) 52, and (d) 66 mol %.

**Molecular Structure of Graft Copolymers.** Figure 1 compares the IR spectra of the resulting PP-*g*-PMMA copolymers (III) and hydroxylated polypropylene (II). All of them were derived from the same copolymer (I) containing 0.5 mol % of borane monomer. The IR spectrum of PP-OH is basically indistinguishable from that of i-PP because of the extremely low concentration of hydroxy groups. On the other hand, the absorption band at 1730 $cm^{-1}$, corresponding to ester groups, clearly indicates the existence of PMMA in the graft copolymers. Some graft copolymers obviously contain a very high percent of PMMA. The quantitative compositions were determined by $^1H$ NMR spectra (shown in Figure 2) which were examined in *o*-xylene-$d_{10}$ at 120 °C. The chemical shifts at 3.6 and 1.8 ppm correspond to methyl groups ($CH_3O$) and methylene groups, respectively, in PMMA. The chemical shifts at 1.9, 1.6, and 1.1 ppm correspond to methine, methylene, and methyl groups in polypropylene. The quantitative analysis of the copolymer composition was calculated by the ratio of two integrated intensities at 3.6 and between 2.1 and 1.1 ppm and the number of protons both chemical shifts represent. Parts a–c of Figure 2 indicate 18, 52, and 66 mol % of PMMA, respectively, in PP-*g*-PMMA copolymers.

The results clearly show high grafting efficiency. High concentrations of PMMA can be incorporated in the side chains of polypropylene with a low concentration of homopolymer. Theoretically, if each alkyl group on the boron had equal reactivity toward $O_2$, then only $^1/_3$ of MMA produced would be graft and $^2/_3$ would be MMA homopolymer for the trialkylborane initiator. This improved grafting is attributed to the higher reactivity of the unhindered polymeric primary C–B bond as opposed to the more sterically hindered secondary C–B bonds of the cyclooctyl ring. Oxygen insertion into a cyclooctyl B–C

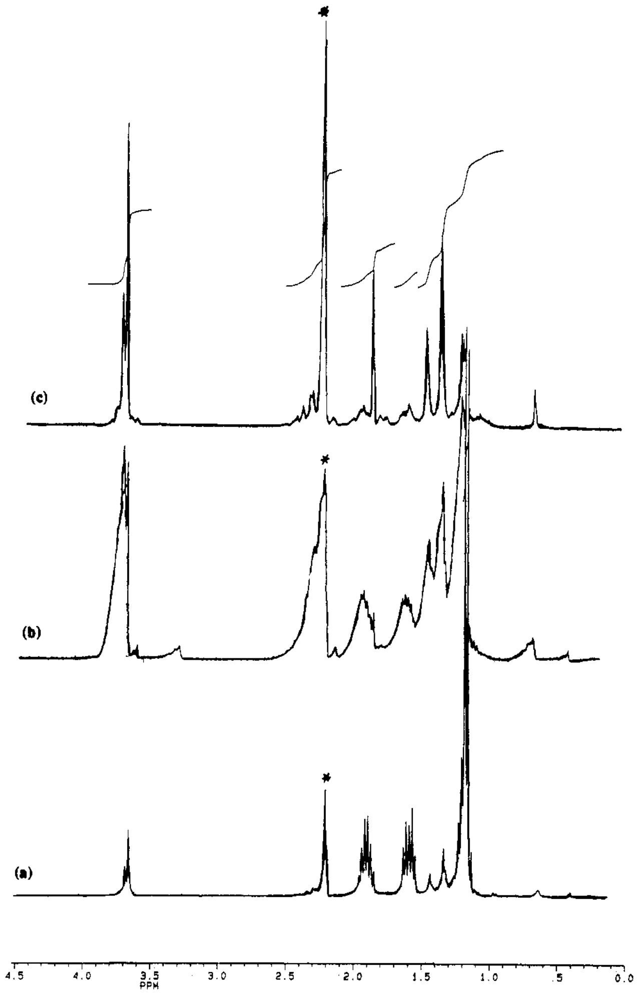


**Figure 2.** $^1H$ NMR spectra of PP-*g*-PMMA graft copolymers, containing (a) 18, (b) 52, and (c) 66 mol % of PMMA.

**Table I. Summary of PP-*g*-PMMA Graft Copolymers**

| run[a] | $O_2$ (mL/h) | MMA/ THF (g) | rxn time (h) | acetone soluble (g) | acetone insoluble (g) | PMMA in copolymer[b] (mol %) |
|---|---|---|---|---|---|---|
| 1 | 1.5/12 | 14/0 | 48 | 0.705 | 8.968 | 66 |
| 2 | 3.0/1 | 14/0 | 2 | 0.120 | 2.251 | 6 |
| 3 | 6 at once | 14/0 | 48 | 0.049 | 2.052 | 1.5 |
| 4 | 1.5/3 | 14/34 | 12 | 0.152 | 5.342 | 52 |
| 5 | diffusion | 14/34 | 48 | 0.095 | 2.413 | 12 |

[a] 2 g of borane-containing polypropylene containing 0.5 mol % borane monomer was used in each reaction. [b] Acetone-insoluable fraction, determined by $^1H$ NMR spectra.

bond would need to distort the cyclooctyl's stable double-chair conformation in order to form the boron peroxide. In addition, the borinate radicals (–BO*) formed during the autoxidation reaction were inactive in the free-radical polymerization. The backbonding of the free radical to the empty p-orbital of the boron may diminish its reactivity to initiate MMA monomers and prevent the PMMA homopolymer.

Table I summarizes the experimental results of the graft copolymers. By varying the reaction conditions, especially the rate of $O_2$ addition, the composition of copolymer was very different. Comparison of runs 1–3 shows the sensitivity of oxygen addition to the graft efficiency. Even though the final stoichiometry of oxygen to boron should be 1:1, the best results in this heterogeneous reaction system are realized when the $O_2$ is introduced slowly so that $O \ll B$ at any time. Excess $O_2$ not only is a poison for free-radical polymerizations but also leads to overoxidation to boronates and borates which are poor free-radical initiators at room temperature. The polarity of the solution also effects the graft reaction. THF is a very good solvent in this reaction. A nonpolar solvent, such as benzene, slows down the graft-from reaction, which may be due to the solubility of $O_2$ in the solvent. In run 5 oxygen was introduced by diffusion of air through the rubber septum which was tightly installed on the top of the reactor. Insufficient $O_2$ in this process leads to a low percent of PMMA formation.

The detailed microstructure of the graft copolymer, in terms of graft density and molecular weight of the PMMA side chain, is very difficult to determine by simple measurements. In fact, in an intrinsic viscosity study carried out in a decalin solution at 135 °C the PP-*g*-PMMA graft copolymers with 30% PMMA showed a significant lower viscosity than PP-OH (II); both were obtained from the same borane-containing polymer (I). The poor solubility of the PMMA side chains in decalin may result in a decrease of the radius of gyration of the graft copolymer. Due to the significant difference in the solubility parameter, it is very difficult to find a single solvent which is good for both segments. However, it seems reasonable to assume that the PMMA side chain in the graft copolymer may have a molecular weight ($M_n \sim 70\,000$) similar to that of isolated homopolymer (acetone-soluble fraction) because both reactions occurred under the same reaction conditions. Under this assumption, the copolymers of runs 1 and 4 may have on average 5 to 3 PMMA side chains along the polypropylene backbone. Details of the graft density and homogeneity of copolymers are under investigation using high-temperature GPC with a light scattering detector. Both graft copolymers were found to be very effective compatibilizers in polymer blends (discussed later).

**Thermal Property Studies.** Thermal properties of graft copolymers were measured by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Figure 3 shows DSC traces of pure i-PP (upper curve, $\Delta H = 62$ J/g), PP-*g*-PMMA with 5% PMMA (middle curve, $\Delta H = 52$ J/g), and PP-*g*-PMMA with 66% PMMA (lower curve, $\Delta H = 22$ J/g). All samples were treated under the same thermal conditions. It is interesting to note that the polymer with 66% PMMA still shows a melting point similar to that of i-PP. In addition, the heat of fusion (J/g of PP) is also very close despite the large differences in their compositions. The propylene segments in graft copolymers maintain most of their crystallinity. This indicates that the graft density must be low as suggested before. The phase separation between PP and PMMA segments was also shown in the glass transition temperature, with only slightly higher $T_g$s in graft copolymers than in pure i-PP. Thermal gravimetric analysis shown in Figure 4 demonstrates that the graft copolymers begin weight loss at 190 °C in air and at 250 °C in argon, whereas i-PP begins weight loss at 220 °C in air and at 360 °C in argon. The thermal decomposition of the graft copolymer obviously starts from the less thermally stable PMMA segments.

**Polymer Blends.** Optical microscopy was used to evaluate the graft copolymer's ability to act as a phase compatibilizer for blends of i-PP and PMMA homopolymers. Polymer solutions were prepared in BHT-inhibited *o*-xylene at 135 °C. The polymer films were then solution cast onto glass microscope slides. After evaporating the xylene under $N_2$ purge, the films were covered with a slide cover. The polymer films were then melted in a hot stage at 180 °C for 15 min. The samples were then allowed to cool quiescently in the hot stage to room temperature for

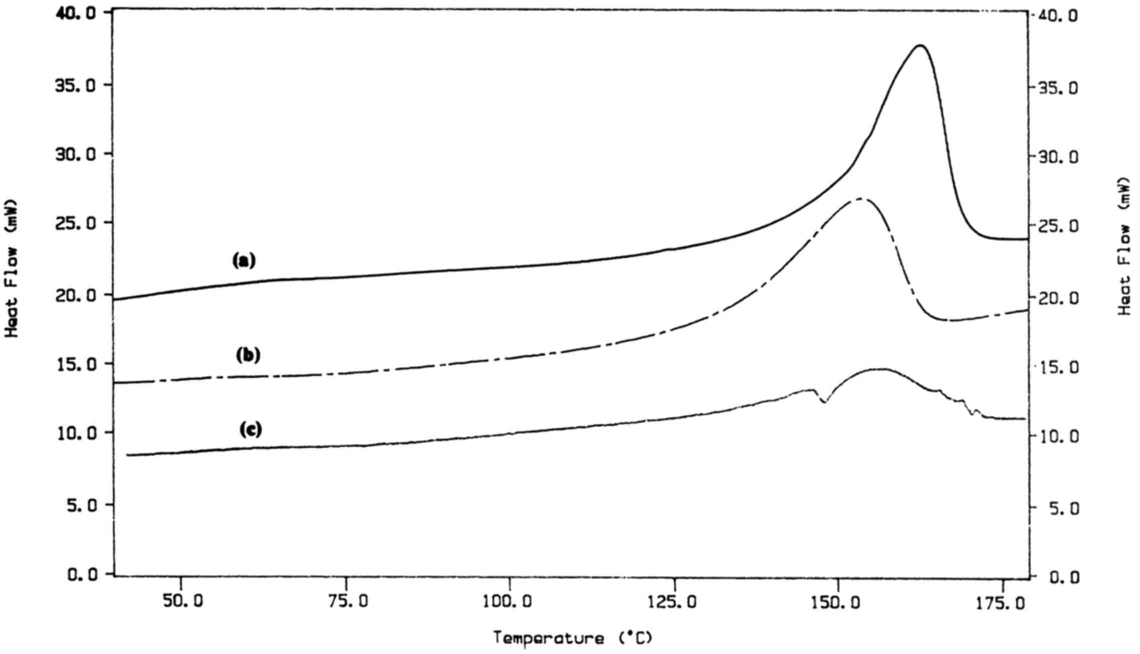


**Figure 3.** DSC curve comparison between (a) i-PP and (b) PP-*g*-PMMA copolymers containing 5 mol % PMMA and (c) 66 mol % PMMA.

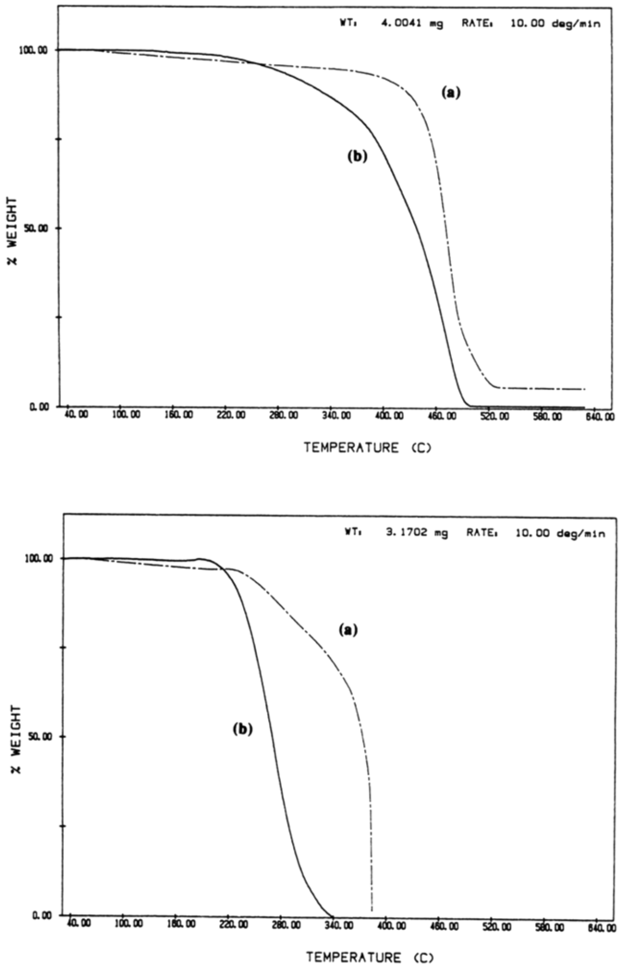


**Figure 4.** TGA curves of (a) i-PP and (b) PP-*g*-PMMA containing 66 mol % PMMA in argon (top) and in air (bottom).

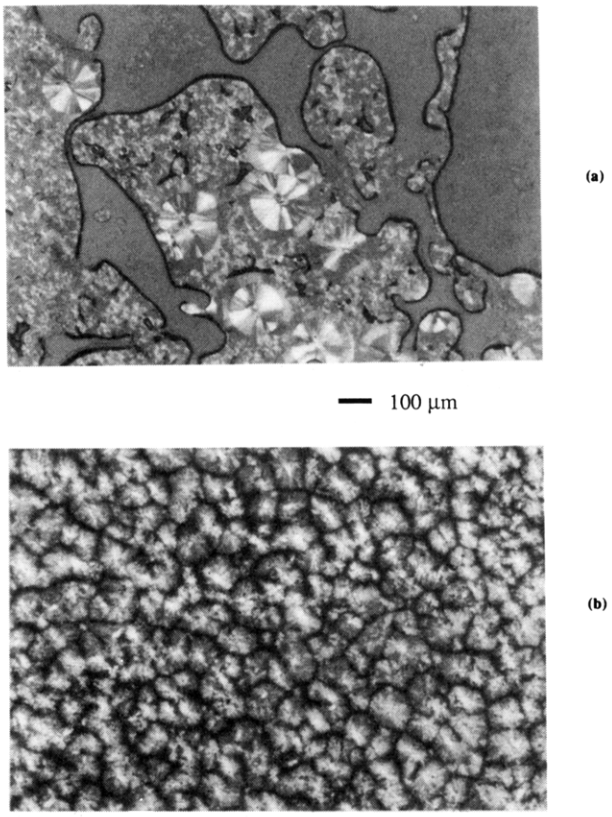


**Figure 5.** Optical micrographs of polymer blends: (a) two homopolymer blends with i-PP/PMMA = 70/30 and (b) two homopolymers with PP-*g*-PMMA containing 30% PMMA, i-PP/PP-*g*-PMMA/PMMA = 70/10/30.

20 min. Figure 5 shows the micrographs with a magnification of 100×. Blend A is a 70/30 wt % mixture of i-PP and PMMA homopolymers that were blended in solution. Two distinct phases are visible, the crystalline i-PP phase and an amorphous PMMA phase. Within the i-PP domain, the spherulite size varies greatly with a few extremely large crystallites and predominantly small spherulites. Blend B is a sample of blend A to which 10 wt % PP-*g*-PMMA has been added in solution. The added graft copolymer was also 30 wt % PMMA so as not to change the overall composition. The most noticeable change in the micrograph is the disappearance of the visibly distinct PMMA domain. Also, the mode of nucleation within the crystalline phase has changed as evidenced by the now relatively homogeneous spherulite size. Both

morphological changes certainly indicate the compatibility of PP-*g*-PMMA in a PP and PMMA blend.

It is interesting to note that both films of the compatibilized blend and the pure graft copolymer formed in the melt press were optically clear. This is very different from pure polypropylene which forms hazy, translucent films. The lack of large spherulites in the graft copolymer and polymer blend may minimize the light scattering.

## Experimental Section

**Instrumentation and Materials.** All room- and high-temperature $^1$H NMR and $^{11}$B NMR spectra were recorded on Bruker WP-200 or Bruker AM-300 spectrometers with the DISNMR software. Quartz NMR tubes were used in $^{11}$B NMR measurements. Fourier transform infrared spectroscopy was performed on a Digilab FTS-60 instrument on solution-cast films on KBr windows. Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer DSC-7, TAC-7 instrument controller. The DSC's were measured from −30 to +200 °C at a heating rate of 20 °C/min. Thermogravimetric analysis was accomplished using the Perkin-Elmer TCS-2 thermogravimetric analyzer using a system thermal analysis microprocessor controller. Weight loss versus temperature was measured under argon and under $O_2/Ar = 30/70$ at a heating rate of 10 °C/min. Viscosity measurements were taken using a cone/plate rotational Brookfield digital viscometer Model DVII. The viscosities of polymer solutions in decahydronaphthalene (decalin) inhibited with BHT were determined at 135 °C. The alcohol-containing copolymers were esterified before measuring their viscosities. Solutions of the copolymers in dry xylene and pyridine were esterified by benzoyl chloride to their respective benzoic ester copolymers to improve their solubility in decalin.

All $O_2$- and moisture-sensitive manipulations were carried out inside of an argon-filled Vacuum Atmospheres drybox. HPLC-grade tetrahydrofuran and toluene were deoxygenated by an argon sparge before refluxing for 48 h and then distilling from their respective green or purple sodium anthracide solution under argon. Isopropyl alcohol was refluxed in $CaH_2$ before distilling under argon. All three solvents were stored in the drybox. The borane-containing polypropylene was prepared by the published method.[12]

**Graft-from Polymerization.** In a typical reaction, 2 g of borane-containing copolymer with 0.5 mol % borane groups was placed in a suspension of 12 g of dry uninhibited MMA and 20 g of THF in a sealed, opaque flask. The reaction was initiated by injecting dry $O_2$ into the reaction flask; about 0.5 mL of oxygen was added hourly. After 12 h of stirring at room temperature the reaction was terminated by removal of MMA and oxygen under vacuum. The polymer solid was then refluxed in 100 mL of methanol before distilling off 20 mL of methanol and isolating by filtration. After drying in a vacuum oven, 3.49 g of white solid was obtained. The polymer was fractionated by acetone extraction in a Soxhlet apparatus for 24 h. Both insoluble and soluble fractions were isolated by vacuum removal of the solvent, resulting in 95% grafted MMA and 5% homopolymer. The acetone-insoluble polymer was 3.41 g of PP-*g*-PMMA which was completely soluble in xylene at elevated temperatures. Only 0.08 g of acetone-soluble polymer was recovered, which was PMMA homopolymer.

## Conclusion

This paper clearly shows the advantages of the borane approach in the preparation of graft copolymers. Despite the heterogeneous reaction conditions, the grafting efficiency can be very high. The delivery of oxygen is a key factor in controlling this graft-from reaction. Overall, the process is simple and general, which can be easily extended to various polyolefin backbones and free-radical-polymerized side chains, such as PMMA, PVA, PAN, and PS. Most of the graft copolymers would be very difficult to obtain by other existing methods. The resulting graft copolymers of PP-*g*-PMMA are effective compatibilizers in controlling the morphology of polyolefin blends. Their mechanical properties are currently under investigation.

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