Macromolecules **1998,** *31,* 5943−5946 **5943**

Maleic Anhydride Modified Polypropylene with Controllable Molecular Structure: New Synthetic Route via Borane-Terminated Polypropylene

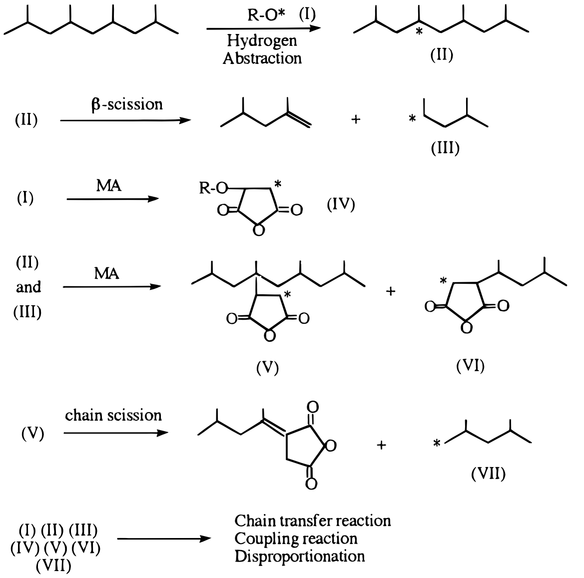
Bing Lu and T. C. Chung*

Department of Materials Science and Engineering,
The Pennsylvania State University,
University Park, Pennsylvania 16802

Received March 24, 1998
Revised Manuscript Received May 27, 1998

Introduction. By far, maleic anhydride (MA) modified polyolefins are the most important class of functionalized polyolefins in commercial applications, due to the unique combination of low cost, high activity, and good processiblity. They are the general choice of material in improving compatibility, adhesion, and paintability of polyolefins. Among them, MA modified polypropylene (PP-MA)[1] is the most investigated polymer, which has found applications in glass fiber reinforced PP,[2] anticorrosive coatings for metal pipes and containers,[3] metal−plastic laminates for structural use,[4] multilayer sheets of paper for chemical and food packaging,[5] and polymer blends[6−8] (PP/polyamide and PP/polyester).

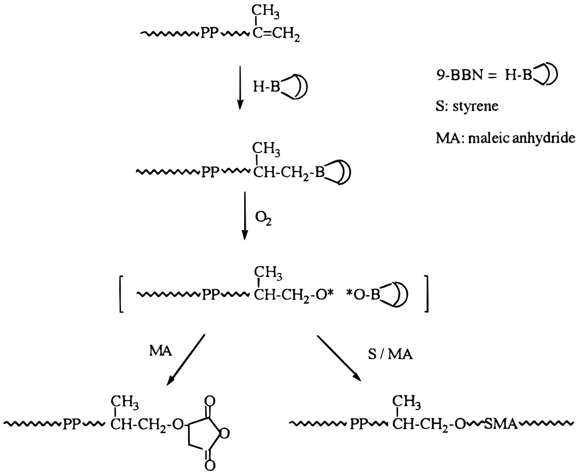
Usually, PP-MA was prepared by chemical modification of preformed PP under free radical conditions,[9−12] as illustrated in eq 1.



(1)

As expected, this MA grafting reaction is accompanied by many potentially undesirable side reactions, such as β-scission, chain transfer, and coupling. The MA incorporation is usually inversely proportional to the resulting polymer molecular weight. In fact, it has been generally suggested that a significant portion of PP-MA polymers have a succinic anhydride group located at the polymer chain end,[11,12] resulting from β-scission. Many experimental results,[13] mainly found in patent literature, have been focused on the reaction conditions (i.e., temperature, initiator, solvent, mixing, etc.) to improve the grafting efficiency and to minimize the undesirable side reactions. However, the inherent complexity of this reaction has greatly limited the progress of achieving PP-MA polymer with controllable molecular structure. The combination of mixed MA structure, reduced PP molecular weight and impurities has significantly reduced PP-MA ability as the interfacial agent in PP blends and composites. Overall, the PP-MA technology barely satisfies the current technological needs.

Results and Discussion. In this paper, a new synthetic route is discussed, which is aimed to prepare MA-modified PP with controllable molecular structure, i.e., PP molecular weight and MA incorporated location and concentration. Equation 2 illustrates the reaction scheme.



(2)

The chemistry involves the usage of borane-terminated PP as the intermediate, which can be effectively prepared and transformed to MA-modified PP with controllable MA concentration and no detectable side reactions, i.e., chain degradation and cross-linking. Usually, the borane-terminated PP (PP-B) was prepared by hydroboration reaction of chain end unsaturated PP (u-PP), obtained from metallocene polymerization[14] or thermal degradation[15] of high molecular weight PP. In turn, PP-B polymer is selectively oxidized by oxygen[16,17] to form a “stable” polymeric alkoxyl radical[18] (associated with the boroxyl radical), which then initiates the free radical reaction of maleic anhydride. Due to the low tendency of homopolymerization of MA,[19] a very low concentration of MA (possibly only a single unit) was incorporated in the PP structure to form MA-terminated PP (PP-*b*-MA). On the other hand, with the presence of styrene in the PP−B/MA mixture, the free radical graft from polymerization takes place to extend the PP chain end with an alternating styrene and MA (SMA) copolymer.[20] In other words, a diblock copolymer PP-*b*-SMA is obtained, containing both PP and SMA segments. The MA concentration in the copolymer is governed by the molecular weight of the SMA segment.

Figure 1 compares IR spectra of the starting u-PP and two corresponding MA-modified PP polymers, i.e., PP-*b*-MA and PP-*b*-SMA, which were prepared and fractionated by the procedures shown in the Experimental Section.

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* To whom all correspondence should be addressed.

S0024-9297(98)00469-0 CCC: $15.00

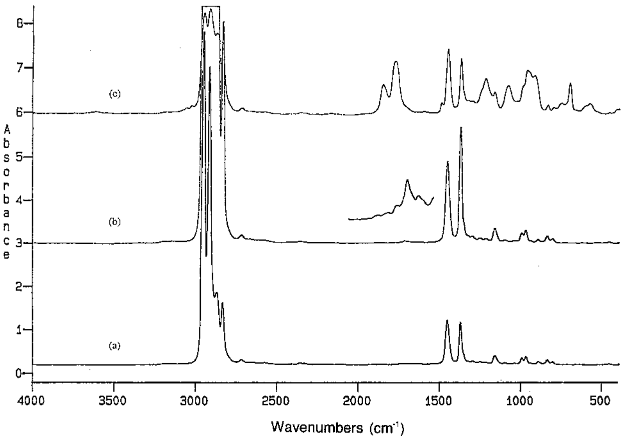

Figure 1. Comparison of IR spectra of (a) PP-3, (b) PP-3-*b*-MA, and (c) PP-3-*b*-SMA-3 polymers in the first reaction set in Table 1.

In Figure 1b, a new weak absorption band centered at 1710 cm^{-1}, corresponding to the $\upsilon_{C=O}$ stretching mode of the acid form, indicates that a very low concentration of MA was incorporated into PP-*b*-MA and most of them were hydrolyzed during the sample handling.

On the other hand, Figure 1c shows several new strong absorption peaks at 1860 and 1780 cm^{-1}, corresponding to two $\upsilon_{C=O}$ vibrational stretching modes in succinic anhydride, at 900−950 cm^{-1}, corresponding to the υ_{C-H} deformation in succinic anhydride, and at 1500, 700, 750, and 580 cm^{-1}, corresponding to styrene υ_{C-H} deformation. Clearly, very high concentrations of MA groups were incorporated with styrene units in the PP-*b*-SMA sample. The concentration of anhydride or/and acid was calculated by a standard industrial method (discussed in the Experimental Section), based on the IR carbonyl group absorption intensity and sample thickness.

Table 1 summarizes the experimental conditions and results of two comparative reaction sets.

In the first set, about 0.2 wt % MA was detected in the PP-3-*b*-MA sample, which is close to the theoretical value (0.16 wt %) of one MA unit per PP chain. With the addition of styrene, the incorporation of MA units dramatically increases, and the concentration is dependent on the reaction time (comparing samples PP-3-*b*-SMA-2 and PP-3-*b*-SMA-3) and styrene concentration (comparing samples PP-3-*b*-SMA-1 and PP-3-*b*-SMA-2). In the PP-3-*b*-SMA-3 sample, 25 wt % MA incorporation indicates about 50 wt % of SMA assuming the alternating copolymer segment existed in this diblock copolymer. In other words, the molecular weight of the SMA segment is about 5.3×10^4, similar to that of the PP segment. Similar results were concluded for the second set, despite the starting u-PP being of very high molecular weight (1.63×10^5) and thus having an extremely low concentration of reactive sites. Due to the sensitivity limit of FTIR spectroscopy, the MA concentration (0.06 wt %) in PP-8-*b*-MA is only an estimation, assuming one MA in each PP chain. However, with the styrene in the reaction mixture, the chain extension took place and the amount of incorporated MA units dramatically increased. IR spectra also show that the concentration of MA is also increased with the increases of styrene concentration and reaction time (comparing samples PP-8-*b*-SMA-1 and PP-8-*b*-SMA-2). Sample PP-8-*b*-SMA-2 contains a high concentration (20 wt %) of MA units with the estimated molecular weight $>2.6 \times 10^5$, assuming an alternating SMA segment in the diblock copolymer.

With the increase of SMA concentration in PP structure, the solubility of polymer gradually reduced. Only the samples containing MA units <1.5 wt % are soluble in decalin for molecular weight determination. However, all the samples are melt processible at 260 °C. It is very interesting to note that all measured PP-*b*-MA and PP-*b*-SMA samples (soluble in decalin) show molecular weights similar to that of the starting u-PP, indicating no detectable degradation or cross-linking reactions happened during MA grafting reactions, which is a great departure from the current peroxide/MA technology discussed in eq 1.

Figure 2 compares three DSC curves of uPP-8, PP-8-*b*-MA, and PP-8-*b*-SMA-2 in the second reaction set discussed in Table 1.

An almost identical melting peak at 162 °C, corresponding to the T_m of the PP polymer, was observed in all samples. A clear new T_g at about 216 °C (corresponding to the alternating SMA copolymer[1]) was shown in the PP-8-*b*-SMA-2 sample. Two thermal transitions almost identical to those of two corresponding PP and SMA polymers indicate clear phase separation between the PP and SMA domains. Both polymer segments in the diblock copolymer must have long consecutive (undisturbed) sequences to form separate domains.

To further examine the presence of MA units in PP-*b*-MA samples, containing only one MA per polymer chain, a reactive polymer blend study was carried out by mixing a small quantity of PP-*b*-MA sample with PP and poly(ω-aminoundecanoic acid) (Nylon 11) in a Brabender mixer at 240 °C for a few minutes. The morphology of the polymer blend was viewed by SEM. Figure 3 compares two SEM micrographs of the reactive blend Nylon 11/PP-3-*b*-MA/PP = 75/5/20 and the corresponding control blend Nylon 11/PP = 75/25 prepared under the same conditions. The magnification is 1500× (micrographs reduced to 64% for publication).

Figure 3a shows inhomogeneous discrete PP domains, with sizes between 15 and 4 μm, embedded in Nylon 11 continuous domain, which indicates limited compatibility between PP and Nylon 11. In Figure 3b, a similar polymer blend containing 5 wt % PP-3-*b*-MA shows a much more homogeneous morphology with uniform spherical PP domains of sizes of about 1 μm. The good dispersion is obviously due to the high degree of emulsification of PP-3-*b*-MA in this reactive process. During the reactive mixing, the MA end group in PP-3-MA reacts with the chain end NH_2 group in Nylon 11 to form PP-*b*-Nylon 11 diblock copolymer, which in situ served as the compatibilizer between PP and Nylon 11 to improve the compatibility of the PP/Nylon 11 blend. It is very interesting to note the effectiveness of MA groups in this blend, considering the fact that only about 0.01 wt % of MA groups is present in the total polymer mixture and most of them were hydrolyzed to acid form.

Experimental Section. In a typical example, the hydroboration reaction was carried out under heterogeneous conditions by suspending u-PP fine powder in THF. A slight excess of 9-borabicyclononane (9-BBN) was used to ensure complete reaction. Usually, the reaction mixture was stirred at 55 °C for 5 h before removing the polymer powder from solution by filtration. On the basis of our previous experimental results,[21] the reaction is almost quantitative, due to very high hydroboration reactivity and high surface area of

Table 1. Summary of Maleic Anhydride Modified PP Copolymers

	preparation condition[a]			product properties				
sample no.	MA (g)	styrene (mL)	time (h)	W_{diblock}[b] (g)	M_v($\times 10^{-4}$)	MA (wt %)	T_m (°C)	T_g (°C)
u-PP-3					5.29	0	145.4	
PP-3-*b*-MA	2	0	4		5.39	9.2	146.8	
PP-3-*b*-SMA-1	2	0.1	4		5.39	1.1	147.2	
PP-3-*b*-SMA-2	2	2	4			9.6	146.5	
PP-3-*b*-SMA-3	2	2	10	2.014		25	146.1	213
u-PP-8					16.3	0	162.3	
PP-8-*b*-MA	2	0	4		16.0	0.06[c]	162.6	
PP-8-*b*-SMA-1	2	0.1	4		16.1	1.0	163.4	
PP-8-*b*-SMA-2	2	2	10	1.653		20	162.6	216

[a] 1 g of borane-terminated PP. [b] Xylene and Acetone Insoluble Portion. [c] Based on theoretical calculation.

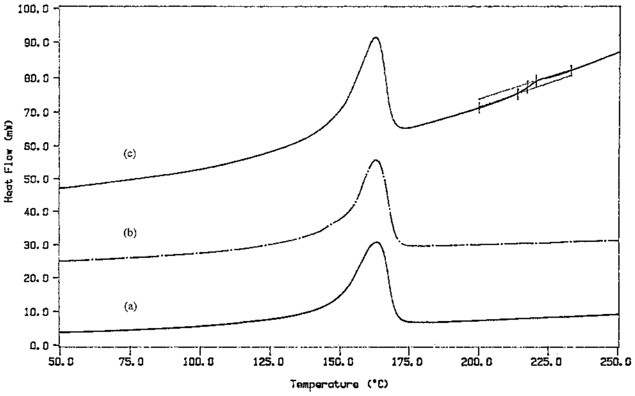

Figure 2. DSC curves of (a) PP-8, (b) PP-8-*b*-MA, and (c) PP-8-*b*-SMA-2 polymers in the second reaction set in Table 1.

reaction sites. While some of the PP segments are crystallized, the polymer chain ends with high mobility are expelled into the amorphous phase, which is swellable by solvent during the reaction. The resulting 9-BBN-terminated polypropylene (PP-9-BBN) was divided into several portions (1 g each); they were then subjected to the oxidation reaction by oxygen in the presence of MA or the mixture of MA and styrene, with various quantities shown in Table 1. The reaction was usually performed at ambient temperature by slowly adding a stoichiometric quantity of oxygen (vs borane) to the suspending polymer solution. After a certain reaction time shown in Table 1, the radical reactions were terminated by precipitating the polymer mixture in 2-propanol. The product, isolated by filtration, was washed repeatedly with acetone. For PP-*b*-SMA sample containing >3 wt % MA, such as PP-3-*b*-SMA-3, the reaction mixture was further subjected to Soxhlet extraction with refluxing xylene and acetone for 24 h to remove unreacted PP (0.182 g) and ungrafted SMA polymer (0.337 g), respectively. The xylene and acetone insoluble but thermally processible portion (2.014 g) is PP-*b*-SMA diblock copolymer. In general, the graft efficiency was very high, and the major portion (>80%) of PP was converted to PP-*b*-SMA diblock copolymer.

The intrinsic viscosity of the polymer was measured in decahydronaphthalene (decalin) dilute solution at 135 °C with a Cannon-Ubbelohde viscometer. The viscosity molecular weight was calculated by the Mark–Houwink equation: $[\eta] = KM_v^{\alpha}$ where $K = 1.05 \times 10^{-5}$ and $\alpha = 0.80$.[22] The MA concentration in the polymer was estmated by the IR spectrum with the following equation: MA wt % = $(k_1A_{1780\mathrm{cm}^{-1}} + k_2A_{1710\mathrm{cm}^{-1}})/d$, wherein d is the film thickness, $A_{1780\mathrm{cm}^{-1}}$ and $A_{1710\mathrm{cm}^{-1}}$ are the peak absorbances, and k_1 and k_2 are the absorption constants for anhydride and acid, respectively. Both k_1 and k_2 were determined by calibration of the known commecial compounds (Uniroyal), assuming the absorption constants are independent of the incorporated MA structures. The melting point (T_m) and glass transition temperature (T_g) were measured by differential scanning calorimetetry (DSC) from the second run with a heating rate of 20 °C/min under nitrogen on a Perkin-Elmer DSC-7 instrument. Scanning electron microscopy (SEM) was used to examine the morphologies of polymer blends. Samples were prepared in a Brabender mixer by mixing various polymers at 240 °C for a few minutes. The mixture was then melt pressed to a film that was cryofractured in liquid N_2 to obtain an undistorted view representative of the bulk material. The surface of the cross-section was sputtered with gold and then viewed with a Topcon International Scientific Intruments ISI-SX-40 using secondary electron imaging.

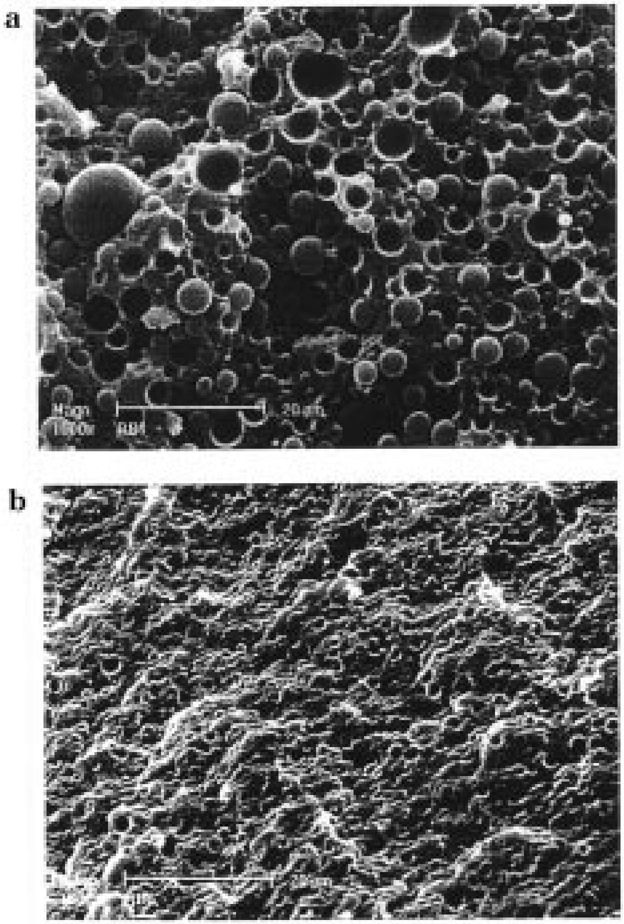

Figure 3. SEM micrographs of (a) the control blend with Nylon 11/PP = 75/25 and (b) the reactive blend Nylon 11/PP-3-*b*-MA/PP = 75/5/20. (1500×). Micrographs reduced to 64% for publication.

Conclusion. It is both scientifically challenging and industrially important to develop a new method to prepare maleic anhydride modified polyolefins with controllable molecular structure. The borane-terminated polyolefin approach provides a promising route. In addition to the incorporation of the desirable amount of MA units, no detectable PP chain degradation and cross-linking reactions ensure the control of PP-*b*-MA molecular weight, similar to the starting PP. Despite the extremely low concentration of MA, PP-*b*-MA appears to be a very effective compatibilizer in the reactive PP/Nylon 11 blend. With the availability of various MA-modified PP polymers with relatively well-defined molecular structure, it is now possible to systematically study the correlation between the molecular structure, i.e., PP molecular weight and MA concentration, and their compatibility in PP blends and composites.

Acknowledgment. The authors are thankful for the financial support from the Polymer Program of the National Science Foundation.

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MA9804693