

Melt-Grafting Mechanism Study of Maleic Anhydride onto Polypropylene with 1-Decene as the Second Monomer

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ABSTRACT: Although polypropylene (PP) grafted by maleic anhydride (MAH) has been successfully commercialized, the grafting mechanism under the existence of a second monomer is not very clear. To simulate the grafting process of MAH onto PP with 1-decene as the second monomer, the MAH/1-decene copolymer and Alder ene reaction product were prepared and grafted onto PP with dicumyl peroxide as the initiator. We found that the grafting of the copolymer and the reactive product greatly improved the grafting degree of MAH. Particularly, the grafting degree with a 3% content of the Alder ene reactive product was 1.89%, which was 178% higher than that of pure MAH-g-PP, the maximum value of which was 0.68%. The molecular weight of the synthesized product affected the grafting efficiency and crystallization behavior

of the grafted system. The system grafted with the Alder ene reaction product showed a higher crystallization temperature and crystalline degree. When the molecular weight of the copolymer was higher than 1700, the improvement of the grafting degree could be neglected. For MAH-g-PP with 1-decene as the second monomer, the possible grafting mechanisms were as follows: first, the formation of MAH/1-decene copolymer or the Alder ene reaction product, and second, the grafting of the previously formed product onto PP, in which, the effect of the Alder ene reaction product was more pronounced. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3724–3732, 2011

Key words: graft copolymers; poly(propylene) (PP); reactive processing

INTRODUCTION

In recent years, the grafting of polar monomers, such as maleic anhydride (MAH), onto polypropylene (PP) has attracted great attention.^{1–4} However, as to the grafting mechanism, there still exists some uncertainty, especially for grafting systems with a second monomer.

Figure 1 shows the widely accepted grafting process of MAH onto PP with an organic peroxide free-radical initiator. First, the decomposition of ROOR leads to the formation of primary free radicals (RO*’s; step a). In step b, RO* reacts with an unsaturated monomer (M; e.g., MAH) to form a saturated free-radical species (RM*). If the latter continues to react with M, an oligomer or a polymer of M will be formed. In step c, RO* reacts with hydrogen atoms of the polymer (e.g., PP), preferentially tertiary ones, to form the corresponding macroradicals (P*’s). Then, in step d, P* is degraded into two shorter segments, or in step e, M is grafted onto P*.

For MAH-grafted PP, because the reactivity of MAH toward free radicals is very low and because of the immiscibility between PP and MAH, the grafting reaction is often accompanied by undesirable chain scission behavior, which results in a relatively low grafting degree and grafting efficiency.⁵ Recently, it has been reported that the grafting degree can be improved and the extent of side reactions can be minimized by the addition of an appropriate second monomer, of which styrene (St) is the most effective.^{6–9} Li and coworkers^{6,7} and Zhang and coworkers^{8,9} proposed a possible mechanism of the grafting of MAH onto PP with St as the second monomer. It is believed that when there is no St in the reactive system, MAH is grafted mostly onto PP as single molecule after the degradation of PP. However, when there is St in the reactive system, St reacts with MAH to form the St–MAH copolymer or St forms a charge-transfer complex with MAH before MAH and St graft onto PP. The formed long chain of MAH and St is grafted onto PP; this leads to an increase in the grafting degree of MAH. For glycidyl methacrylate grafting onto PP with the assistance of St, it has been proposed that St preferentially reacts with the PP macroradicals to form more stable styryl macroradicals, which then copolymerize with glycidyl methacrylate to form branches.^{10–12}

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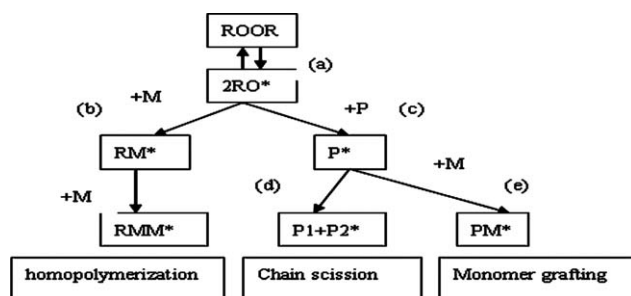


Figure 1 Sketch of grafting process of M onto PP.

In our previous study,¹³ the influence of 1-decene on the melt-grafting behavior of MAH onto PP was examined. We found that the value of the grafting degree increased from 0.68% for pure MAH-g-PP to 1.43% for the system with a 1-decene/MAH molar ratio of 0.3, whereas the maximum value with St as the second monomer was 0.98% under an St/MAH molar ratio of 1.0. As one kind of α -olefin, 1-decene is more effective than St. It has been reported that α -olefin can react with MAH through the Alder ene reaction or can copolymerize with MAH to form an α -olefin/MAH copolymer.^{14–20} Possible grafting mechanisms are proposed here and are shown in Figure 2. One mechanism is that the copolymer formed by 1-decene and MAH is grafted onto PP. The other mechanism is that 1-decene reacts with MAH through the Alder ene reaction, and the formed product is grafted onto PP. We examined which mechanism was more effective, whether the copolymer was grafted onto PP, and what the upper limit of the molecular weight was that could improve the grafting degree.

To simulate the grafting process of MAH onto PP with 1-decene as the second monomer, in this study, we first prepared and then characterized the copolymer and Alder ene reaction product between 1-decene and MAH. Then, they were grafted onto PP under the melt state. A 1-decene/MAH molar ratio of 0.3 was used because the system with this ratio exhibited the highest improvement of grafting efficiency for PP.¹³ Chemical titration, differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) spectroscopy were used to characterize the influence on the grafting behavior.

EXPERIMENTAL

Materials

The sample of PP was commercially obtained from Maoming Petrochemical Co. (Maoming, China). It had a density of 0.91 g/cm³ and a melt flow rate of 3.0 g/10 min (ASTM D 1238). Dicumyl peroxide (DCP) and benzoyl peroxide (BPO) were obtained from Shanghai Dongyi Chemical Agent Co. (Shanghai,

China), which were dried at room temperature under 0.02 MPa. The MAH monomer we used was commercially available (analytical grade). 1-Decene was obtained from Leqing Zhongyi Petrochemical Co. (Leqing, China). Xylene, acetone, propenyl alcohol, deuterioacetone, tetrahydrofuran (THF) and *p*-hydroxyanisole were all reagent grade and were used without further purification.

Preparation of the MAH/1-decene copolymer and the Alder ene reaction product

During the polymerization of the MAH/1-decene copolymer, MAH was first dissolved in xylene, and then, 1-decene was added to the solution. The molar ratio of 1-decene to MAH was 0.3. The mixture was decanted into a three-necked flask, and BPO was added. The concentration of the initiators was varied to produce samples with different molar masses. The flask was evacuated by nitrogen for 15 min before the nitrogen flow was reduced and the system was heated to 120°C. The reaction was run for 5 h, after which the solution was added dropwise to cold propenyl alcohol. The sample was collected and reprecipitated from THF into cold propenyl alcohol and dried *in vacuo* at 60°C for 24 h. The reactive products with different contents of BPO were free-flowing, pale yellow powders and were denoted as samples A, B, and C. Table I lists the detailed chemical conditions for samples A, B, and C.

The Alder ene reaction in the presence of *p*-hydroxyanisole, which was used as an additive, was prepared. The molar ratio of 1-decene to MAH was set 0.3. The mixture of MAH, 1-decene, and *p*-hydroxyanisole was decanted into a three-necked flask. The reaction temperature was 180°C, and the reaction time was 16 h. The reactive product was a brownish yellow liquid and was denoted as sample D.

Melt grafting of the synthesized product onto PP

A Haake Rheomix 600 mixer (Thermo Electron Corp., Karlsruhe, Germany) was used to prepare the graft-modified PP. Determined amounts of PP, synthesized product, and DCP were premixed by hand in a small container before they were charged into

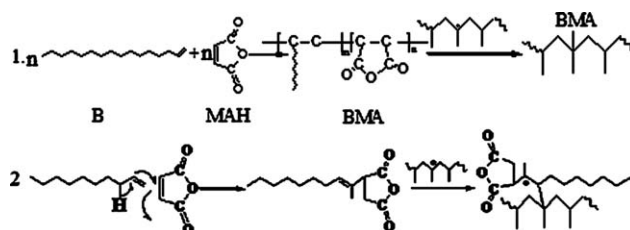


Figure 2 Possible mechanisms of MAH melt grafting under the existence of 1-decene. BMA is the copolymer of 1-decene (represented by B) and MAH.

TABLE I
Copolymerization and Alder Ene Reaction Conditions
between MAH and 1-Decene

Sample name	BPO/MAH molar ratio	1-Decene/MAH molar ratio	Xylene/MAH volume ratio	Reaction temperature (°C)	Reaction time (h)
A	0.005	0.3	1	120	5
B	0.01	0.3	1	120	5
C	0.03	0.3	1	120	5
D	—	0.3	—	180	16

the mixing chamber. The mixing temperature, time, and rotor speed were held constant at 190°C, 3 min, and 90 rpm for all runs. The reaction product was removed from the mixing chamber and added to liquid nitrogen to stop any further reaction.

Purification of the melt-grafted PP

The grafted PP was xylene soluble and acetone insoluble, whereas the MAH/1-decene copolymer and Alder ene reaction product could dissolve in both xylene and acetone. On the basis of this, the separation of the graft copolymers and other components in the raw grafted samples was performed as follows: several grams of raw grafted PP samples were first packed into filter paper and were then boiled with refluxing xylene for 0.5 h in a round flask. The solution was precipitated in hot acetone, then filtered by a Buchner funnel, repeatedly washed with fresh acetone, and then dried in a vacuum oven at 60°C to a constant weight. Thus, samples were obtained for determining the grafting degree.

Characterization of the MAH/1-decene synthesized product and the grafted polymer

Molecular weight and chemical composition

We measured the intrinsic viscosity of the synthesized product by dissolving 5 g of product in 1 dL of acetone and measuring the viscosity at 30°C using an Ubbelohde viscometer (Shanghai Lunjie Instrument Company, Shanghai, China). The molecular weights of the synthesized copolymers (samples A, B, and C) were measured with GPC (Viscotek model 350, Houston, USA) with THF as a solvent. The chemical composition was tested with a Varian Znova ¹H-NMR spectrometer (Palo Alto, USA) operating at 400 MHz. The solid samples were dissolved in dimethyl sulfoxide (DMSO) at a concentration of 0.25 g/mL. The molecular weight and the purity of sample D were analyzed by a Hewlett-Packard 5973A mass spectrometer interfaced directly with a Hewlett-Packard 6890 gas chromatograph (Palo Alto, USA) equipped with a DB-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm). The operating conditions were as follows: the temperature was ramped

from 40 to 120°C at 20°C/min and then from 120 to 280°C at 40°C/min; finally, the temperature was held at 280°C for 7 min. Helium was used as the carrier gas.

Chemical titration

The grafting degree was defined as the weight percentage of MAH in the grafted PP polymers. It was determined by means of acid–alkali titration^{21,22} and carried out with the following procedures. About 1 g of purified sample was first dissolved in 100 mL of refluxing xylene for 0.5 h, in which a few drops of water were added to hydrolyze all of the anhydride functions. Then, the hot solution was titrated immediately with a 0.025 mol/L KOH/C₂H₅OH solution after the addition of four drops of 1% phenolphthalein in ethanol as an indicator. Titration was stopped when the coloration remained for 30 s. The equation to calculate the grafting degree was as follows:

$$\text{MAH}(\%) = \frac{(V_2 - V_1)C}{2m} \times 98.06 \times 10^{-3} \times 100\% \quad (1)$$

where V_2 and V_1 represent the volumes of the KOH/C₂H₅OH solution used for the titration of the blank and grafted samples (mL), respectively; C is molar concentration of the KOH/C₂H₅OH solution (mol/L); 98.06 is the molecular weight of MAH (g/mol); m is the weight of the grafted sample (g); and the number 2 indicates that one anhydride group could change into two carboxylic acid groups after the anhydride rings were opened. The data presented here are the average of at least three repeated analyses, and their relative mean deviation was less than 5%.

FTIR analysis

The purified graft samples and the MAH/1-decene synthesized product were pressed into 100-μm films by the compression of a 0.1–0.2 g sample between Teflon-covered aluminum sheets with 1 MPa of pressure at 190°C for 30 s. The hot-pressed film was submitted to infrared analysis in a PerkinElmer PE 1600 spectrophotometer (Massachusetts, USA) with a resolution of 4 cm⁻¹ and 64 scans per spectrum.

DSC analysis

The crystallization behaviors were investigated by with a Netzsch DSC 200 differential scanning calorimeter (Selb, Germany) at a heating/cooling rate of 10°C/min. All operations were carried out under a nitrogen environment. The melting temperature and crystallization temperature were determined as the peak maximum and minimum of the melting and crystalline peak, respectively. The sample weights were between 4 and 7 mg.

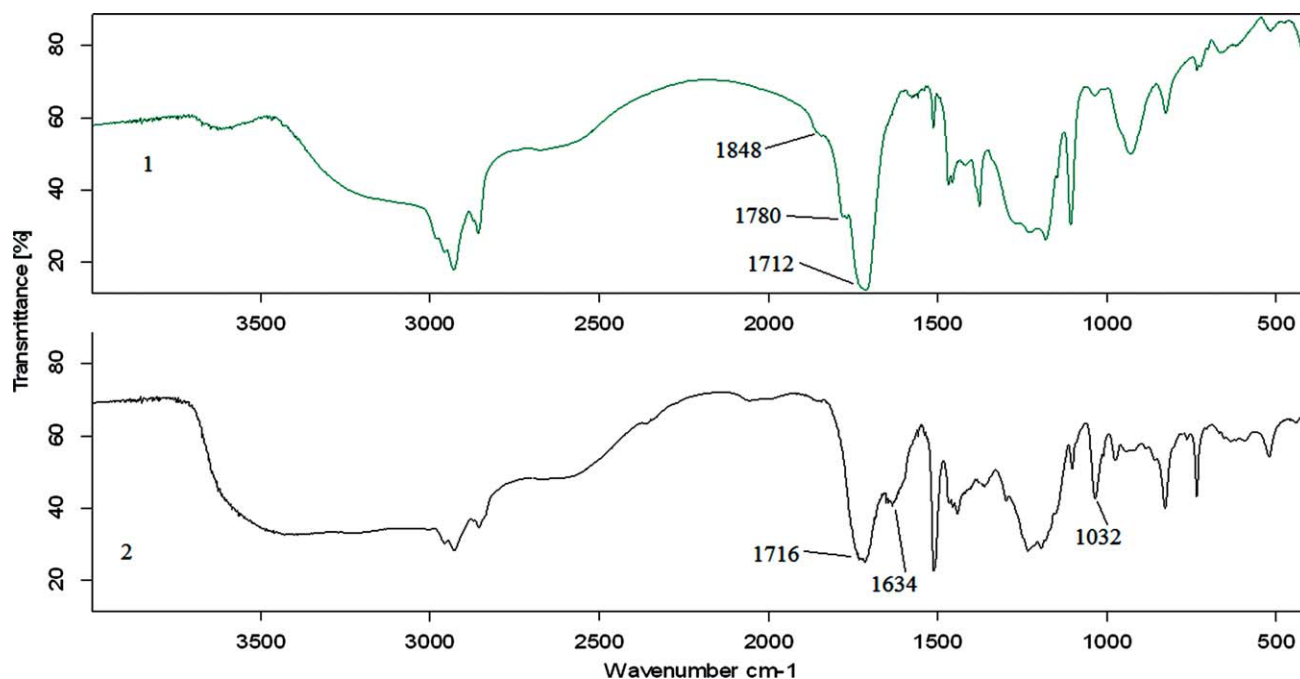
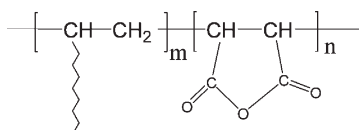


Figure 3 FTIR curves of the synthesized products: (1) copolymer of sample B and (2) Alder ene reaction product. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

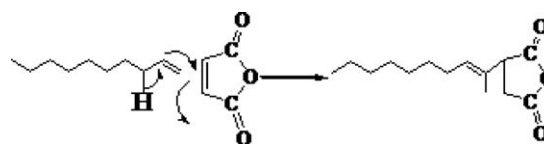
RESULTS AND DISCUSSION

Characterization of the synthesized product between MAH and 1-decene

In this study, to simulate the grafting process of MAH onto PP under the assistance of 1-decene, the MAH/1-decene copolymer and Alder ene reaction product were first synthesized and characterized. Figure 3 shows the FTIR curves of the synthesized products. For the copolymer, the following bands appeared: those for anhydride at 1712, 1780, and 1848 cm^{-1} ; the band of C—O at 1230 and 1067 cm^{-1} ; and the band of C—H at 1370 cm^{-1} . There was no peak around 1600 cm^{-1} ; this indicated the disappearance of C=C. The $^1\text{H-NMR}$ spectroscopy of the copolymer in Figure 4(a) shows the chemical shifts of C—H in MAH at 3.38 ppm, CH_3 in 1-decene at 0.83 ppm, and C—H and CH_2 in 1-decene around 1.22 ppm. The chemical shift at 2.50 ppm was attributed to DMSO because of the existence of part CH in its structure. Both FTIR and $^1\text{H-NMR}$ results proved the existence of MAH and 1-decene in the synthesized copolymer. The possible structure of the copolymer is proposed as follows:



The Alder ene reaction between 1-decene and MAH can be represented by the following equation:



Its FTIR curve is also included in Figure 3. The major difference between the Alder ene reactive product and the copolymer was the appearance of the band at 1634 cm^{-1} , which was the special band of C=C. Figure 4(b) shows its $^1\text{H-NMR}$ curve. In addition to the chemical shifts of C—H and CH_2 in MAH around 3.7 ppm, CH_3 in 1-decene at 0.82 ppm, and CH and CH_2 in 1-decene around 1.22 ppm, the chemical shift of C=C around 6.27 ppm appeared; this proved the existence of C=C in its molecular structure. Figure 5 gives its gas chromatography (GC)/mass spectrometry (MS) results. In the GC curve, we observed that a significant peak appeared at a time of 13.22 min and, around it, there were three small peaks; this indicated that the Alder ene reaction product was of high purity. Figure 5(b) gives the MS curve corresponding to the peak at 13.22 min. The maximum mass-to-charge ratio was 238. Compared with the upper chemical structure, we found that 238 was just the molecular weight of the Alder ene reaction product. All of the results supported the previously presented chemical structure.

To characterize the molecular weight of the synthesized product, the intrinsic viscosity was tested, and the results are shown in Figure 6. The intrinsic

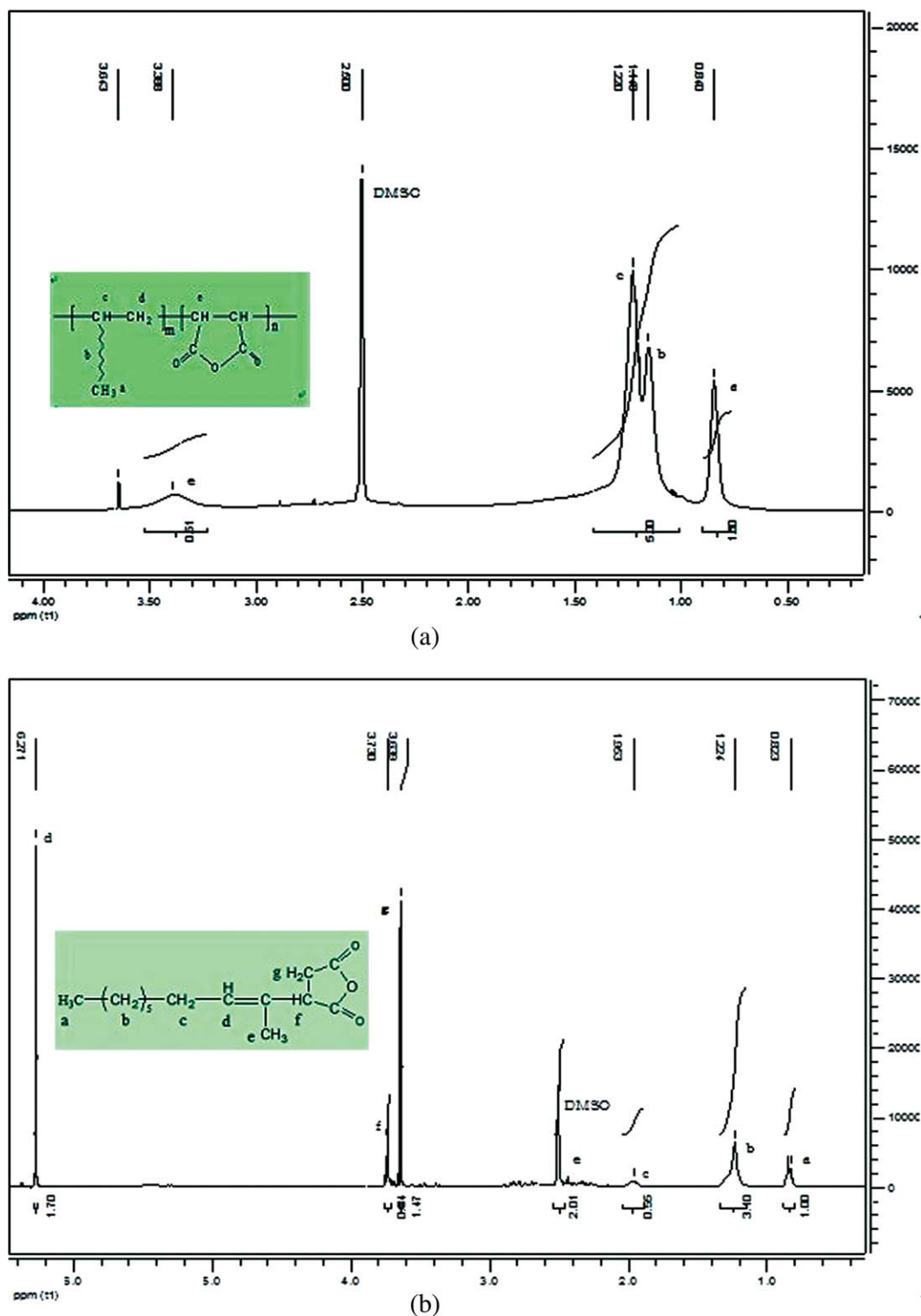


Figure 4 $^1\text{H-NMR}$ curves of the synthesized product: (a) MAH/1-decene copolymer of sample B and (b) Alder ene reaction product. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

viscosities of the synthesized copolymer were higher than that of the Alder ene product. Sample D exhibited oil characterization and showed the lowest intrinsic viscosity; this was in agreement with the previous GC/MS results.

Analysis of the melt-grafted PP

The FTIR spectra of the grafted PP samples with a synthesized product addition content of 3% are illustrated in Figure 7. For samples A, B, and D, we

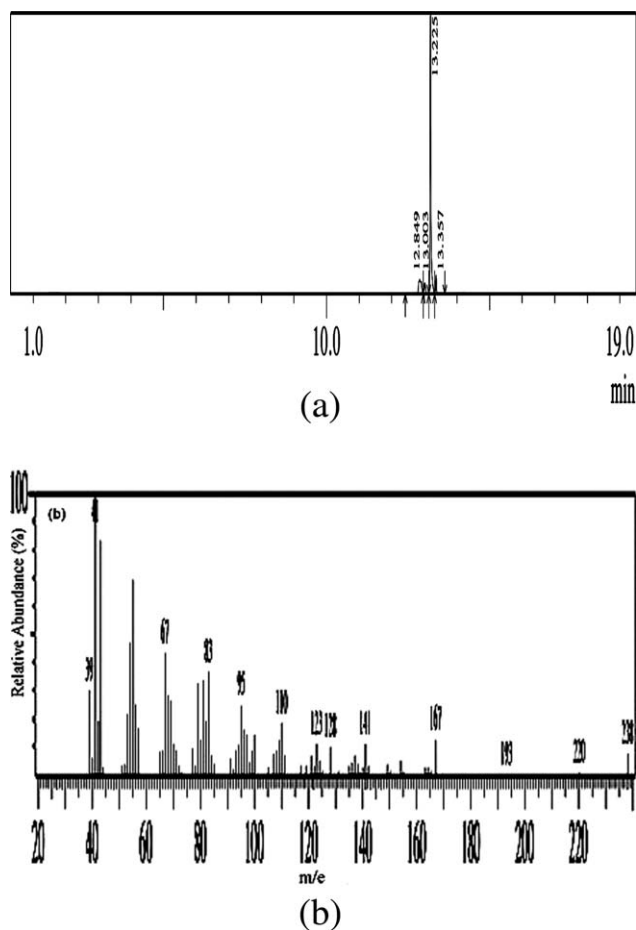


Figure 5 GC/MS results of the Alder ene reaction product: (a) GC and (b) MS curves. m/e is the mass-to-charge ratio.

observed around the band at 1710 cm^{-1} , a small and wide peak, which was assigned to the absorption of the carbonyl groups ($\text{C}=\text{O}$) of cyclic anhydride. We confirmed that the MAH/1-decene copolymer and the Alder ene reaction product were successfully grafted onto the PP backbone. The peak heights at 1710 cm^{-1} of samples B and D were higher than that of sample A; this means that the grafting degrees of samples B and D were higher than that of sample A.

Table II gives the grafting degrees with different contents of samples A, B, C, and D obtained under a DCP content of 0.3%. In our previous study,¹³ for a pure MAH-g-PP system, the maximum grafting degree under a DCP content of 0.3% was 0.68% and, at a 1-decene/MAH blend ratio of 0.3, a maximum value of the grafting degree of 1.43% was obtained. As shown in Table II, with the same content of synthesized product, the grafting degree of melt-grafted PP increased from sample A to D. For sample B, C, and D, the grafting degree was higher than that of the pure MAH grafted system, and particularly at the content of 3% for sample D, a value of the grafting degree of 1.89% was obtained. This was 178% higher than that of the pure MAH grafted system

and 93% higher than that of the system with St as the second monomer, the maximum value of which was 0.98% under an St/MAH molar ratio of 1.0.¹³ Except for sample A, both the grafting of the copolymer and Alder ene reactive product improved the MAH grafting efficiency, of which the influence of the Alder ene reaction product was more pronounced. This gives us a new method for improving the grafting efficiency of MAH onto PP. For sample A, the grafting degree was lower than that of the pure MAH grafted system, and it did not induce improvement of the grafting efficiency. Figure 6 shows that the intrinsic viscosity of sample A was higher than those of samples B and C. Copolymer A, with a higher intrinsic viscosity, led to a bigger obstacle for the copolymer approaching P^* , as shown in Figure 1; this resulted in a lower grafting efficiency.

Figure 8 gives the DSC curves of PP grafted with samples B, C, and D. Apparently, the melting peak temperature, the endothermic melting area, and the crystallization temperature for sample D were higher than those of samples B and C. Compared with samples B and C, sample D showed a lower intrinsic viscosity, and the grafted chain on PP was shorter. The movement ability of the molecular chain and the crystallization ability were higher. The direct results were a higher melting temperature and a higher crystallization degree.

Grafting mechanism of MAH-g-PP with 1-decene as the second monomer

Li and coworkers^{6,7} and Zhang and coworkers^{8,9} reported that the addition of St reacted with MAH to form an St-MAH copolymer or St formed a charge-transfer complex with MAH, and the formed product was grafted onto PP, which resulted in a higher grafting degree. Davis and coworkers^{14–20} proved that α -olefin could copolymerize with MAH

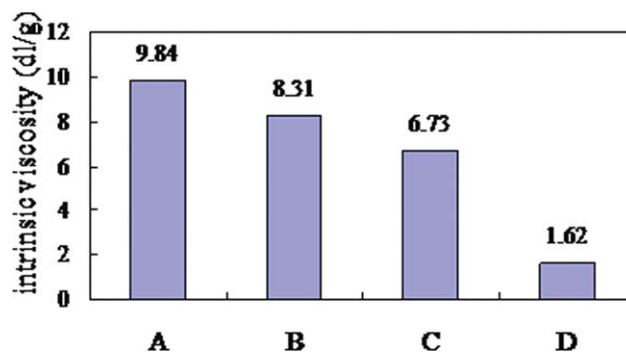


Figure 6 Intrinsic viscosities of the MAH/1-decene copolymer and Alder ene reaction product. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

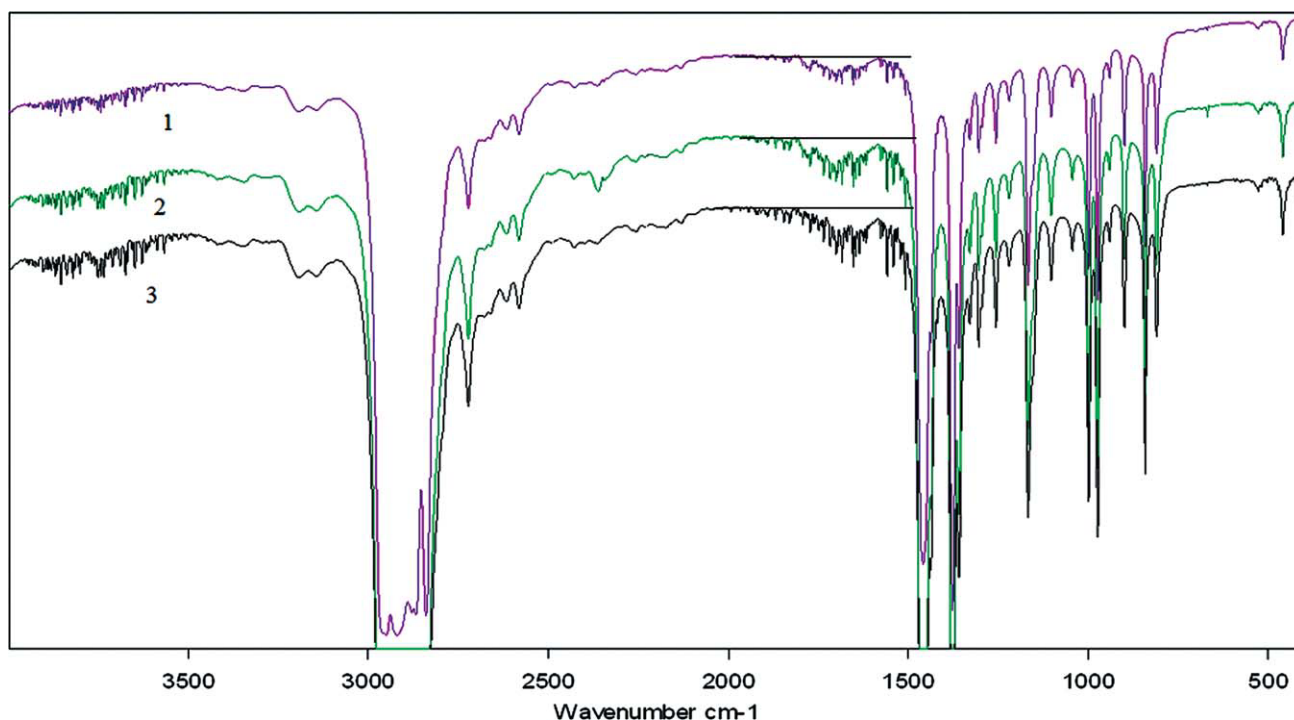


Figure 7 FTIR curves of the melt-grafted PP with a synthesized product addition content of 3%: samples (1) A, (2) B, and (3) D. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to form an α -olefin/MAH copolymer or had reactivity with MAH through the Alder ene reaction. In this study, an MAH/1-decene copolymer and Alder ene product were synthesized and grafted onto PP. As shown in Table II, for samples B, C, and D, the grafting degrees were higher than that of pure MAH-g-PP, as reported in our previous article.¹³ For the melt grafting of MAH onto PP under the assistance of 1-decene, some MAH was directly grafted onto PP, and the remaining MAH was involved in the copolymerization and Alder ene reaction. The formed product was then grafted onto PP; this led to a higher grafting degree because the 1-decene part (with a solubility parameter of $7.0 \text{ cal}^{0.5} \text{ cm}^{-1.5}$,²³) in the chemical structure of the MAH/1-decene copolymer and Alder ene reaction product showed a higher affinity to PP (with a solubility parameter of $7.4 \text{ cal}^{0.5} \text{ cm}^{-1.5}$) than pure MAH (with a solubility parameter of $17.8 \text{ cal}^{0.5} \text{ cm}^{-1.5}$,²⁴). From the previously discussed chemical

titration and FTIR results, we observed that both the copolymer and the Alder ene reaction product were beneficial for the improvement of the grafting degree and proved the mechanism suggested in Figure 2. Compared with that of the MAH/1-decene copolymer, the effect of the Alder ene reaction product on the grafting degree was more pronounced.

From the results shown in Figure 6 and Table II, we found that when the intrinsic viscosity of the synthesized product was higher than 8.3, the grafting

TABLE II
Grafting Degrees of PP with Different Contents of Samples A, B, C, and D

Sample	Content (%)		
	1	2	3
A	0.24	0.33	0.62
B	1.20	1.41	1.61
C	1.25	1.58	1.70
D	1.32	1.56	1.89

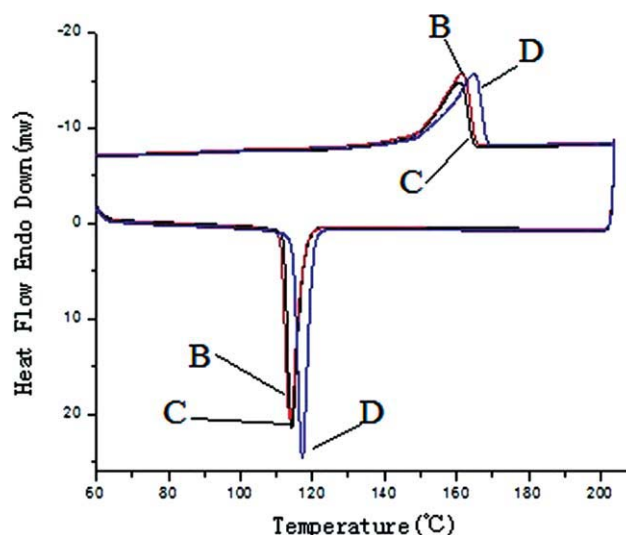
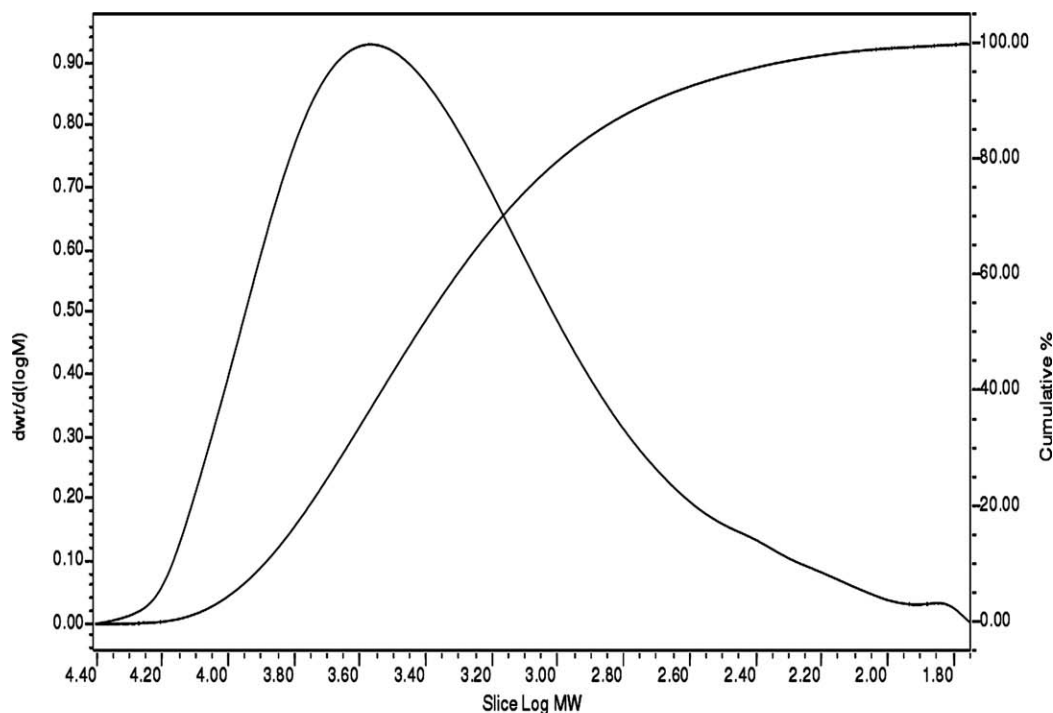
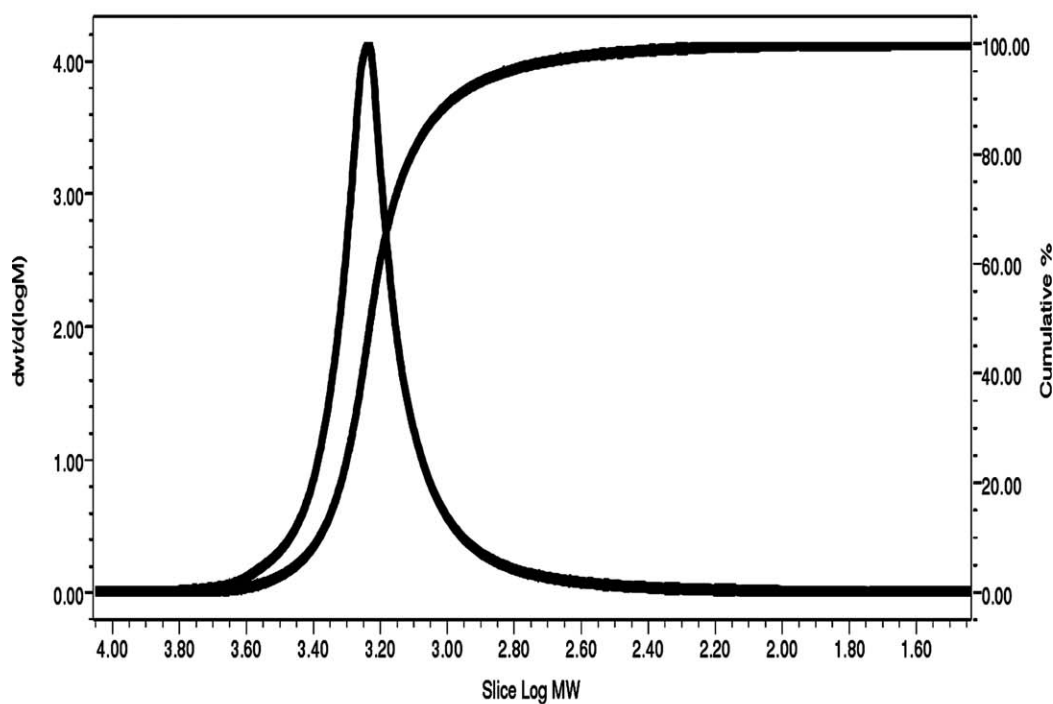


Figure 8 DSC curves of grafted PP at a heating/cooling rate of $10^\circ\text{C}/\text{min}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(a)



(b)

Figure 9 GPC curves of samples (a) A and (b) B. MW: molecular weight; $dwt/d(\log M)$: differential weight distribution.

efficiency was very low, even lower than that of the pure MAH grafted system. Figure 9 gives the GPC results of samples A and B. The corresponding weight-average molecular weights were 3.6 and 1.7 kg/mol, respectively. Then, we deduced that when the molecular weight of the synthesized copol-

mer was higher than 1.7 kg/mol, there was no improvement in the grafting efficiency. For MAH-g-PP with 1-decene as the second monomer, because of the higher molecular weight of the formed MAH/1-decene copolymer, this made the approach of the copolymer to PP difficult and resulted in a

worse grafting degree. Therefore, there was an upper limit for the molecular weight of the MAH/1-decene copolymer for improving the grafting degree.

CONCLUSIONS

In this study, an MAH/1-decene copolymer and Alder ene reaction product were synthesized to simulate the melt-grafting process of MAH onto PP with 1-decene as the second monomer. Chemical titration, DSC, and FTIR were used to investigate the grafting behavior. The results show that when the molecular weight of the copolymer was higher than 1.7 kg/mol, there was no improvement in the grafting efficiency. With decreasing molecular weight, the grafting degree increased, especially for the Alder ene reaction product. A maximum grafting degree of 1.89% was obtained, which was 178% higher than that of the pure MAH grafted system. For MAH grafted onto the PP system with 1-decene as the second monomer, the formed MAH/1-decene copolymer and Alder ene product were grafted onto PP, and this resulted in a higher grafting degree.

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