

# Synthesis of Multifunctional Polypropylene via Solid Phase Cografting and Its Grafting Mechanism

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Received 11 December 2000; accepted 24 May 2001

**ABSTRACT:** Functional monomers, maleic anhydride (MAH) and vinyl acetate (VAc), were used as comonomers in the solid-phase grafting of polypropylene (PP). Quantitative determination of the graft level of both MAH and VAc performed by titration and FTIR methods allowed for a good appreciation of the interaction of MAH and VAc. A product with high-graft level of both VAc and MAH was obtained when the feeding molar ratio of MAH/VAc approached 1 : 1. The melt flow rate (MFR) of the grafted PP decreased with the increase in the feeding amount of VAc. It was proposed that MAH and VAc molecules could form a kind of stable transition state during the graft polymerization and that the reactivity of both monomers were enhanced. The resulting multifunctional PP offers possibility for the development of novel PP-based polymer blends and composites, thus extending the application field of PP. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 929–935, 2002; DOI 10.1002/app.10121

**Key words:** polypropylene; solid-phase grafting; comonomers; maleic anhydride; vinyl acetate

## INTRODUCTION

Synthesis of functional polypropylene (PP) is a very active field in recent years because it can improve the polar deficiency of pure PP molecules and provide compatibility with a large number of polar polymers in polymer blends and composites, extending the application field of PP.<sup>1–8</sup>

Solid-phase grafting method is a promising method to synthesize functional PP. A few articles have been published, involving the solid-phase grafting of single-functional monomer, such as maleic anhydride (MAH), onto PP.<sup>9–10</sup> However, there are two main disadvantages when single MAH monomer was used: first, the MAH

graft level is limited because of the structural confinement of MAH molecule; second, the melt flow rate (MFR) of the grafted PP is very high, which means that PP molecules suffer severe degradation in the grafting process.

In this study, vinyl acetate (VAc) was used as a comonomer in the process of solid-phase grafting MAH onto PP for the goal of obtaining a multifunctional PP with a high-graft level and a proper MFR. The effect of different MAH/VAc feeding ratios on the graft level of both the monomers and the MFR of the products was studied. The grafting mechanism was also discussed.

## EXPERIMENTAL

### Materials

PP powder (trademark, PPH223; MFR = 4.6 g/10 min) was provided by Jinzhou Petroleum Chemi-

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*Journal of Applied Polymer Science*, Vol. 84, 929–935 (2002)  
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cal Group of China. Maleic anhydride and vinyl acetate, both analytically pure reagent, were purchased from Beijing Chemical Reagent Co. Benzoyl peroxide (BPO), industrial product, was recrystallized before use.

### Grafting Process

The solid-phase grafting process was performed in a 500-mL three-necked flask equipped with an agitator, operating at 60 rpm. Five grams of MAH dissolved in 5 g xylene were added to the flask containing 50 g PP powder and a certain amount of VAc. It was heated to 110°C under nitrogen. BPO was added to the flask at 16-min intervals. The reaction was terminated after 32 min of the last batch of BPO. The reaction products were extracted with acetone to remove the unreacted monomers and oligomers. The purified products were dried at 80°C for 1 h.

### Determination of Graft Level

#### Titration

The acid value of the grafted PP was determined by titration. Two grams of dried grafted PP and 80 mL xylene were added to a 250-mL three-necked flask. It was refluxed for 20 min to dissolve the grafted PP completely. The system was then cooled down and excessive 0.1 mol L<sup>-1</sup> KOH-ethanol standard solution was added. It was then refluxed further for 6 h to make all MAH neutralized and all VAc saponified. The system was back titrated by 0.1 mol L<sup>-1</sup> acetic acid-xylene standard solution after cooling down. Phenolphthalein was used as the titration indicator. A blank titration was carried out by using the same method. The acid value (AV; mmol KOH g<sup>-1</sup>) of the product could be calculated.

#### FTIR Spectroscopy

For FTIR analysis, samples were compression-molded into thin films between aluminum sheets on a laboratory hot press at 200°C under 10 MPa. FTIR spectra were determined on a Nicolet 560 FTIR spectrometer. Being the characteristic peaks of anhydride and internal standard peak of PP, the absorption peaks at 1860 and 810 cm<sup>-1</sup> were used to determine the MAH content in the grafted PP. An IR working curve, obtained by using the PP-g-MAH samples with known MAH content, was used to determine the definitive MAH content in the grafted PP sample.

The definitive VAc content in the grafted PP sample could be calculated from the AV and MAH content. The graft level of MAH and VAc ( $G_{\text{MAH}}$  and  $G_{\text{VAc}}$ ) mentioned in this article was defined as the weight percentage of grafted MAH or VAc to PP.

### MFR of Grafted PP (PP-g-MAH/VAc)

The MFR of the grafted PP was determined under the standard test conditions of 230°C, 2.16 kg.

## RESULTS AND DISCUSSION

### FTIR Characterization

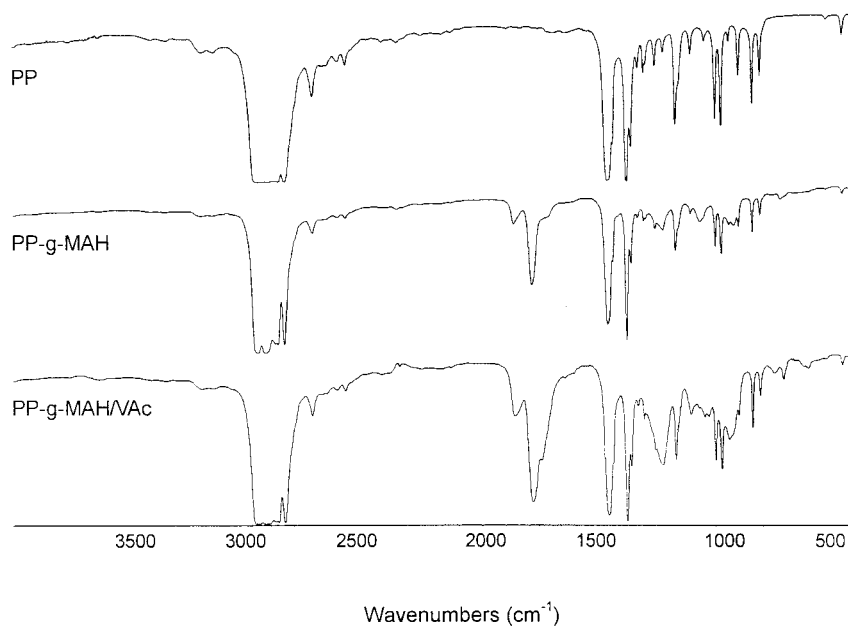
The FTIR spectrum of PP-g-MAH/VAc showed two peaks at 1860 and 1780 cm<sup>-1</sup>, which are the characteristic peaks of the carbonyl group in MAH. In addition, as illustrated in Figure 2, a shoulder peak appears at 1720–1745 cm<sup>-1</sup> in the zoomed absorbance spectrum of PP-g-MAH/VAc. This shoulder peak is the stretching vibration peak of the ester carbonyl group in VAc, which overlaps with the peak of the carbonyl group of anhydride. Therefore, it is confirmed that both MAH and VAc were grafted onto the PP backbone.

### MAH and VAc Graft Level

As mentioned above, the isolated peak of anhydride near 1860 cm<sup>-1</sup> can be used to characterize the graft level of MAH in PP-g-MAH/VAc. Several PP-g-MAH samples with known MAH content, prepared in our laboratory, were analyzed by FTIR. The absorbance peak height ratio of 1860 to 810 cm<sup>-1</sup> and the MAH content were fitted by linear fitting method. The expression of the fitted equation is

$$Y = 0.88075 + 1.93747X$$

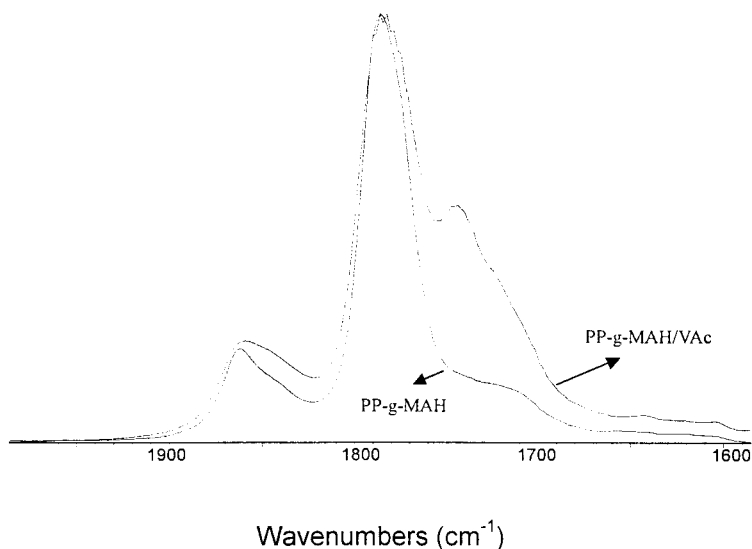
where  $Y$  is the MAH content;  $X$  is the peak height ratio; and the correlation coefficient,  $R$ , is 0.9976. Thus, the MAH content in PP-g-MAH/VAc can be obtained from the above expression and the VAc content can be calculated from the acid value after subtracting the contribution of MAH. The acid value and the graft level of MAH and VAc in different grafted samples are given in Table I. The feeding amounts of MAH and BPO were both fixed to 10 wt % of PP in the grafting process.



**Figure 1** FTIR spectra of PP, PP-g-MAH, and PP-g-MAH/VAc.

The results in Table I show that the graft level of MAH and VAc both initially increase with the increase in VAc feeding amount up to 10%. When the VAc feeding amount exceeds 10%, the graft level of MAH begins to decrease, but that of VAc still remains increasing. The MAH graft level increases remarkably and reaches the maximum value at the VAc feeding amount of 8 and 10%. It is known that the MAH molecule almost cannot

homopolymerize because of its steric hindrance resulted from 1,2-substitution and its electron acceptor property. Therefore, the MAH graft level is limited when used to graft onto PP alone. In our laboratory, the MAH graft level can only reach 1% in the melt extrusion grafting process and about 4% in the normal solid-phase grafting process at the same MAH and initiator feeding amount. However, as shown in Table I, the graft level of



**Figure 2** Absorbance peaks of PP-g-MAH/VAc and PP-g-MAH at 1600–2000  $\text{cm}^{-1}$ .

**Table I** MAH and VAc Graft Level in Different PP-g-MAH/VAc Samples

$W_{\text{VAc}} \times 100$	Acid Value (mmol KOH g <sup>-1</sup> )	$H_{1860\text{cm}^{-1}}^{-1}/H_{810\text{cm}^{-1}}^{-1}$	$G_{\text{MAH}} \times 100$	$G_{\text{VAc}} \times 100$
0	0.7770	1.62	3.96	0
2	0.8183	1.34	3.48	1.32
4	0.9408	1.36	3.52	2.48
6	1.0664	1.47	3.73	3.37
8	1.3160	2.02	4.79	3.91
10	1.6428	2.29	5.32	6.39
12	1.6408	1.56	3.91	9.36
10 <sup>a</sup>	0.3752	0	0	3.34

$W_{\text{VAc}}$ , VAc feeding amount.

<sup>a</sup> Without MAH.

MAH and VAc could reach 5.32 and 6.39%, respectively, when MAH and VAc were used together in the process of solid-phase grafting.

#### MFR of PP-g-MAH/VAc

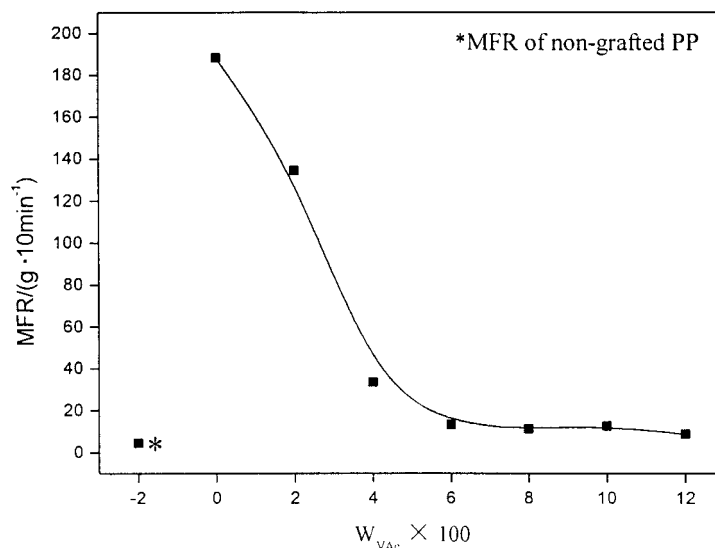
The effect of the VAc feeding amount on the MFR of grafted PP is shown in Figure 3.

It is evident that the MFR value decreases dramatically in the beginning with the increase in VAc feeding amount and levels off as the VAc feeding amount exceeds 6%. If no VAc was introduced into the solid-phase grafting process, the MFR of the product was very high (188 g/10 min<sup>-1</sup>) compared with that of original PP (5 g/10 min<sup>-1</sup>). This indicates that PP underwent serious degradation in the MAH grafting process. Thus,

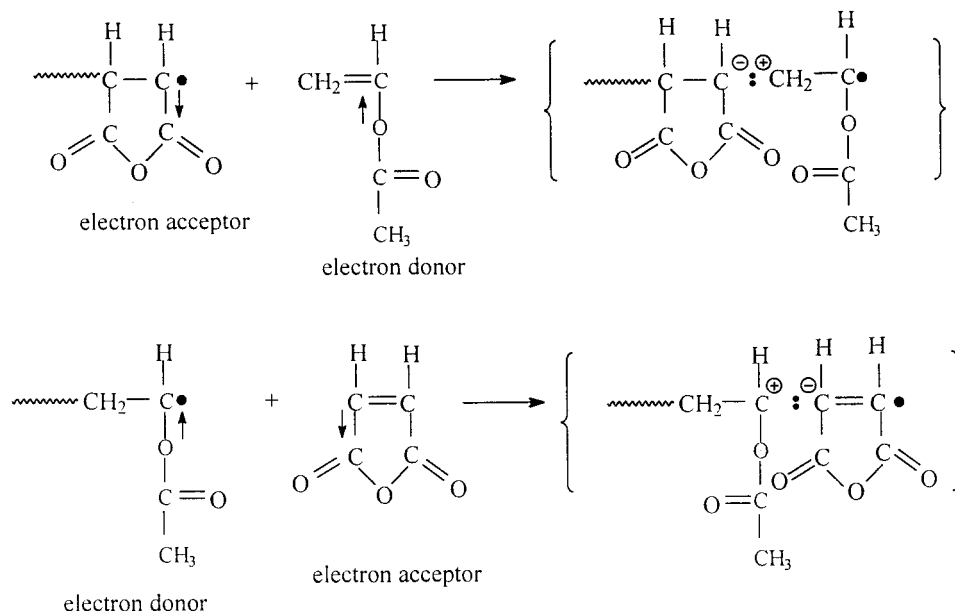
we can conclude that VAc can efficiently prohibit the degradation of PP when added to the solid-phase grafting of MAH onto PP.

#### Mechanism of MAH/VAc Cografting Process

The MAH molecule is a 1,2-substituted five-member ring, so its steric hindrance has a prominent effect on its reactivity. After one MAH molecule has grafted onto the PP backbone, the formed macromolecular free radical almost cannot continue to react with another MAH molecule. Further, MAH grafting needs a new PP free radical, which is initiated by initiator or chain transfer. Therefore, the graft level of MAH was usually very low and a large amount of initiator was needed.



**Figure 3** Plot of MFR of PP-g-MAH/VAc as a function of VAc feeding amount.



**Figure 4** Schematic mechanism of the transition state of MAH/VAc formed in the process of the graft polymerization.

The steric hindrance of VAc is small and can easily react with the macromolecular radical and continue grafting with MAH. Furthermore, it is known that the effect of polar factor is very important in copolymerization.<sup>11</sup> A transition state is first formed when propagating free radicals attack the monomer in the addition reaction. When monomer with a double bond polarized by electron donor group (or electron acceptor group) reacts with the free radical polarized by electron acceptor group (or electron donor group), the formed transition state is more stable. The addition reaction is easy to propagate in this state.

The ester group in the VAc molecule is an electron donor group, and the anhydride group in MAH is an electron acceptor group. Either VAc free radical and MAH monomer or MAH free radical and VAc monomer can form a stable transition state. Consequently, the grafting activity of both monomers increase in the solid-phase grafting process and high-graft level of both monomers are achieved. Figure 4 illustrates the possible transition state of MAH/VAc in the process of the graft copolymerization. It is obvious that the transition state of MAH/VAc is easy to form as the feeding mole ratio of MAH/VAc approaches 1 : 1. The

**Table II** Feeding Ratio of MAH/VAc, Mole Ratio of Grafted MAH/VAc

Feeding Mass Ratio (MAH/VAc)	Feeding Molar Ratio (MAH/VAc)	Grafted MAH <sup>a</sup> (g)	Grafted MAH <sup>a</sup> (mole)	Grafted VAc <sup>a</sup> (g)	Grafted VAc <sup>a</sup> (mol)	Molar Ratio of Grafted MAH/VAc
10/0	—	3.96	0.040	—	—	—
10/2	4.39	3.48	0.035	1.32	0.015	2.33
10/4	2.19	3.52	0.036	2.48	0.029	1.24
10/6	1.46	3.73	0.038	3.37	0.039	0.97
10/8	1.10	4.79	0.049	3.91	0.045	1.09
10/10	0.88	5.32	0.054	6.39	0.074	0.73
10/12	0.73	3.91	0.040	9.36	0.109	0.37
0/10	—	—	—	3.34	0.039	—

<sup>a</sup> Monomer grafted onto 100 g PP.

**Table III** IR Wavenumbers of Ester Carbonyl Group in Different Grafted PP Samples

Feeding Mass Ratio (MAH/VAc)	Feeding Molar Ratio (MAH/VAc)	Wavenumber of Ester Carbonyl Group (cm <sup>-1</sup> )
10/2	4.39	1720
10/4	2.19	1724
10/6	1.46	1724
10/8	1.10	1745
10/10	0.88	1745
10/12	0.73	1726

graft level of both monomers will be higher under this condition.

The feeding ratio of MAH/VAc and the corresponding molar ratio of grafted MAH/VAc are shown in Table II. The data in Table II show that the graft level of both monomers without the addition of the other one is quite similar, almost 0.04 mol in 100 g of PP. When the feeding molar ratio of MAH/VAc is 2 : 1, the molar ratio of grafted monomers is around 1. This is probably an indication of the transition state formation. When VAc is in a higher proportion, it grafts more than MAH. Therefore, the graft chain of VAc homopolymer may be formed.

In addition, it can be seen from Table III that the IR peak of the carbonyl group in VAc shifts to a higher wave number and approaches the maximum (1745 cm<sup>-1</sup>) when the feeding molar ratio of MAH/VAc approaches 1. This fact may due to the strong electron acceptor group near the ester carbonyl group. The only probability is the action of the adjacent anhydride group. It is clear that the grafted units of MAH and VAc tend to alternate in graft chain under this condition and the mechanism we have proposed can also be proven.

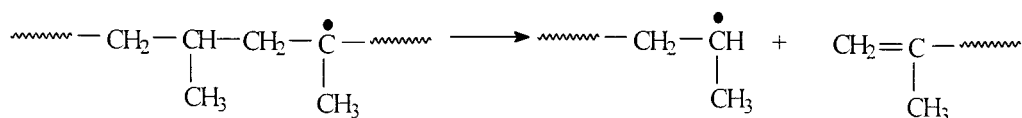
In the process of MAH grafting,  $\beta$ -scissions of PP tertiary carbon free radicals tend to take place, which lead to the degradation of PP. Mean-

while, MAH free radicals formed in the grafting process are difficult to react with another MAH monomer, so the probability of transfer reaction to PP macromolecules increases. Consequently, more  $\beta$ -scission reactions take place. The MFR of MAH-grafted PP thus becomes very high, as indicated in Figure 3. The schematic mechanism of  $\beta$ -scission of PP radical is demonstrated in Figure 5.

When VAc is added, either MAH free radical or VAc free radical on the PP macromolecule can quickly react with the other monomer. The probability of transfer reaction to PP is cut down when compared with single MAH grafting. Thus, it is reasonable to point out that fewer PP macromolecular free radicals are produced and the chance of  $\beta$ -scission diminishes, which results in lower MFR.

## CONCLUSIONS

MAH and VAc can be cograftered onto PP via solid-phase grafting. The graft level of both MAH and VAc gradually increases with the increase in the feeding amount of VAc within the range of 0 to 10%. Further increase in the feeding amount of VAc results in the decrease of the graft level of MAH, but that of VAc still remains increasing. At 8 and 10% feeding amount of VAc, the graft level of MAH increases remarkably and reaches the maximum value. The maximum graft level of MAH reaches 5.3% and that of VAc can reach 6.5% simultaneously. The MFR of grafted PP decreases dramatically in the beginning with the increase in the feeding amount of VAc and reaches a plateau as it exceeds 6%. The grafting mechanism is proposed that MAH and VAc can form a stable transition state in the solid-phase grafting process. High-graft level of both MAH and VAc are obtained as the feeding molar ratio of MAH/VAc approaches 1 : 1. MAH/VAc monomers tend to alternate copolymerization under this condition.

**Figure 5** Schematic mechanism of the  $\beta$ -scission of PP radical.

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