

# Modification of Polypropylene via the Free-Radical Grafting Ternary Monomer in Water Suspension Systems

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**ABSTRACT:** Maleic anhydride, styrene, and butyl acrylate were grafted onto polypropylene (PP) via free-radical polymerization. The grafted product, polypropylene-*g*-(maleic anhydride-styrene-butyl acrylate) (PP-*g*-PMSB), was prepared in a water suspension system, and a non-grafted polymer, poly(maleic anhydride-styrene-butyl acrylate) (PMSB'), was produced at the same time. The optimal synthesis conditions were determined by orthogonal experiments. The crystallinity, thermal stability, melt flow rate, and hydrophilicity of the grafting samples were investigated in the presence or absence of PMSB'. The results indicate that the grafting percentage ( $G_p$ ) of PP-*g*-PMSB and the content of PMSB' ( $C_m$ ) increased as the monomer content increased under the optimum reaction conditions. All of these ternary monomers were grafted

onto the PP backbone as long-chain branches. With increasing  $G_p$ , PP-*g*-PMSB's polarity and thermal stability increased, the crystallinity decreased, and the molecular distribution became narrower. The contact angle decreased to 72.12° when  $G_p$  was 6.87%. With increasing  $C_m$ , the crystallinity and thermal stability of the grafting products decreased compared to PP-*g*-PMSB and the molecular distribution grew wider. The contact angle decreased to 63.51° when  $C_m$  was 3.64%; this indicated that the presence of PMSB' further improved the hydrophilicity of the grafted products. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** branched; graft copolymers; polyolefins; thermal properties

## INTRODUCTION

As one of the most important general-purpose resins, polypropylene (PP) has lots of advantages: low cost, excellent performance, and wide usage in various fields. However, PP is restricted in its applications because of its nonpolarity and poor compatibility with other polymers.<sup>1</sup> Graft modification offers an effective approach for improving the polarity of PP. The grafting of polar monomers onto the PP backbone has been an important practice, which has given PP the performance that is needed.

Maleic anhydride (MAH) is one of the most commonly used monomers for grafting onto the PP matrix.<sup>2</sup> MAH has many unique properties, including a low cost and high polarity. It also has a lone pair of electrons on the oxygen of its molecule, which makes it easy to blend or bond with other materials because of the empty orbital. Also, MAH can be transformed into a living polymer with carboxyl groups via hydrolysis. Then, a series of new functionalized polymers<sup>3,4</sup> can be formed via the reaction

between the carboxyl group and compounds that contain hydroxyl, amino, and epoxy groups. However, because of its low reactivity and structural confinement, the content of anhydride is very low in the grafting process and leads to a limited degree of polymerization. Furthermore, the toxicity of MAH also restricts its utility and adds many difficulties to the manipulative process.<sup>5</sup>

In recent years, people have come to realize that grafting a single monomer onto the PP matrix cannot satisfy its production requirements. Therefore, the use of a comonomer and a coagent has received increasing interest because these compounds can improve the grafting percentage ( $G_p$ ) and limit side reactions. Coiai et al.<sup>6</sup> used furan and thiophene derivatives to control the degradation of PP during its radical functionalization with MAH in the melt and found that 3-(2-furanyl) propenoate and 3-(2-thienyl) propenoate could form stable macroradicals with isotactic PP macroradicals to limit the decrease of the average molecular weight (MW). In the case of 3-(2-furanyl) propenoate, coupling reactions of the formed macroradicals could lead to a high formation of branched MW architectures. Li et al.<sup>7</sup> studied the free-radical melt grafting of the multi-monomer system of MAH/styrene (St) onto PP with a single-screw extruder. They showed that the maximum MAH grafting degree was obtained

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when the molar ratio of MAH to St was approximately 1 : 1. St, as added to the melt-grafting system as a comonomer, could react with MAH to form a St-MAH copolymer before the two monomers grafted onto PP and significantly enhanced the MAH grafting degree onto PP and limited or weakened the degradation of PP. We studied the free-radical water suspension grafting of a multimonomer system of MAH/St onto PP and found that with the increasing addition of St to the system, the MAH grafting degree increased. It was proven that when the mass ratio of MAH to St was approximately 1 : 3, the MAH grafting degree reached 3.10%.<sup>8</sup> Zhang et al.<sup>9</sup> studied the melt grafting of a multimonomer system of MAH/butyl acrylate (BA) onto PP and pointed out that in the cografting process, with the dosage of MAH at a constant amount (4 mass %), the grafting degree attained a maximum (1.34 mmol/g of PP) when the amount of BA was 3 mass %; that was double that with one monomer and higher than any value (0.36 mmol/g PP) ever reported.

The aqueous-phase suspension grafting method not only inherits the advantage of the solution grafting method, which has many unique properties, including a low reaction temperature, simple technology and equipment, low degradation degree of PP, and manageable reaction conditions, but also has the merit of an easy postprocess and little pollution. However, in the grafting reaction, the undesired ungrafted homopolymer<sup>10</sup> and copolymer usually affect the properties of the original PP. At present, the effects of the ungrafted polymers on the target production (grafted PP) have seldom been reported. In this study, the grafting ternary monomer system of a hard monomer, MAH/St, and a soft monomer, BA, onto PP was examined. The grafting reaction first used swelling in the solid phase. After that, the reaction was carried out in a boiling water suspension under mechanical mixing. The synthesis conditions were determined with orthogonal experiments. The effects of the monomer content on the grafting reaction were examined. Variations in the thermal stability, melt flow rate (MFR), and hydrophilicity of the product were examined in the presence and absence of non-grafted polymers.

## EXPERIMENTAL

### Materials

Porous polypropylene granules (T30S) were supplied by Daqing Petrochemical (Daqing, China). The benzoyl peroxide (BPO) initiator was purchased from Shanghai Shanpu Chemical Co. (Shanghai, China). St was purchased from Tianjin

Kuang-Fu Fine Chemical Industry Research Institute (Tianjin, China). BA was supplied by Tianjin Yongda Reagent Development Center (Tianjin, China). Anhydrous ethanol was supplied by Shanghai Nanxiang Chemical Reagent Co. (Shanghai, China). MAH, xylene, and acetone were purchased from Tianjin Damao Chemical Reagent Co. (Tianjin, China). BPO was used after it was recrystallized twice from methanol. St and BA were purged to remove hydroquinone inhibitor with an inhibitor remover disposable column (Aldrich Chemical Co., Milwaukee, Wisconsin) and distilled under reduced pressure before use. Pure BPO, St, and BA were stored at 0°C before use. MAH monomer (a chemically pure reagent), anhydrous methanol, xylene, and acetone were used as received.

### Grafting process

The aqueous-phase suspension grafting process was performed in a 500-mL, three-necked flask equipped with a twin-blade mechanical stirrer operated at 100 rpm, a condenser tube, and a thermometer. The reaction temperature was 100°C, and the temperature of the flask was maintained with an accuracy of  $\pm 1.0^\circ\text{C}$ . First, the grafting monomers, interface agent, and initiator were added to the flask. After the monomers and initiator dissolved to form a mixed solution, the porous PP was added. Then, the solution was agitated by swelling in an oil bath at 60°C for 90 min to ensure that the mixture was absorbed by the PP granules. Subsequently, 200 mL of distilled water was added to the system, and the temperature was raised to start the grafting reaction. The whole process accompanied the mechanical stirring. After the filtering and drying process when the reaction was over, the primary graft product was obtained.

### Poly(maleic anhydride-styrene-butyl acrylate) (PMSB') measurement

The primary graft product samples were immersed and washed by anhydrous ethanol several times to remove the interface agent, initiator, and unreacted monomers. Then, the washed sample was dried, and the dried sample was marked as PP-*c*-PMSB'. The content of PMSB' ( $C_m$ ) could be calculated as follows:

$$C_m = (m_1 - m_0)/m_0 \times 100\% - G_p$$

where  $m_0$  is the weight of the original PP,  $m_1$  is the weight of the grafted product washed by ethanol, and  $G_p$  is the grafting percentage of the polypropylene-*g*-(maleic anhydride-styrene-

butyl acrylate) (PP-g-PMSB) synthesized in the same experiment.

### $G_p$ and grafting efficiency ( $G_e$ )

The  $G_p$  and  $G_e$  measurement were done according to the literature.<sup>11</sup>

### Gel fraction determination, Fourier transform infrared (FTIR) spectral analysis, thermogravimetric-differential thermal (TG-DAT) analysis, MFR determination, and water contact angle measurement

The gel fraction determination, FTIR spectral analysis, TG-DAT analysis, MFR determination, and water contact angle measurement were done according to the literature.<sup>1</sup> The FTIR spectra were recorded on a TENSOR27 FTIR spectrometer (Bruker, Inc., Karlsruhe, Germany) from 4000 to 400  $\text{cm}^{-1}$  with a 0.5- $\text{cm}^{-1}$  resolution. TG-DAT analysis was carried out on a PerkinElmer RIS Diamond TG-DAT (PerkinElmer Inc., Waltham, Massachusetts).

### MFR, dwell ratio ( $D_r$ ), and melt strength ( $M_s$ ) measurements

MFR,  $D_r$ , and  $M_s$  were measured by a  $\mu$ PXRZ-400 melt indexer (Jilin University, Changchun, China). Measurement was performed at 230°C with a load of 2.16 kg.  $D_r$  and  $M_s$  were calculated according to the following equations:

$D_r$  was calculated as follows:

$$D_r = (D - D_0)/D_0$$

where  $D_0$  is the diameter of the orifice (2.095 mm) and  $D$  is the diameter of the extruded samples that were just extruded from the machine (mm).

$M_s$  was calculated as follows<sup>12</sup>:

$$M_s = 0.85\Delta L^2 r_0^2 / \text{MFR}$$

where  $\Delta L$  is the length of the cord required for a 50% decrease in the diameter of the cord (mm),  $r_0$  is the radius of the cord as it first emerged from the die (mm), and MFR is the melt flow rate (g/10 min).

### X-ray diffraction (XRD) analysis

The crystallinity of the graft copolymer was determined by X-ray diffraction (XRD) analysis with a D/MAX-2200 X-ray diffractometer (Rigaku Co., Tokyo, Japan) with Cu target radiation over the range  $2\theta = 10\text{--}80^\circ$ . The tube voltage was 40 kV, and the tube current was 30 mA. The samples were processed in 0.4 mm thick films by compression molding at 200°C for 1 min.

### Gel permeation chromatography (GPC) analysis

The average MWs, including the number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and viscosity-average molecular weight ( $M_v$ ), were measured at 135°C by a Waters 150CV GPC instrument (Waters Co., Milford, Massachusetts) with *o*-dichlorobenzene as the solvent. The machine, equipped with an online degasifier attached to a viscometer, detected the intrinsic viscosity of the samples, and a refractive-index detector detected the concentration of the samples (Chromatography Workstation 2010). The calibration was made with narrow MW distribution polystyrene standards, and calculations were carried out by Millennium software (Millennium Software, Inc., Deer Island, Oregon).

## RESULTS AND DISCUSSION

### Optimized reaction conditions

In Table I, A is the initiator content, B is the xylene dosage, C is the swelling time, D is the reaction time, and E is the grafting rate. In our work, we took the level of the grafting rate ( $G_p$ ) as the standard to measure the quality of the grafting reaction. The free-radical grafting reaction in the water suspension system was a heterogeneous system. First, xylene dissolved BPO, St, MAH, and BA and made them form a mixed solution; this solution was able to strongly swell PP. Therefore, xylene could be used as a carrier for the monomers and an initiator to swell and wet PP. Moreover, St also had a certain ability to swell PP, so the addition of St enhanced the extent of swelling of PP. The optimized reaction conditions were determined by orthogonal experiments [ $L_9(3^4)$ ], which were designed on the basis of the following factors: the content of the initiator, amount of xylene, swelling time, and reaction time. The results are summarized in Table I. When the synthesis conditions were  $A_3B_2C_1D_3$ ,  $G_p$  reached a maximum value of 1.55%. In our work, we chose  $G_p$  as a criterion; therefore, the optimization synthesis conditions were  $A_3B_2C_1D_3$ . According to the value of  $G_p$ , the influencing factors could be arranged as follows:  $A > D > B > C$ . The reason was that with increasing concentration of initiator and reaction time, there was a lot of initiator decomposition, and more active sites on the PP particles formed; this enhanced  $G_p$ . At the same time, the appropriate interface agent and swelling time also gave some advantages to the grafting reaction.<sup>11</sup> However, when the content of BPO was relatively high, it decreased the grafting degree because of the formation of more active sites on the monomers, which led to the speeding of monomer self-polymerization and a negative impact on the length of the side chains.

TABLE I  
Results of the Orthogonal Experiments for the Grafting Reaction

Level	Factor				
	A: Initiator content (%)	B: Xylene dosage (%)	C: Swelling time (h)	D: Reaction time (h)	E: Grafting rate (%)
1	0.075	4.3	1.0	1.5	1.22
2	0.075	8.6	1.5	2.0	1.34
3	0.075	12.9	2.0	2.5	1.27
4	0.015	4.3	1.5	2.5	1.40
5	0.015	8.6	2.0	1.5	1.09
6	0.015	12.9	1.0	2.0	1.16
7	0.15	4.3	2.0	2.0	1.44
8	0.15	8.6	1.0	2.5	1.55
9	0.15	12.9	1.5	1.5	1.30
$K_1$	1.277	1.353	1.310	1.203	
$K_2$	1.217	1.327	1.347	1.313	
$K_3$	1.430	1.243	1.267	1.407	
R	0.213	0.110	0.080	0.204	

The reaction temperature was 98°C, and the total mass of monomers was 3 g.

$K_1$ ,  $K_2$ ,  $K_3$  were the variances of level for 1, 2 and 3 respectively in each column factors, and R was the range of in each column factors.

### Influence of the monomer concentration

According to the optimized reaction conditions determined by the orthogonal experiments, the effects of the monomer concentration on  $G_p$ , the content of the gel,  $G_e$ , and  $C_m$  are shown in Figure 1. It can be seen that as the concentration of the monomers increased,  $G_p$  monotonously increased; however,  $G_e$  monotonously decreased. When the concentration of the monomers was 3 wt %,  $G_p$  was 1.54%, and  $G_e$  reached 51.49%. However, when the concentration of monomers was 15 wt %,  $G_p$  was 6.87%, and  $G_e$  decreased to 40.1%. The PMSB' content increased relatively steadily. When the monomers concentrations was over 12 wt %, there were few gels formed. As is well known, the grafting reaction and monomer self-polymerization are a pair of competitive reactions. With the monomers diffused and the amount of reaction regions on the PP backbone increased,  $G_p$  began to increase. Most of the monomers reacted with the PP microradical when the concentration of monomer was low, and then, the dominant reaction was the grafting reaction. Therefore,  $G_p$  increased when the monomer increased. However, monomer self-polymerization and copolymerization began to react when the monomer concentration reached a certain amount. It is well known that PP is a semicrystalline polymer, so the grafting reaction only occurred at definite amounts of crystal defects and amorphous areas, and this reduced the number of active sites.<sup>1</sup> Then, many of the homopolymers and copolymers formed and prevented the grafting reaction from proceeding. Higher  $G_p$ 's led to more branched chains, so it was easier to form the crosslinking product. Also, when there were more active sites of the macroradical, PP crosslinked by itself and formed a three-dimensional network.<sup>13</sup>

### FTIR spectroscopy analysis (Fig. 2)

According to the method discussed in our previous article,<sup>8</sup> we synthesized the graft copolymer polypropylene-*g*-(maleic anhydridestyrene) (PP-*g*-PMS) with St, MAH, and PP. The IR spectra of pure PP, PP-*g*-PMS, and PP-*g*-PMSB showed the presence of a band at 1782  $\text{cm}^{-1}$  in PP-*g*-PMS (characterizing the carbonyl group of MAH), which was absent from the spectrum of the pure PP. This indicated that MAH was grafted onto PP. However, the band present at 1720  $\text{cm}^{-1}$  (characterizing the carbonyl of maleic acid) indicated that MAH hydrolyzed partly with the process of grafting. The absorption at 1600  $\text{cm}^{-1}$  was assigned to the characteristic absorption of the C=C bond of the benzene ring, and the bands at 754 and 700  $\text{cm}^{-1}$  were characteristic of the absorption of the C-H bond of the benzene ring. The characteristic peaks of PP-*g*-PMSB were similar to the

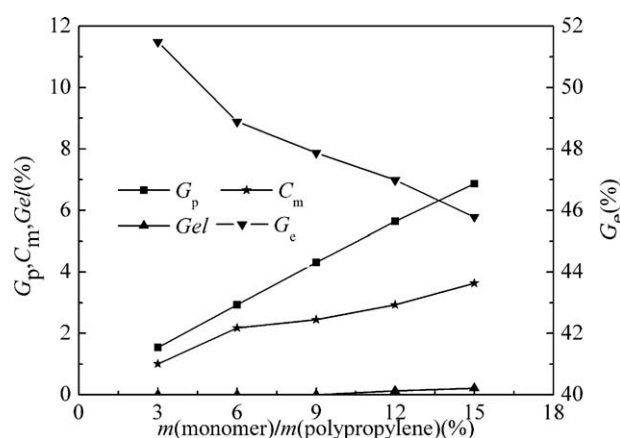
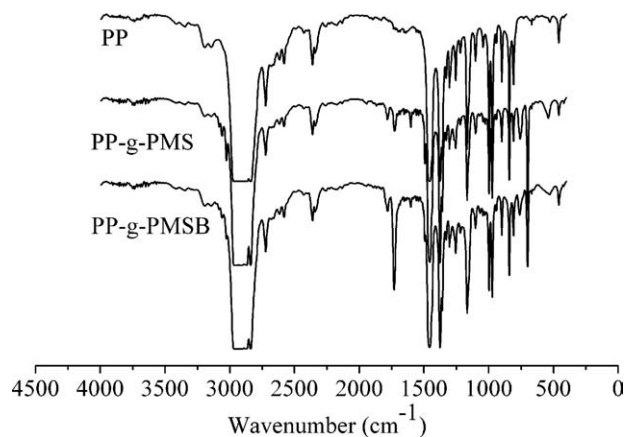


Figure 1 Effect of the monomer amount ( $m$ ) on the grafting reaction.



**Figure 2** FTIR spectra of the virgin PP, PP-g-PMS, and PP-g-PMSB.

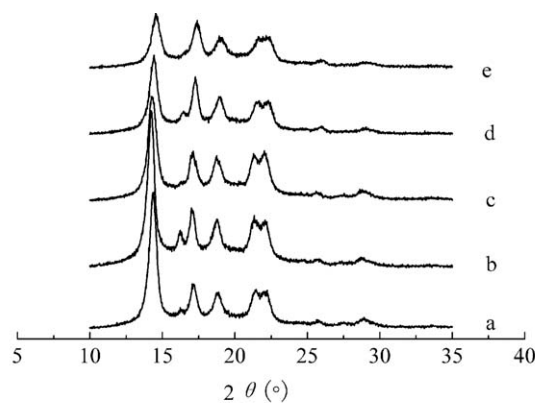
characteristic peaks of PP-g-PMS. However, the band present at  $1720\text{ cm}^{-1}$  was obviously stronger because of the carbonyl group of the BA.<sup>14</sup> In conclusion, the FTIR spectroscopy analysis indicated that MAH, St, and BA were grafted onto the backbone of PP.

### MW determination

Table II shows the MW distribution data obtained by GPC of the polypropylene untreated and modified samples. As is shown, the average MW values ( $M_n$ ,  $M_v$ , and  $M_w$ ) of the grafted polymer PP-g-PMSB were slightly larger than those of pure PP. The values became larger and the PDI became narrower with increasing  $G_p$ . The results obtained indicate that the free-radical grafting reaction in the water suspension system had mild reaction conditions and that the grafting reaction mostly occurred on the shorter molecular chains of PP. Furthermore, the addition of St and BA largely suppressed the degradation of the main chains of PP. In general, the MW of a nongrafted polymer is close to that of a grafted polymer with branch chains.<sup>15</sup> The  $M_n$  value of PMSB' was 10,703, and the PDI value was 1.9388; this indicated indicate that long grafted branch chains were formed onto the grafted product and that the length of the branch chains was very close.

**TABLE II**  
GPC Results Analysis of the Samples

Sample	PP	PMSB'	PP-g-PMSB $G_p$		PP-c-PMSB $C_m$	
			2.93	6.87	2.18	3.64
$M_n$	53,970	10,703	55,219	63,187	48,027	45,454
$M_v$	191,019	37,342	191,021	207,499	190,539	170,663
$M_w$	229,137	20,751	226,778	247,011	207,772	203,140
PDI	4.2456	1.9388	4.1069	3.9092	4.3261	4.4691



(a) virgin PP (b) PP-g-PMSB,  $G_p=2.93\%$  (c) PP-c-PMSB,  $C_m=2.18\%$   
(d) PP-g-PMSB,  $G_p=6.87\%$  (e) PP-c-PMSB,  $C_m=3.64\%$

**Figure 3** XRD patterns of the virgin PP, PP-g-PMSB, and PP-c-PMSB.

Because of the presence of PMSB', the  $M_n$ ,  $M_v$ , and  $M_w$  values of PP-c-PMSB were lower than those of PP-g-PMSB, and the value of PDI broadened.

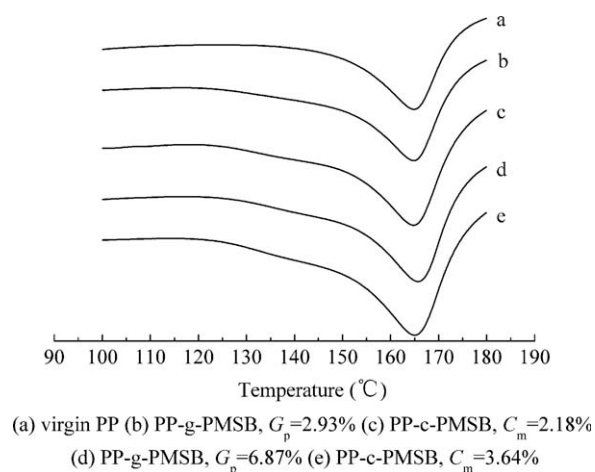
### X-ray diffraction analysis

As is well known, the most common and the most stable crystal form of PP is the  $\alpha$  crystal. In contrast, the  $\beta$  crystal of PP is easily tensile, has a higher thermal deformation temperature, and has better toughness; these properties give PP better application prospects. Figure 3 shows the XRD spectrum of the pure PP and grafted products. As is shown, the characteristic diffraction peaks of  $\alpha$ -PP at  $2\theta = 14.02$ ,  $17.24$ ,  $18.86$ , and  $21.68^\circ$  were all present in PP, PP-c-PMSB, and PP-g-PMSB; however, the characteristic diffraction peaks of  $\beta$ -PP were present at  $2\theta = 16.58^\circ$ .<sup>16</sup> This indicated that PP-g-PMSB had the ability to induce nucleation. With increasing  $G_p$ , the diffraction peaks' intensity of PP-g-PMSB became weaker, and PP-c-PMSB weakened more obviously. The reason was that the graft polypropylene contained so many branched chains, which could become entwined with each other; this led to the destruction of some of the tacticity and hindered the speed of chain-segment diffusion, migration, and the arrangement of tacticity. The higher  $G_p$  was, the harder the crystallinity of the grafted product was. Therefore, the crystallinity of the grafted product declined with increasing  $G_p$ ,<sup>17</sup> and the existence of PMSB' also hindered the  $\alpha$  and  $\beta$  crystals formed.

### Differential thermal analysis (DTA) analysis and thermogravimetric analysis (TGA)

#### DTA

DTA measurements were performed for the virgin PP and the graft polypropylene samples. The DTA

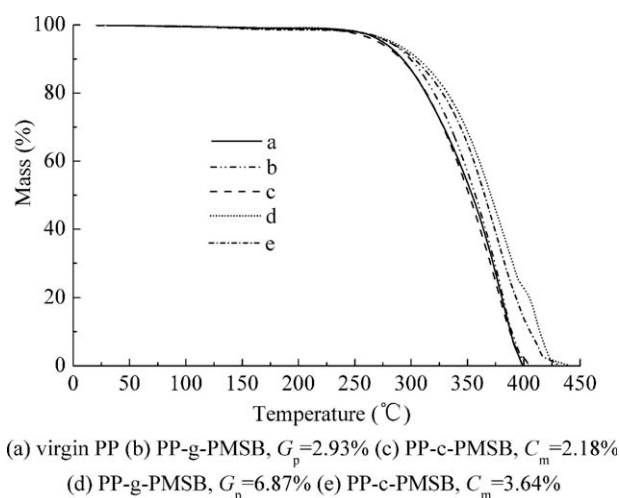


**Figure 4** DTA patterns of the virgin PP, PP-g-PMSB, and PP-c-PMSB.

measurement curves of the samples are shown in Figure 4. As is shown, PP-g-PMSB and PP-c-PMSB all emerged in a new, narrow-temperature transition range from 123.2 to 152.1°C because of the glass-transition process of PMSB' and the branched chains of the grafted products.<sup>18</sup> This result was consistent with the conclusion received from the GPC analysis that there were long grafted chains on the PP backbone during the grafting reaction. Because the PP-c-PMSB contained a certain amount of ungrafted PMSB', the endothermal peak area was larger. As stated, the melting point of the virgin PP was about at 165.0°C, which was close to the melting point of PP-g-PMSB and PP-c-PMSB; this indicated that the grafting reaction primarily occurred at the amorphous and crystal defects on the PP backbone.

#### TGA

Figure 5 shows the TGA results of the virgin PP and grafted samples with different  $G_p$  values. It can be seen from this figure that PP-g-PMSB had a higher onset thermal degradation temperature. The temperature when the virgin PP lost 50% of its mass was 353.5°C; however, the temperatures at 50% mass loss of the PP-g-PMSBs with 2.93 and 6.87%  $G_p$  were 358.2 and 373.8°C. This was because the addition of St and BA prompted the PP microradicals to react with the monomers before the degradation of the



**Figure 5** TGA patterns of the virgin PP, PP-g-PMSB, and PP-c-PMSB.

main chains of PP, and this formed more stable radicals and restrained the degradation of PP. In addition, the tertiary hydrogen atoms of PP were gradually substituted by the polarity monomers with increasing  $G_p$ . Therefore, the polarity monomers resulted in the redistribution of the density of the electron cloud of the intermolecular chemical bonds, which strengthened the bond energy between the atoms and enhanced the thermal stability of PP.<sup>19</sup> It is also known from Figure 5 that the thermolysis temperatures of PP-c-PMSB were all lower than those of PP-g-PMSB because there were no C—C bonds between PMSB' and the main chains of PP, and this phenomenon led to thermolysis of PP-c-PMSB in advance under high temperature. When  $G_p$  of PP-g-PMSB was 6.87% and  $C_m$  of PP-c-PMSB was 3.64%, there was little weight loss existing on the thermogravimetry curves because there were some gels existing in the graft products.

#### MFR, $D_r$ , and $M_s$ measurements

The MFR data of the virgin and grafted PPs are listed in Table III. It was observed that the MFR values of PP-g-PMSB decreased gradually with increasing  $G_p$ . At the same time, we discovered that  $D_r$  and  $M_s$  increased constantly, and the clarity of the extruded samples declined. The reason may have

**TABLE III**  
**MFR,  $D_r$ , and  $M_s$  Data of the Virgin and Grafted PPs**

Sample	PP	PP-g-PMSB $G_p$ (%)					PP-c-PMSB $C_m$ (%)				
		1.54	2.93	4.31	5.64	6.87	0.85	2.18	2.45	2.93	3.64
MFR (g/10 min)	4.20	5.52	4.15	3.06	2.55	2.12	5.86	4.35	4.58	4.72	5.27
$D_r$	0.064	0.10	0.20	0.39	0.53	0.72	0.083	0.16	0.25	0.37	0.55
$M_s$ ( $10^4$ Pa s)	0.43	1.52	2.25	3.27	4.72	5.74	1.32	1.86	2.75	3.67	4.89

**TABLE IV**  
Water Contact Angle Data of the Virgin and Grafted PPs

Sample	PP	PP-g-PMSB $G_p$ (%)					PP-c-PMSB $C_m$ (%)				
		1.54	2.93	4.31	5.64	6.87	0.85	2.18	2.45	2.93	3.64
Water contact angle ( $^\circ$ )	90.26	89.32	87.56	83.63	78.56	72.12	87.37	82.25	74.33	68.59	63.51

been the ternary monomer grafted onto the PP backbone, which could have formed long branched chains and led to a higher branched degree and poorer tacticity of the products. Meanwhile, the winding effect of the side chains with the main chain of PP increased,  $M_s$  increased, and the crystallinity decreased. The MFR values of the PP-g-PMSB samples with  $G_p$  of 1.54% were all larger than those of virgin PP; this indicated that with low  $G_p$ , the degradation of the PP backbone was greater than its heat resistance. However, the MFR values of the PP-c-PMSB samples increased gradually with  $C_m$  above 2.18%; this was related to the increase in  $C_m$  on the PP surface. The reason may have been that there were no chemical bonds between the starting PMSB' and the PP backbone; PMSB' began to fuse when it was heated, and this could have lubricated the surface of PP and was good for extrusion. In other words, PMSB' played a plasticizer role.

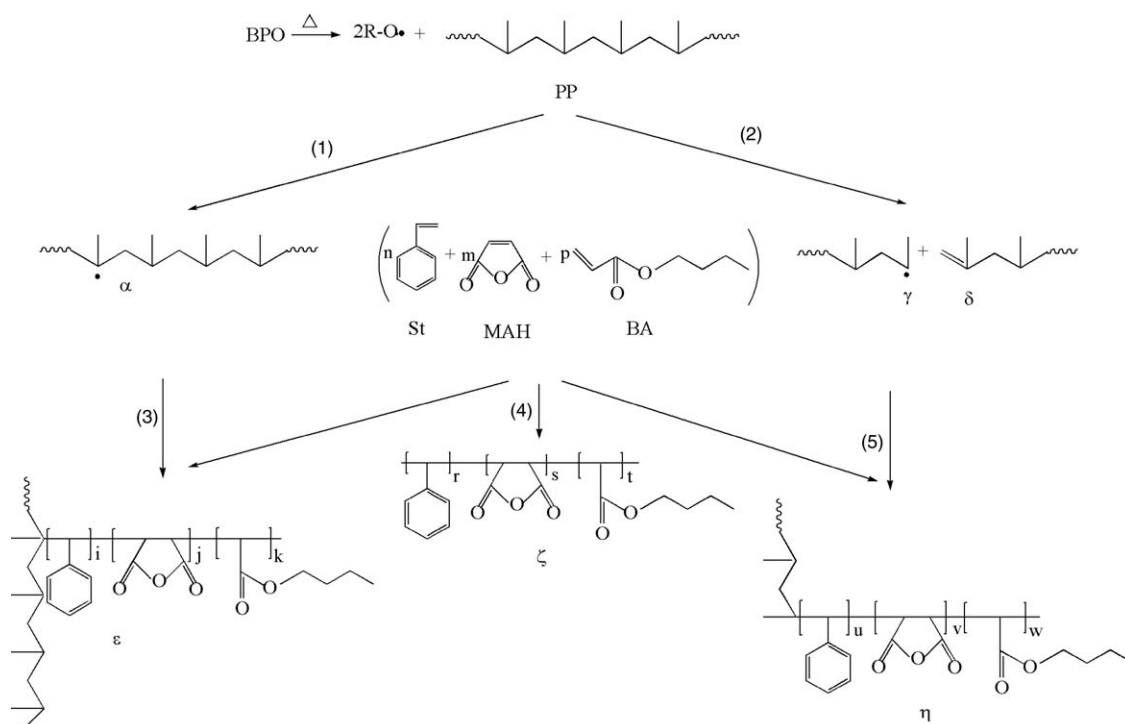
virgin PP was  $90.26^\circ$ , and the contact angle of PP-g-PMSB decreased from  $89.32$  to  $72.12^\circ$  with increasing  $G_p$ . When  $G_p$  was low, the contact angle of PP-g-PMSB changed slightly. However, when the contact angle was  $72.12^\circ$ , the hydrophilicity of the polymer improved efficiently. The contact angle of PP-c-PMSB decreased more obviously than that of PP-g-PMSB with the content of ungrafted PMSB' increased, and when  $C_m$  was 3.64%, the contact angle of PP-c-PMSB decreased to  $63.51^\circ$ ; this indicated that the presence of PMSB' further improved the hydrophilicity of the grafted polymer. The reason for the decrease in the contact angle was complicated, and the change in the polymer's polarity surface was an important factor. When the samples were processed into films by compression molding in the melt, PP-g-PMSB and PMSB' could diffuse to the surface of the polymer;<sup>20</sup> this led to a decrease in the contact angle.

### Contact angle measurements

The contact angle data of the virgin and grafted PPs are listed in Table IV. As shown, the contact angle of

### Reaction mechanism

In our research, the grafting reaction took place at the molecular level. First, the solid-phase swelling



**Figure 6** Reaction mechanism of St, MAH, and BA grafting onto PP.

process diffused the initiator and monomer uniformly in the pores and surfaces of the PP granules. With the help of the interface, they could be absorbed into the inner and micropore regions of the PP granules. After that, the dispersion medium (water) began to transfer mass and heat. Also, the grafting reaction mainly occurred in the amorphous and microdefect region of crystallinity. The mechanism of free-radical grafting of the ternary monomers (St, MAH, and BA) onto the PP granules in the water suspension system is shown in Figure 6.

Generally speaking, first, the primary radical formed by decomposition of the initiator in the free-radical grafting system.<sup>21</sup> Then the primary radical generated a macroradical by hydrogen abstraction from the backbone of the PP (reaction 1); this started the free homopolymerization of the monomers (reaction 4) and/or degradation (reaction 2). The macroradical could react with the monomers (reaction 3) and form a target molecule. Meanwhile, St and BA were electron donors and had higher reactivities, which could react with the macroradical quickly and suppress the degradation and other side reactions; this was the main reaction route. The results received from the GPC analysis exactly demonstrated this point. The products of reactions 3 and 5 could react with each other and form a gel. The products of reaction 2 were  $\gamma$  and  $\delta$ . Because of the low reaction temperature,  $\delta$  had little chance to react with the monomers.<sup>22</sup> With the increasing addition of monomers, the homopolymer formed by the monomers also increased. Therefore,  $G_p$  was elevated and so was the content of ungrafted polymer and the content of gel. Because the reaction process was in the water, MAH may have partially hydrolyzed.

## CONCLUSIONS

This study concerned the performance of ternary monomers (MAH, St, and BA) in the free-radical grafting modification of PP in a novel water suspension system. The optimal synthesis conditions were determined by orthogonal experiments. The effects of the chemical and processing parameters were discussed. The effect of the monomer content on the grafting reaction were examined to study the crystallinity of the products, variations of the thermal stability, MFR, and hydrophilicity of the product when

there was nongrafted polymer and no nongrafted polymer. The grafted polymer of PP synthesized in our experiment contained lower gel content and lower degree of degradation. Meanwhile, the thermal stability,  $M_s$ , and hydrophilicity were efficiently improved.

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