Synthesis and Characterization of a Macromolecular Surface Modifier for Polypropylene

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ABSTRACT: A novel macromolecular surface modifier, a polypropylene-*graft*-poly(butyl methylacrylate) copolymer, was synthesized through the coupling of polypropylene containing maleic anhydride with monohydroxyl-terminated poly(butyl methylacrylate). The effects of the raw ratio, reaction temperature, and molecular weight of the branches on the graft reaction were studied. The graft copolymers were characterized with IR, ^{1}H-NMR, thermogravimetry, and differential scanning calorimetry. The results of attenuated total reflection/Fourier transform infrared and contact-angle measurements indicated that polypropylene-*graft*-poly(butyl methylacrylate) could diffuse preferably onto the surface and be used as a surface modifier for polypropylene. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3413–3419, 2006

Key words: additives; graft copolymers; poly(propylene) (PP); surfaces

INTRODUCTION

Polypropylene (PP) has become one of the largest polymers in use because of its low price, excellent properties, and convenient processing. However, because of its low surface energy and relatively high crystallinity, PP products are difficulty to dye, adhere, and coat, and its compatibility with polar polymers is also poor. Many approaches, such as plasma oxidation, solution oxidation, and radical grafting reactions, have been used to increase its surface reactivity and hydrophilicity.[1–4] However, limits such as pollution and complicated processes still exist in many applications.

Blending with a surface modifier is widely recognized as a potential technique to functionalize the surface properties of polymers because of its convenience in processing. The technique relies on a small amount of a surface modifier to modify the surface properties[5] and includes blending the surface modifier with an excess of the host polymer and diffusing the modifier to the surface of the product.

In the past years, polymer surface modification has been accomplished by blending,[6–10] but many interconflictive results have been obtained because of the effects of the solvents with which the samples were formed via solvent casting and because the modifiers were not easy to attain on account of the complicated synthesis methods.[11–14] In our previous work,[15,16] several surface modifiers for polyethylene were also synthesized and used to improve its hydrophilicity, and thermoform was used to form polymer films to avoid the effects of solvents and their properties on surface modification. Therefore, the effects of the molecular structure, including the molecular weight of the functional groups and the length and density of the side chains, on the modification can be determined by the study of the surface modification of modifiers with different molecular structures.

In this work, the interaction between the surface modifier and host polymer is examined so that the surface modifier can anchor to the host polymer and keep its lasting effectiveness, whereas the relatively strong interactive force does not hinder the surface modifier from preferably diffusing to the surface.

For these reasons, block or graft copolymers of PP with relatively low molecular weights may be suitable surface modifiers of PP. However, because of the difficulty of obtaining terminally functionalized PP oligomers, graft copolymers of PP could be the most feasible choice for functionalizing the surface of PP, especially for industry.

The aim of this work was to prepare graft copolymers suitable for the surface modification of PP and to study the surface and bulk properties of blends of the graft copolymers with PP. Polypropylene-*graft*-poly

(butyl methylacrylate) (PP-*g*-PBMA) graft copolymers were synthesized and characterized so that the most suitable structure of the graft copolymers could be chosen. The graft copolymers were prepared by the reaction of PP with maleic anhydride to form polypropylene-grafted maleic anhydride (MPP) and by further coupling with monohydroxyl-terminated poly(butyl methylacrylate)s (PBMA-OHs) of various molecular weights. In another article, the effect of PP surface modification on graft copolymers will be reported.

EXPERIMENTAL

Materials

The MPP copolymer with 3.5% maleic anhydride was synthesized by a radical solution graft reaction. The molecular weight of PP was 5000, 9000, or 15,000 (Shanghai Petroleum Co., Shanghai, China). Butyl methylacrylate (BMA) was purified to remove any hindrance and a small amount of water before use. 2,2′-Azoisobutyronitrile (AIBN) was recrystallized with ethylene alcohol. Acetic anhydride and pyridine were distilled before use, and other reagent-grade chemicals such as *o*-xylene, *p*-toluene sulfonic acid, and mercaptoethylene alcohol (TEG) were used as received without further purification.

Synthesis of PBMA-OH[17]

The polymerization of BMA was initiated by AIBN in toluene at 60°C in a four-necked glass equipped with a stirrer, a thermometer, a nitrogen gas inlet, and a condenser. TEG was used as the chain-transfer reagent to control the molecular weight and ensure the sought polymer with hydroxyl-terminated groups. Before the reaction, air was replaced by the passage of nitrogen into the glass. After 30 min of reaction, the polymerization was terminated via cooling to room temperature and pouring into a large quantity of petroleum ether, and the deposit was dissolved in toluene and reprecipitated again until no monomer or TEG was detected; it was then dried in a vacuum oven at 80°C for 24 h. The conversion of the monomer rate was about 13%.

Preparation of PP-*g*-PBMA

The graft reactions of PBMA-OH with MPP were carried out in a 250-mL, four-necked glass at 140°C in *o*-xylene in the presence of *p*-toluene sulfonic acid under N$_2$. *p*-Toluene sulfonic acid was used as the catalyst. During the reaction, xylene was distilled off and allowed to pass through a layer of 4-Å molecular sieves before reentering the reactor to remove any water that formed during the reaction. After the enactment time, the reaction mixture was cooled to 100°C, poured into acetone three times, precipitated, and filtered. The gross graft copolymer was refined with ethylene alco-hol until no PBMA-OH was detected. The purified grafted polymer was dried *in vacuo* at 80°C for 24 h.

Measurements of the hydroxyl value and molecular weight of PBMA-OH

The hydroxyl value of PBMA-OH was determined with acetic anhydride/KOH standard solution titration. A sample of PBMA-OH of about 3 g was dissolved in a 15-mL acetic anhydride/pyridine solution. After the sample was completely dissolved, the solution was refluxed at 100°C for 1 h, and then 5 mL of distilled water was added and refluxed for 10 min. The solution was titrated with a 0.5 mol/L potassium hydroxide solution to the end point with phenolphthalein as a red indicator. The blank titration was performed at the same time. The hydroxyl value of PBMA-OH was calculated with the following relation:

$$\text{Hydroxyl value} = [(V_0 - V) \times M \times 56.11]/W \quad (1)$$

where V are V_0 are the volumes of KOH/ethanol standard solutions of the sample and blank, respectively (mL); M is the concentration of the KOH standard solution (mol/L); and W is the sample weight (g).

For PBMA-OH, the number-average molecular weight (M_n) was calculated with the following relation:

$$M_n = (56.11 \times 1000)/\text{Hydroxyl value} \quad (2)$$

Characterization

Fourier transform infrared (FTIR) spectra were obtained with a Nicolet 210 FTIR spectrometer. Its measurement scope was 600–4000 cm^{-1}, and the scanning velocity was 32 times. ^{1}H-NMR measurements were run on a Varian Inova 500 NMR spectrometer in *o*-dichlorobenzene at 70°C. The thermogravimetric analysis (TGA) was performed on a NetzschTG-209 thermogravimetric analyzer (Bavaria, Germany) via the heating of the samples from 50 to 700°C under air or nitrogen. Both types of experiments were carried out at a flow rate of 40 mL/min and a heating rate of 20°C/min. A TA Instrument DSC 2910 differential scanning calorimeter was used to investigate the thermal behavior of the graft copolymers. The analysis was performed at a heating and cooling rate of 10°C/min. Each specimen was heated to 200°C at a rate of 10°C/min and held for 2 min to remove the residual thermal influence. The sample weight was approximately 5 mg.

Blend preparation and characterization

Blends of PP-*g*-PBMA/PP were prepared via solvent mixing. The films were obtained via melt casting in a stainless steel mold at 190°C. The composition of the blending film surface was investigated with attenuated total reflection/Fourier transform infrared (ATR–FTIR)
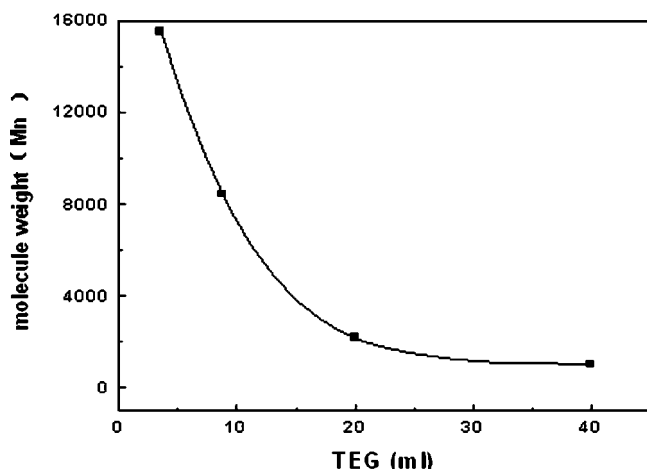
Figure 1 Influence of chain transfer on the molecular weight.

spectroscopy with a Nicolet 210 FTIR spectrometer with an attenuated total reflection accessory at an angle of incidence of 45°.

Contact-angle measurements

The contact angles of the film surfaces were determined with a Dataphysics, Inc., OCA-20 contact-angle goniometer (Stuttgart, Germany) at the ambient temperature. All measurements were preformed with the sessile drop method and made with drops of 1 μL after about 15 s. The reported values were the averages of eight measurements at various places on the same film sample. The values of the contact-angle measurements varied by ±3°.

RESULTS AND DISCUSSION

Synthesis of PBMA-OH

PBMA-OH was synthesized with AIBN as the initiator and mercaptoethylene alcohol as the chain-transfer re-

agent. Under a BMA/AIBN molar ratio of 100 : 1, a series of PBMA-OHs with various molecular weights were obtained by the alteration of the amount of TEG. The results are shown in Figure 1. A small amount of TEG could lower the molecular weight of PBMA-OH rapidly. However, its effect was less and less as its amount increased. In comparison with TEG, the chain transfers of the solvent, initiator, and growing polymer chains could be neglected. The polymerization degree of the polymer with chain transfer (P_n) can be expressed as follows:

$$\frac{1}{P_n} = \frac{1}{P_{n,0}} + C_s \times \frac{[S]}{[M]} \tag{3}$$

where $P_{n,0}$ is the polymerization degree without the chain-transfer reagent; C_s is the constant of chain transfer of TEG; and [S] and [M] are the concentrations of TEG and BMA, respectively. The molecular weight of the polymer was lowered as the concentration of the chain-transfer reagent increased. In the experiment, PBMA-OH with molecular weights of 690, 1030, 2200, 8850, and 15,500 were synthesized and used to graft onto PP.

Preparation of PP-*g*-PBMA

PP-*g*-PBMA graft copolymers with different constitutional structures and grafted rates were achieved by the esterification of MPP with PBMA-OH. MPP with a relatively low concentration of maleic anhydride was a semicrystalline polymer similar to PP with a melting point of 148°C according to differential scanning calorimetry (DSC), and the solvents for it were *o*-xylene and toluene at their boiling points. Therefore, *o*-xylene was chosen to carry out the esterification to obtain high reaction rates. Furthermore, the esterification was an equilibrium reaction, and the removal of the water that formed in the reaction was very important to obtain

TABLE I
Reaction Conditions and Graft Ratios of MPP

Functional group ratio (MPP/PBMA)	Time (h)	Molecular weight of PBMA	Molecular weight of MPP	Graft ratio of MPP (%)[a]
1 : 0.5	12	2,200	5,000	13.7
1 : 1	12	2,200	5,000	32.9
1 : 2	12	2,200	5,000	34.0
1 : 3	12	2,200	5,000	41.9
1 : 2	6	2,200	5,000	29.8
1 : 2	18	2,200	5,000	35.7
1 : 2	24	2,200	5,000	38.2
1 : 2	12	2,200	9,000	32.6
1 : 2	12	2,200	15,000	33.2
1 : 1	12	690	5,000	11.9
1 : 1	12	1,030	5,000	14.1
1 : 1	12	2,200	5,000	32.9

[a] The contents of PBMA in the graft copolymers were measured by ^{1}H-NMR.

high conversion rates. In the experiments, the reaction solvent was continuously distilled off and passed through 4-Å molecular sieves to ensure the removal of water from the system.

By the alteration of the raw ratio or reaction time, a series of PP-g-PBMAs with different graft ratios were obtained. The results are shown in Table I. The grafting ratios increased with an increasing molar ratio of PBMA-OH to maleic anhydride in MPP. On the other hand, a reaction time of 12 h was necessary to reach the maximum conversions of maleic anhydride in MPP. In comparison with the esterification of small molecules, a prolonged reaction time was needed because of the limitations arising from polymer–polymer interactions and the relatively low concentration of hydroxyl groups and maleic anhydride in MPP.

Assumed that each maleic anhydride group in MPP reacted only with one molecule of PBMA-OH and that the reactions were complete, we found that the content of poly(butyl methylacrylate) (PBMA) was 44.0% according to the content of maleic anhydride in MPP and the molecular weight of PBMA-OH. We concluded that the graft reactions dealt only with the reactions of anhydride and hydroxyl groups and that the esterification of hydroxyl and carboxyl groups did not occur. Therefore, the reaction path can be shown as illustrated in Figure 2.

Graft copolymers with different constitutional structures were also synthesized by the alteration of the molecular weight of MPP or PBMA-OH. In those experiments, MPPs of several molecular weights were chosen to react with PBMA-OH, the molecular weight of which was 2200. Unlike the general rule, the molecular weight of MPP had no effect on the graft reaction; all three kinds of graft copolymers had the same grafting rates of 33 wt % by esterification. On the other hand, PBMA contents of 11.9, 14.1, and 32.9 wt % were obtained by the reaction of MPP samples with PBMA-OH with molecular weights of 690, 1030, and 2200, respectively. The grafting rates increased with the increasing molecular weight of PBMA-OH. However,
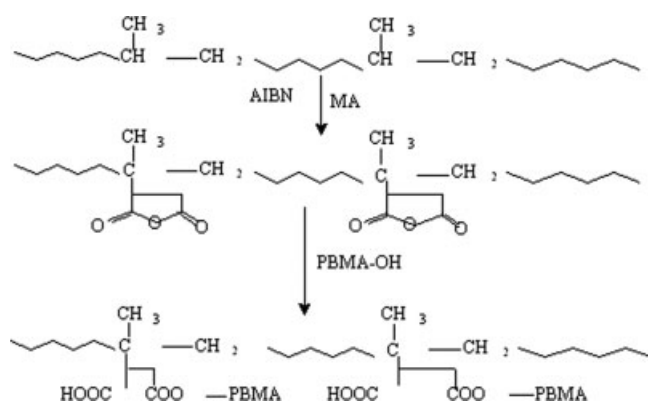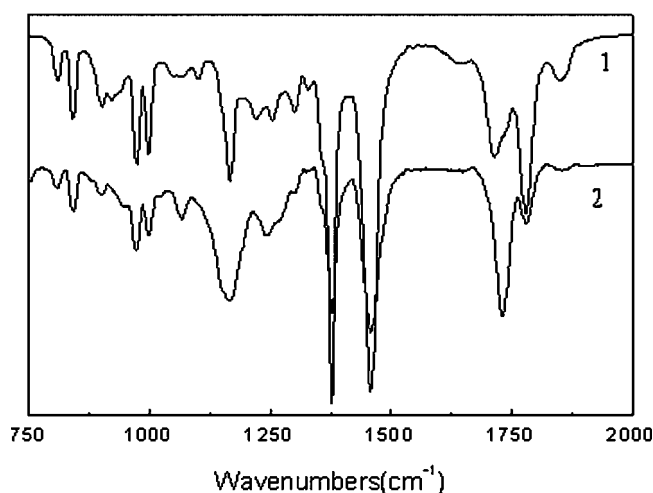

Figure 3 IR spectra of (1) MPP and (2) PP-g-PBMA.

the molar graft rates decreased with the increasing molecular weight of PMMA-OH. This indicated that the higher molecular weight of PBMA-OH blocked the esterification reaction. The product of PBMA-OH with a higher molecular weight was the grafting copolymer with a long side chain and a lower density (and vice versa). The effects of the structure of graft copolymers on the surface modification of PP will be reported in another article.

IR analysis of PP-g-PBMA

The FTIR spectra of MPP and PP-g-PBMA are shown in Figure 3. Four new bands at 1268, 1242, 944, and 972 cm^{-1}, attributed to PBMA, appeared for the PP-g-PBMA sample. The intensity of the band at 1731 cm^{-1}, attributed to the carbonyl groups of PP-g-PBMA, was much stronger for the MPP sample. Furthermore, in comparison with MPP, the band intensities at 1780 and 1854 cm^{-1}, attributed to maleic anhydride of MPP, decreased for the PP-g-PBMA sample. All these results showed that the copolymer contained PBMA grafts.
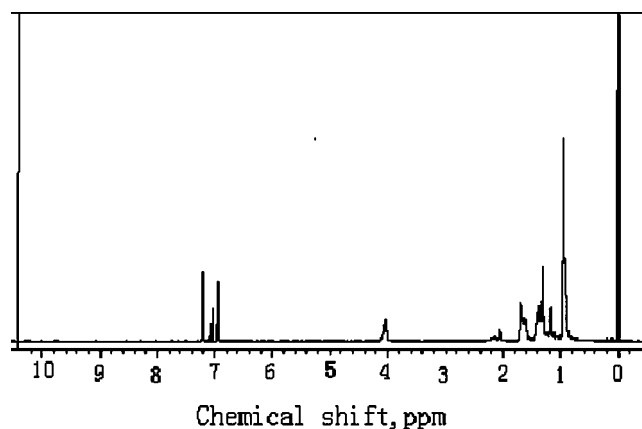

Figure 2 Grafting PP with PBMA-OH by esterification.

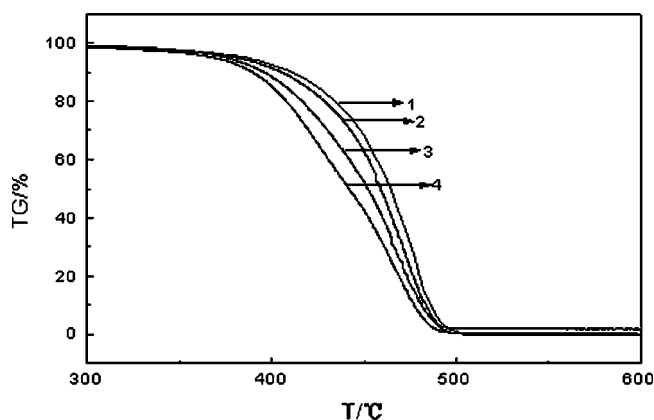**Figure 4** ^{1}H-NMR spectrum of graft copolymer PP-g-PBMA.

Figure 5 TGA thermograms of MPP and PP-*g*-PBMA in N$_2$: (1) PP-*g*-PBMA with 32.9% PBMA, (2) PP-*g*-PBMA with 41.9% PBMA, (3) PP-*g*-PBMA with 51.4% PBMA, and (4) MPP.

^{1}H-NMR of PP-*g*-PBMA

The grafted copolymers were also analyzed by ^{1}H-NMR, and a typical NMR spectrum is shown in Figure 4. The copolymer contained the characteristic signals of PP at 0.93 ppm for [dCH$_3$], 1.42 ppm for [mCH$_2$], and 1.74 ppm for [mCH]. On the other hand, the copolymer also showed stronger signals of PBMA at 4.0 ppm, which were related to the OCH$_2$ proton from PBMA. These results verified that PBMA-OH as branches was grafted onto the PP molecular chains. The contents of PBMA in the graft copolymers were also measured with ^{1}H-NMR.

TGA of PP-*g*-PBMA

Thermal stability is an issue for polymer processing and product durability. To investigate whether the copolymers were suitable as surface modifiers of PP in processing, the thermal and thermo-oxidative degradation of PP-*g*-PBMA was investigated with TGA. The
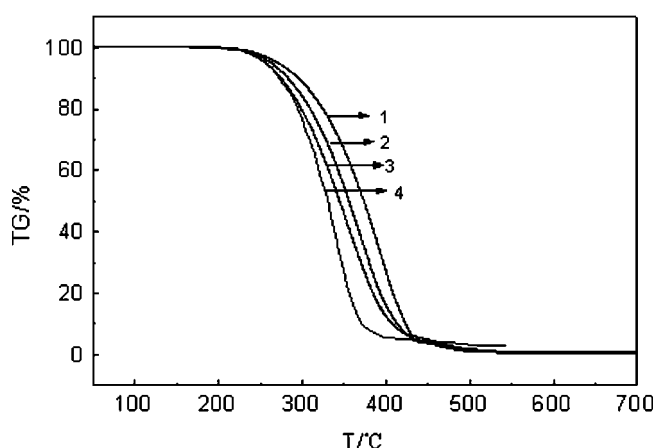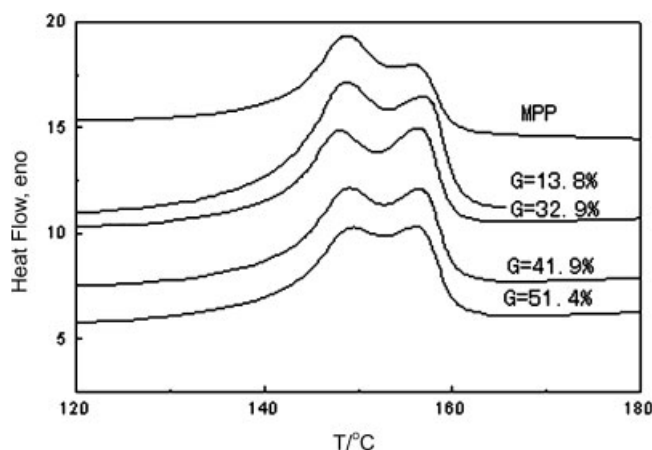

Figure 7 DSC melting thermograms of MPP and PP-*g*-PBMA.

results are shown in Figures 5 and 6. The thermo-oxidative degradation temperatures were far below the thermal degradation temperatures, with more than a 100°C difference for the grafted copolymer 50 wt % retention temperature. However, the initial degradation temperatures for the copolymers all exceeded 250°C, which was higher than the processing temperature for PP; this indicated that the copolymers would be suitable for the surface modification of PP in terms of the thermal stability. Furthermore, the PP-*g*-PBMA copolymers appeared more stable than their raw material MPP in air, indicating that the PBMA pendants had a positive effect on the backbone of PP. On the other hand, the opposite effect of the PBMA contents in the copolymer on the decomposition temperature in air and in N$_2$ was observed (Figs. 5 and 6). The samples containing higher contents of PBMA displayed higher thermal stability in N$_2$. In contrast, samples with lower contents of PBMA exhibited higher thermooxidation stability in air. The differences could be attributed to their different mechanisms in decomposition. In addition, the results showed that the length of the PBMA
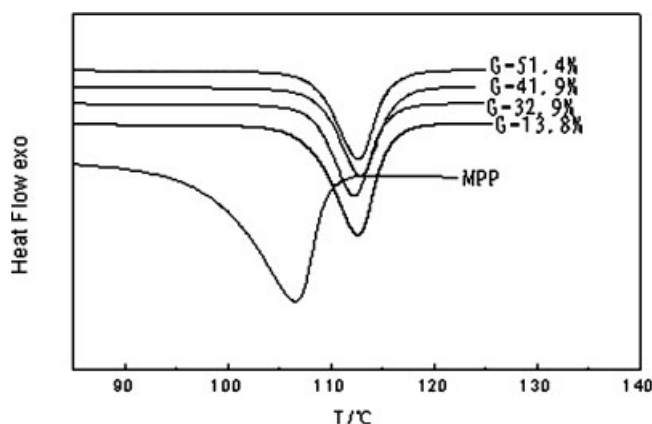

Figure 6 TGA thermograms of MPP and PP-*g*-PBMA in air: (1) MPP, (2) PP-*g*-PBMA with 13.8% PBMA, (3) PP-*g*-PBMA with 32.9% PBMA, and (4) PP-*g*-PBMA with 41.9% PBMA.

Figure 8 DSC cooling thermograms of MPP and PP-*g*-PBMA.

TABLE II
DSC Melting Temperatures and Crystallinity

Sample	PBMA (wt %)	ΔH_m (J/g)	Crystallinity (%)	T_{m1} (°C)	T_{m2} (°C)
MPP	3.50	134.00	64.1	148.86	156.85
PP-g-PBMA1	13.8	95.91	45.9	148.73	156.82
PP-g-PBMA2	32.9	87.49	41.8	147.97	156.3
PP-g-PBMA3	41.9	84.03	40.2	148.34	156.56
PP-g-PBMA4	51.4	70.60	33.8	149.49	156.14

The molecular weights of PP and PBMA were 5000 and 2200, respectively. The crystallinity of the PP phase was compared to 209.08 J/g. T_{m1} is the first melting temperature, and T_{m2} is the second melting temperature. ΔH_m is the melt heat.

pendants and PP backbone posed no effect on the thermal stability in both air and N_2, indicating that the backbone structure was the overwhelming factor for thermal stability in air or N_2.

DSC thermograms of PP-g-PBMA

DSC thermograms of MPP and PP-g-PBMA with different PBMA contents are shown in Figures 7 and 8, and the parameters drawn from the curves are listed in Tables II and III. Grafting PBMA onto PP did not result in a significant change in the melting temperature of PP but did result in an increase in the crystallization peak temperatures. All the copolymers showed two melting peaks due to two crystalline structures, the α and β forms, similarly to that reported for PP.[18] It is important that the surface modifier could form a similar crystalline structure with the host polymers so that the surface modifier could incorporate with the host polymer to avoid easily coming off the surface. On the other hand, the PBMA pendants had an effect on the degree of crystallization of the copolymer. With increasing contents of PBMA in the copolymers, the degree of crystallization was reduced rapidly.

Surface modification of PP with PP-g-PBMA

PP-g-PBMA was blended with PP by solvent mixing, and then the blend melt was cast in a stainless steel mold at 190°C. The thickness of the cast film was about

TABLE III
DSC Cooling Temperatures and Crystallinity

Sample	PBMA (% w/w)	ΔH_m (J/g)	Crystallinity (%)	T_c (°C)
MPP	3.50	146.85	70.2	106.54
PP-g-PBMA5	13.8	94.57	45.2	112.62
PP-g-PBMA6	32.9	87.15	41.7	112.25
PP-g-PBMA7	41.9	79.81	38.2	112.87
PP-g-PBMA8	51.4	71.96	34.4	112.64

The molecular weights of PP and PBMA were 5000 and 2200, respectively. The crystallinity of the PP phase was compared to 209.08 J/g. T_c is the cooling temperature. ΔH_m is the melt heat.

100 μm. Transmission FTIR and ATR–FTIR were used to measure the concentration of PP-g-PBMA in the bulk and on the surface, respectively. On the basis of the ATR–FTIR principle, a surface layer of about 3 μm was involved. From the FTIR and ATR–FTIR spectra, the ratios of 1735 cm^{-1} to 1103 cm^{-1}, which represent the characteristic absorptions of PP-g-PBMA and PP, were used to express the concentration of PP-g-PBMA. The results are shown in Figure 9. The concentration of PP-g-PBMA on the surface was higher than that in the bulk, especially for the samples with a low concentration of PP-g-PBMA. This indicated that PP-g-PBMA could preferably diffuse to the surface of the blends and could be used as a surface modifier. The details of the use of graft copolymers as surface modifiers for polyolefin will be reported in another article.

Water contact angles have been shown to be very sensitive to the nature of the functional groups in a few angstroms of the upper layer on the surface for functionalized polymers. The functionalized PP in this work had essentially two types of functional groups: a polar portion contributed by the PBMA units and a nonpolar portion contributed by the PP units. The contact angles for the blending surface were uniformly much less than the contact angle found for the surface of pure PP (Table IV). This reflected a preferential
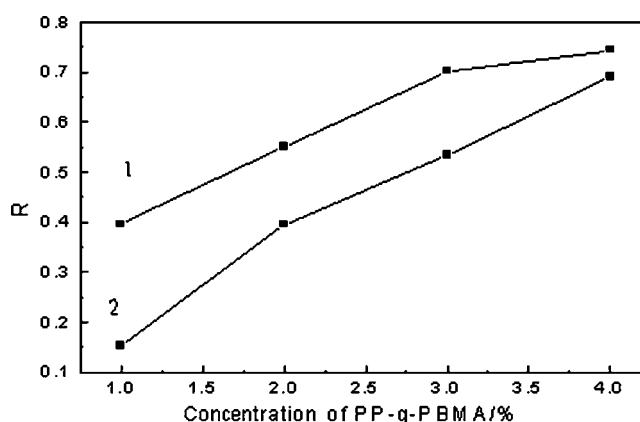

Figure 9 Surface modification of PP with PP-g-PBMA: (1) concentration of PP-g-PBMA on the surface and (2) concentration of PP-g-PBMA in the bulk.

TABLE IV
Contact Angles of PP/PP-*g*-PBMA Blend Films

Copolymer loading (wt %)	0	1	2	3	4
Contact angle (°)	119.8	101.7	96.9	95.2	95.2

migration of PBMA blocks to the contact-angle interface when the blend film was formed in the steel. Steel is a high-energy substrate, so PBMA was expected to be in contact with steel, and PP was expected to transfer to the inside of the film. The data of Table IV also show that there was an effect of the weight percentage of PP-*g*-PBMA. The contact angle gradually increased as the weight percentage of PP-*g*-PBMA decreased, and this was consistent with the results of ATR–FTIR, although various depth regimes are used for contact-angle and ATR–FTIR analysis techniques.

CONCLUSIONS

The results of FTIR and ^{1}H-NMR confirmed the grafting of PBMA-OH onto MPP. By the alteration of the reaction conditions, a series of PP-*g*-PBMA with different microstructures were obtained. The grafting of PBMA onto MPP did not change the melting temperature but increased the crystallization temperature of the copolymers. The temperatures of thermal and thermooxidative degradation of PP-*g*-PBMA were also influenced by the content of PBMA in PP-*g*-PBMA, but

they all exceeded 250°C, higher than that of the processing of PP. The results of ATR–FTIR and contact-angle measurements indicated that the PP-*g*-PBMA additive could preferably diffuse to the surfaces of blends and would be suitable as a novel surface modifier for PP.

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