

Influence of the Reaction Conditions on the Solid-State Graft Copolymerization of Methyl Methacrylate and Polyethylene/Polypropylene *In Situ* Alloys

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ABSTRACT: Graft copolymers of poly(methyl methacrylate) (PMMA) with spherical, high-porosity polyethylene (PE)/polypropylene (PP) *in situ* alloys were synthesized by a solid-state reaction. The effects of the amount of the free-radical initiator, the feed ratio of the methyl methacrylate (MMA) monomer, the reaction temperature, and the composition of the alloys on the grafting degree of PMMA were studied. A greater amount of the initiator and a higher reaction temperature led to a higher grafting degree. The grafting degree first increased with the feed ratio of MMA but leveled off at a higher feed ratio. The obtained graft copolymer was fractionated by temperature gradient extraction fractionation into six fractions, and each fraction was

characterized by Fourier transform infrared and differential scanning calorimetry. The structures of these fractions were ungrafted ethylene-propylene random copolymers and ethylene-propylene segmented copolymers, ethylene-propylene block copolymers having PE and PP segments of different lengths and grafted by PMMA, PP grafted by PMMA, and nearly pure PP. Most PMMA was grafted on propylene segments, and thus the grafting degree decreased as the content of ethylene units in the alloys increased. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 195–202, 2005

Key words: alloys; copolymerization; polyethylene (PE); poly(propylene) (PP)

INTRODUCTION

Polyolefins are a class of important commercial plastics with excellent processability and relatively low cost. However, polyolefins exhibit poor compatibility with other resins because of their nonpolarity. For the same reason, polyolefins have poor adhesion, printing, and dyeing properties. This limits their applications.

To improve the properties of polyolefins, polar polymer units are usually grafted to them. Such graft copolymerizations are usually conducted by a solution process,^{1,2} a melt process,^{3,4} or a solid-state graft copolymerization process.^{5–9} A lot of solvent is used in the solution process to dissolve polyolefins, and this is not friendly to the environment. The melt process also has two shortcomings: a high reaction temperature results in the degradation of polyolefins and greater power consumption. In contrast, the solid-state graft copolymerization process can be carried out at comparatively low temperatures and atmospheric pressure. However, in the traditional solid-state graft copolymerization process, a toxic interfacial agent such as benzene, toluene, or xylene is still needed to enhance the specific surface area that can contact the polar monomer.

Currently, polyolefin alloys can be produced *in situ* by means of a multiple-reactor technique and a spherical catalyst technique. Polyolefin *in situ* alloys based on this technique usually have excellent mechanical properties with respect to both toughness and stiffness. Another very important characteristic of polyolefin *in situ* alloys is their high porosity (from 10 to more than 40 vol % of the alloys). Such characteristics make polyolefin *in situ* alloys especially suitable for graft copolymerization with polar monomers through a solid reaction because the specific surface area of polyolefin *in situ* alloys is sufficient for contact with polar monomers and no interfacial agent is needed. Nevertheless, to the best of our knowledge, so far there is no open literature reporting the graft copolymerization of a polyolefin *in situ* alloy with a polar monomer yet. The objective of this work was to develop an efficient and low-cost process to produce a methyl methacrylate (MMA) grafted copolymer of a polyolefin *in situ* alloy. The reaction conditions of the solid graft copolymerization, including the amount of the free-radical initiator, the feed ratio of the MMA monomer, the reaction temperature, and the composition of the polyolefin alloys, were studied.

EXPERIMENTAL

Preparation of the polyethylene (PE)/polypropylene (PP) *in situ* alloys

Prepolymerization was first carried out by the homopolymerization of propylene at atmospheric pres-

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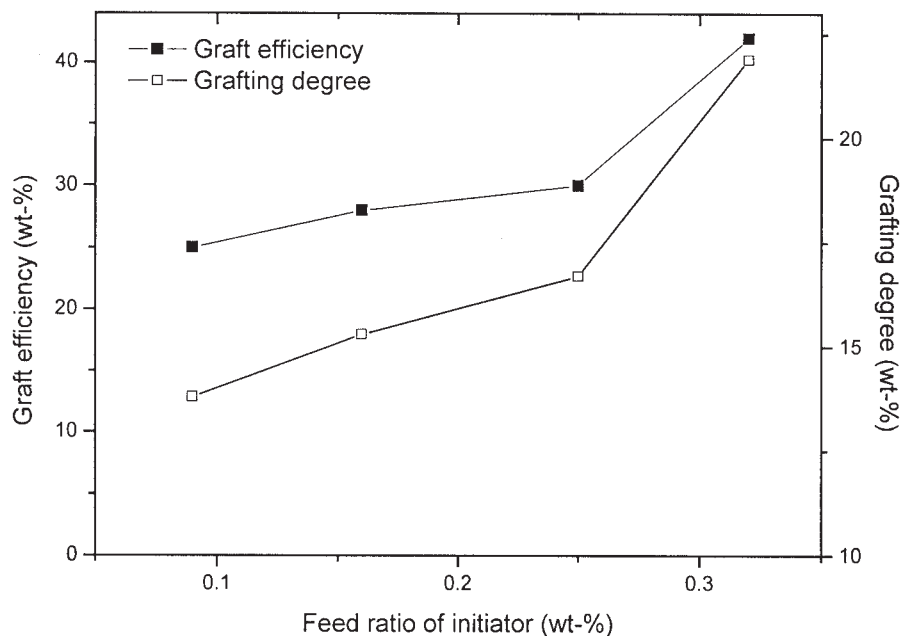


Figure 1 Effect of the amount of the initiator on the grafting degree at 114°C with 4 mL (3.776 g) of MMA.

sure in a well-stirred flask bottle containing 40 mL of petroleum ether (60–90°C) at 50°C for 30 min. A high-yield, spherical $\text{TiCl}_4/\text{MgCl}_2 \cdot \text{ID}$ (ID = internal donor) catalyst (DQ-1, kindly donated by the Beijing Research Institute of Chemical Industry, Beijing, China) was used in the polymerization, with $\text{Al}(\text{C}_2\text{H}_5)_3\text{-Ph}_2\text{Si}(\text{OCH}_3)_2$ as a cocatalyst (Al/Ti = 60, Al/Si = 25).

The product obtained in the prepolymerization stage was then transferred into a 0.5-L jacketed Büchiglasuster reactor (Flawil, Switzerland) with a helical tape stirrer to ensure good mixing inside the reactor. Moreover, 50 mL of petroleum ether was added for every experiment to prevent prepolymerized particles from sticking to one another and to the reactor wall. A pressurized two-stage polymerization was then conducted: the first stage was ethylene homopolymerization in a nearly gas-phase mode at 60°C and 0.6 MPa for 60 min, and the second stage was successive gas-phase propylene homopolymerization at 60°C and 0.8 MPa for 120 min. In the first stage, spherical PE granules 0.5–2.5 mm in diameter were produced, and residual ethylene in the particles was completely removed before propylene was fed into the reactor. The porosity of the polymer particle thus obtained was 47 vol %.

Graft copolymerization of MMA and the alloy

MMA was distilled after being washed with a sodium hydroxide solution and stored in refrigerator. Benzoyl peroxide (BPO), used as a free-radical initiator, was purified by recrystallization.

A 50-mL, round-bottom flask was purged with nitrogen, and 5 g of PE/PP alloy particles and half of the prescribed amount of MMA was introduced into the reactor; then, the mixture was heated to the designated temperature. Vigorous shaking was applied to mix the reactant thoroughly. BPO was dissolved in the remaining MMA. When the reaction system reached the designated temperature, a mixture of BPO and MMA was added to the reactor. The shaking of the flask was continued until the copolymerization was finished.

The reaction product was extracted with vinyl acetate for 24 h. The extracted polymer was dried in a vacuum oven for 4 h.

Fractionation of the graft copolymer

A modified Kumagawa extractor was used to carry out temperature gradient extraction fractionation (TGEF) of the polymer.¹⁰ *n*-Octane was used as the solvent to successively extract the sample at different controlled temperatures (room temperature, 90, 110, and 120°C). Five fractions were collected by the extraction of 2 g of each sample at 25, 90, 110, 120, and >120°C, and they were named fraction A, fraction B, fraction C, fraction D, and fraction E, respectively. Purified fractions were obtained after the concentration of the extract solutions, precipitation of the polymer, and washing and drying of the fractions *in vacuo*. Then, fraction E was further extracted with propanoic acid at 120°C. The part dissolved by propanoic acid at 120°C was named fraction F, and the remaining polymer was named fraction G.

Thermal analysis

Differential scanning calorimetry (DSC) analysis of the fractions was performed on a PerkinElmer Pyris 1 thermal analyzer (Wellesley, MA) under a high-purity nitrogen atmosphere. An approximately 4-mg sample was sealed in an aluminum crucible, melted at 180°C for 5 min, and then successively annealed at 130, 120, 110, 100, 90, 80, 70, and 60°C, each for 12 h. Then, the DSC scan was recorded at a heating rate of 5°C/min from 30 to 180°C.

Scanning electron microscopy (SEM) analysis

The intersection morphology of the PE/PP *in situ* alloy particle and its grafted copolymer was observed with a JSM T20 scanning electron microscope (Tokyo, Japan).

Fourier transform infrared (FTIR) analysis

FTIR spectra of the alloys, copolymers, and their fractions were recorded on a Bruker Vector 22 FTIR spectrometer (Karlsruhe, Germany). A thin film of the sample was prepared by hot pressing.

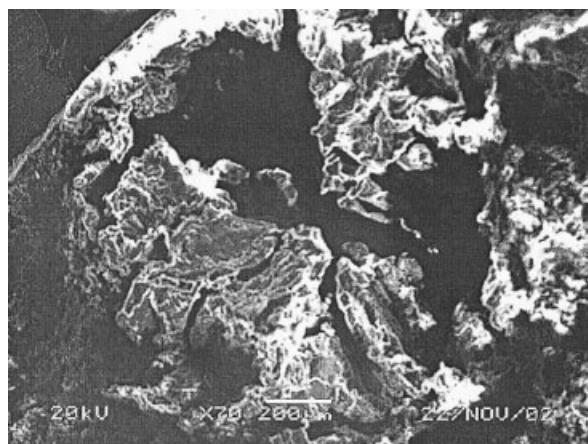
RESULTS AND DISCUSSION

Effect of the initiator amount

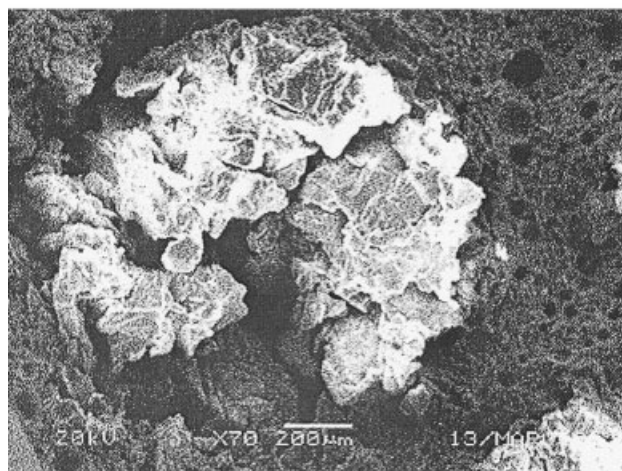
The influence of the initiator concentration on the grafting degree [expressed as the weight percentage of grafted poly(methyl methacrylate) (PMMA) in the (PE/PP)-*g*-PMMA product] is shown in Figure 1. The degree of grafting was 21.9 wt % when the initiator concentration was 0.32 wt % (weight percentage of BPO to the PE/PP *in situ* alloy). Obviously, an adequate increase is beneficial for initiating more MMA grafting on the chain of PE/PP *in situ* alloys.

The intersection morphology of the PE/PP *in situ* alloy and its grafted copolymer is shown in Figure 2. The PE/PP *in situ* alloy used in this work indeed has very high porosity. After graft copolymerization, the particle was not broken, and the spherical outer shape was retained. However, the color of the particle turned from white to ivory-white, and the morphology of the internal part of the particle changed sharply. It became compact, and the porosity of the particle decreased from 47 to 21 vol %. Obviously, the graft copolymerization mainly occurred in the hole inside the particle and the tiny pores in the shell. Therefore, the porosity of the particle is an important factor that influences the upper limit of the grafting degree.

The graft polymer samples extracted by ethyl acetate were analyzed by infrared spectroscopy. A typical FTIR spectrum of a sample is shown in Figure 3. Four distinct peaks can be observed in the FTIR spectra, which clearly identify the presence of PMMA in the copolymer. The strong band at 1730 cm⁻¹ confirms the



(a) PE/PP alloy



(b) PE/PP alloy grafted by PMMA

Figure 2 SEM micrographs of the intersection morphology of (a) the PE/PP alloy particle and (b) its grafted copolymer.

presence of carbonyl groups of MMA in the grafted polymer. The bands at 1268, 1240, 1190, and 1150 cm⁻¹ indicate the presence of C—C—O—C groups. Because the copolymer was extracted by ethyl acetate, it is clear that the PMMA peaks identified in the infrared spectrum come from the copolymer, not from the PMMA homopolymer.

Effect of the reaction temperature

The effect of the temperature on the grafting degree is presented in Figure 4. The grafting degree increased from 16.7 to 29.6 wt % when the reaction temperature increased from 108 to 120°C. The effect of temperature on the graft copolymerization can be considered two-fold. On the one hand, raising the reaction temperature can speed up the polymerization of MMA. On the other hand, a high temperature promotes the swelling of the PE/PP alloy particle, and more MMA can enter

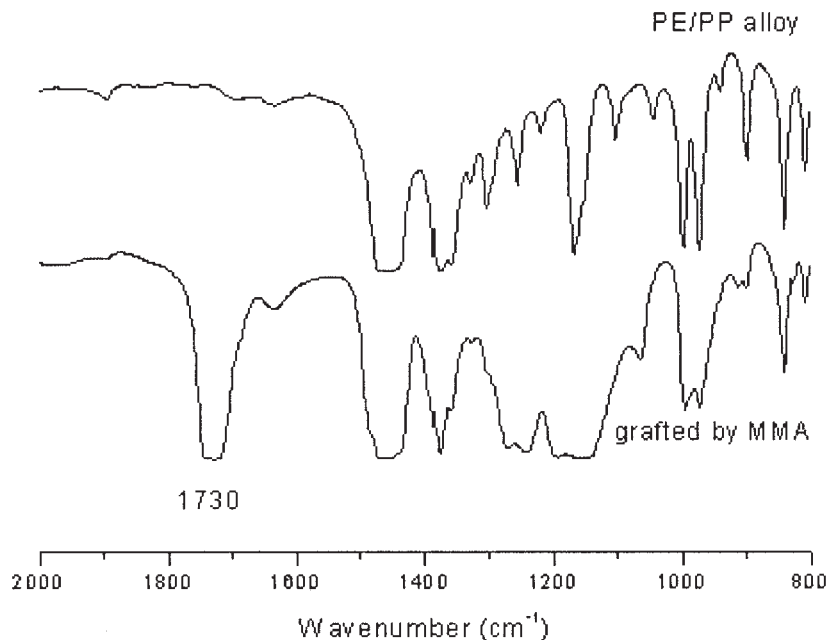


Figure 3 FTIR spectra of the PE/PP *in situ* alloy without and with PMMA.

the pores of the particles and react with the polyolefin chains. Therefore, the reaction temperature has a strong effect on the grafting degree.

Effect of the feed ratio of MMA

The effect of the MMA feed ratio on the grafting degree is shown in Figure 5. There is a maximum in the profile at 75 wt % (weight percentage of MMA to

the alloy), which may result from two competitive reactions: the graft copolymerization of MMA with the PE/PP alloy and the homopolymerization of MMA. At low levels of the MMA feed ratio (≤ 75 wt %), the internal surface area of the PE/PP alloy particles is large enough to absorb most of the MMA monomer, so the graft copolymerization is the main reaction, and more MMA leads to a higher grafting degree. However, at high levels of the MMA feed ratio, the

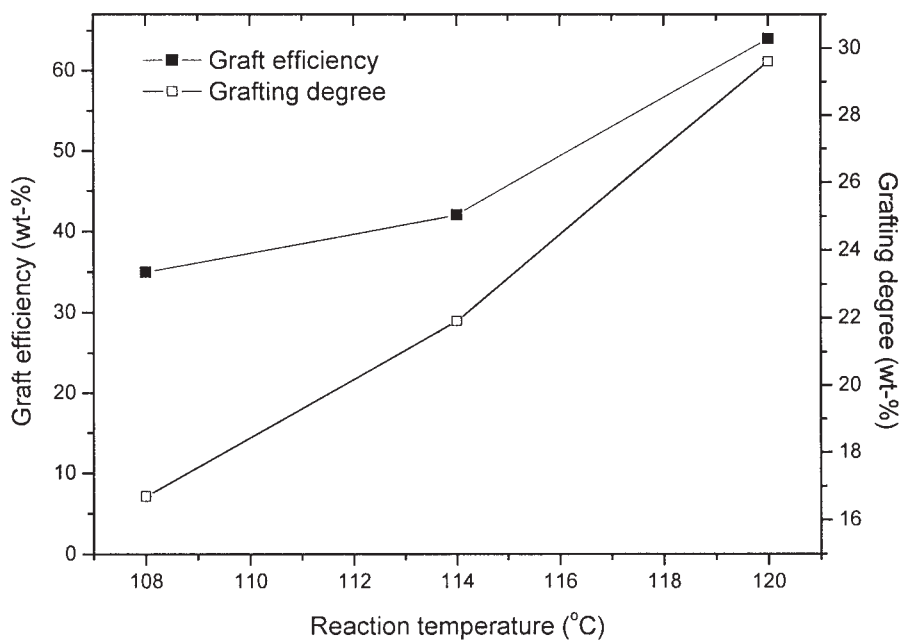


Figure 4 Effect of the reaction temperature on the grafting degree with 0.32 wt % initiator and 4 mL of MMA.

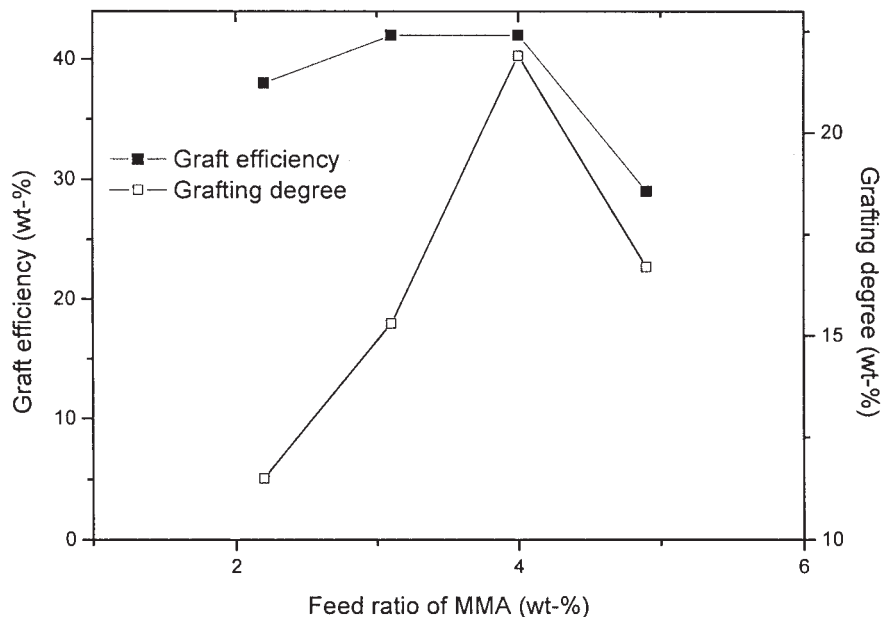


Figure 5 Effect of the feed ratio of MMA on the grafting degree at 114°C with 0.32 wt % initiator.

homopolymerization of MMA becomes the dominant reaction because much of the MMA molecule cannot reach the polyolefin chains. Therefore, the graft efficiency drops at a high MMA feed ratio.

Effect of the composition of the PE/PP *in situ* alloys

A series of polyolefin particles was used in the solid-state graft polymerization to investigate the effect of

the matrix composition on MMA grafting. The matrix materials included PE, PE/PP alloys of different ethylene contents, and PP. As shown in Figure 6, the grafting degree decreased with an increase in the ethylene content. The difference between the ethylene unit and propylene unit is that there is a tertiary carbon on the propylene unit. Because tertiary radicals can be generated by the initiator more easily than secondary radicals, PMMA was mainly grafted on the propylene unit.

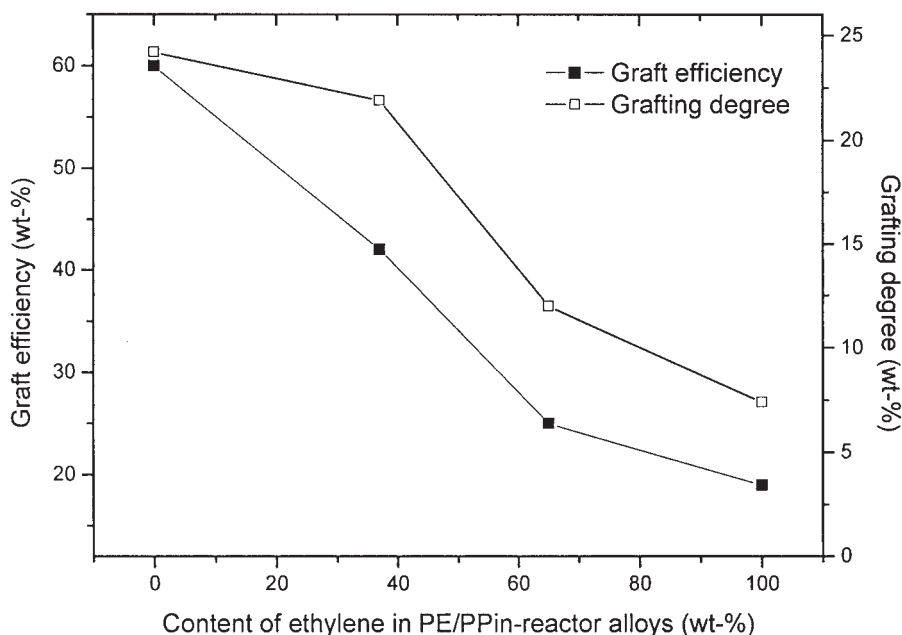


Figure 6 Effect of the composition of the alloys on the grafting degree at 114°C with 0.32 wt % initiator and 75 wt % MMA.

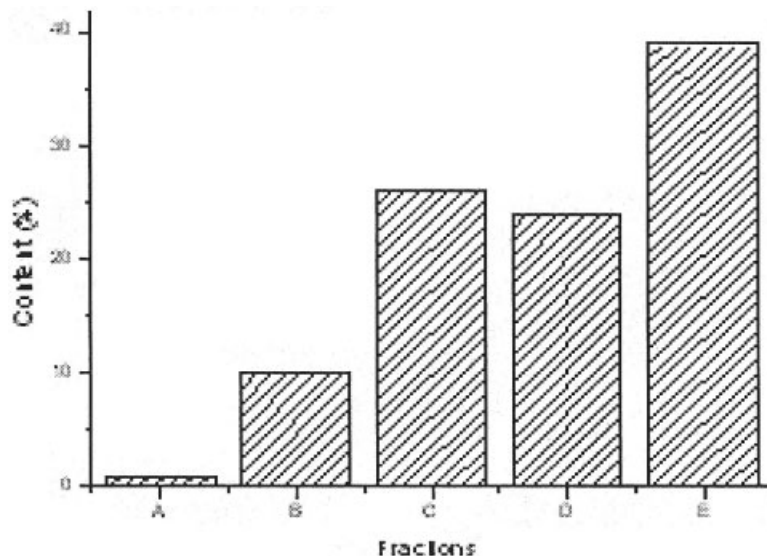


Figure 7 Fraction distribution of the PMMA grafted copolymer.

Fractionation of the MMA graft copolymer

In our previous study,¹¹ we found that PE/PP *in situ* alloys could be fractionated into five fractionations: an ethylene-propylene random copolymer (25°C), an ethylene-propylene segmented copolymer (90°C), PE (110°C), a PE-*b*-PP block copolymer (120°C), and PP ($\geq 120^\circ\text{C}$). To understand the structure of the graft copolymer and the mechanism of graft copolymerization, we fractionated one typical graft copolymer into five fractions by TGEF. The result is shown in Figure 7. The amount of fraction A is very low (1 wt %), whereas the amount of fraction E is as high as 39 wt %. In other words, fraction E is the main component of the graft copolymer. The fractionation results show us that the composition distribution of the graft copolymer is not uniform. Considering that PMMA is a polar polymer that cannot be dissolved in the nonpolar *n*-octane, we further fractionated fraction E into two fractions, fractions F and G. The results show that about 90 wt % of fraction E exists in fraction F, which is soluble in boiling propanoic acid.

FTIR analysis of the fractions

To clarify the structure of each fraction, FTIR spectroscopy analysis was performed on all samples. Figure 8 shows that there is no absorption or very weak absorption at 1730 cm^{-1} in the spectra of fractions A and B. However, the bands at 1730 cm^{-1} in the spectra of fractions C–E are strong, and that in fraction E is the strongest. This finding shows that there is little or no PMMA in fractions A and B, and most PMMA is in fractions C–E, especially in fraction E. We found that the PE/PP *in situ* alloy could be fractionated into five fractionations.⁵ Through FTIR analysis, we have con-

cluded that fraction A is an ethylene-propylene random copolymer, fraction B is an ethylene-propylene segmented copolymer, and fractions C and D are ethylene-propylene block copolymers grafted by PMMA. Figure 9 shows the FTIR spectra of fractions F and G. From the spectra, we know that fraction F is PP grafted by PMMA and that fraction G is mainly pure PP. This result indicates that PMMA is mainly grafted on the propylene unit, in agreement with the conclusion drawn from the effect of the matrix composition on the grafting degree.

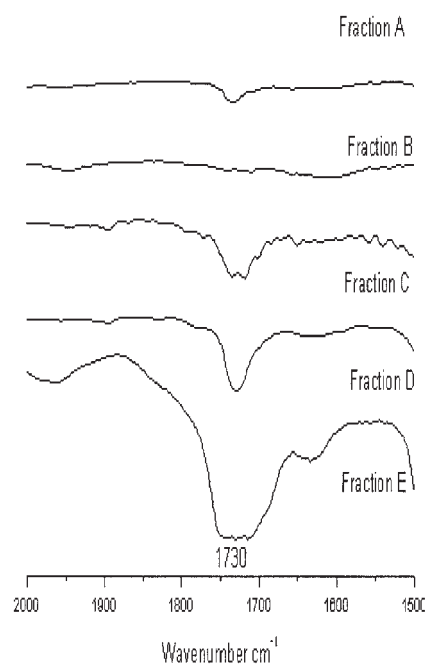


Figure 8 FTIR spectra of fractions A–E.

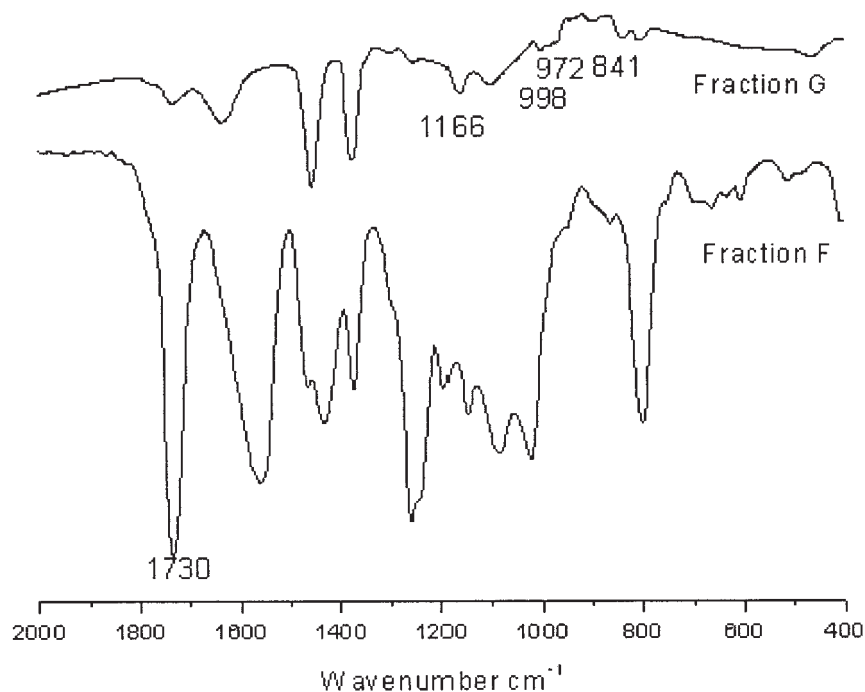


Figure 9 FTIR spectra of fractions F and G.

It becomes quite clear that the graft copolymer is composed of five components: (1) an ungrafted ethylene-propylene random copolymer, (2) an ungrafted ethylene-propylene segmented copolymer, (3) an ethylene-propylene block copolymer having PE and PP segments of different lengths and grafted by PMMA, (4) PP grafted by PMMA, and (5) nearly pure PP.

Thermal analysis of the fractions

A thermal analysis of the annealed samples was also conducted to verify the chain structures of the different fractions. Multistep annealing of the samples ensures that PE and PP segments of different lengths form lamellae of different thicknesses, and thus the DSC melting curve can reflect the presence of these different lamellae. As shown in Figure 10, the DSC melting curves of fractions B–E are very different from one another. Fraction B shows several endothermic peaks in the range of 129–164°C. The peak at 129°C is strong. This endotherm is mainly caused by the melting of PE lamellae. This means that the PE segments in this fraction are long enough to form crystals. The peaks at higher temperatures are comparatively weak. These endotherms are mainly caused by PP lamellae of relatively low thickness, and they show that the PP segments in this fraction are long enough to form crystals but there are also many short PP segments, as the fusion enthalpy is much smaller than that of a PP homopolymer. From this, we can deduce that fraction

B is an ethylene-propylene segmented copolymer with long PE segments.

The DSC curve of fraction C shows two melting peaks at temperatures close to the melting temperatures of PE and PP. However, the peak at 166°C is weak. On the basis of the results of FTIR analysis, it can be said that this fraction is mainly composed of a PE-*b*-PP block copolymer with PP and very long PE segments grafted by PMMA.

The melting curve of fraction D shows two melting peaks at temperatures similar to those of PE and PP, respectively. This means that the PE and PP segments in this fraction can form perfect crystals independently. On the basis of the results of FTIR analysis, it can be said that this fraction is mainly composed of a PE-*b*-PP block copolymer with very long PE and PP segments grafted by PMMA. The weak endothermic peak around 140°C may be due to the grafted PP segments, as the presence of PMMA branches may influence the crystallization of PP segments.

Finally, in the melting curve of fraction E, there is no melting peak in the temperature range of PE melting, and the peak in the temperature range of PP melting is very weak and shows a broad shoulder. From this fact, we can say that the PE segment is not long enough to form crystals. The PP segments in this fraction are long, but their crystallization is seriously hindered by the high level of MMA grafting. On the basis of the results of FTIR analysis, it may be said that fraction E is mainly composed of a PE-*b*-PP block copolymer with long PP segments and very short PE segments,

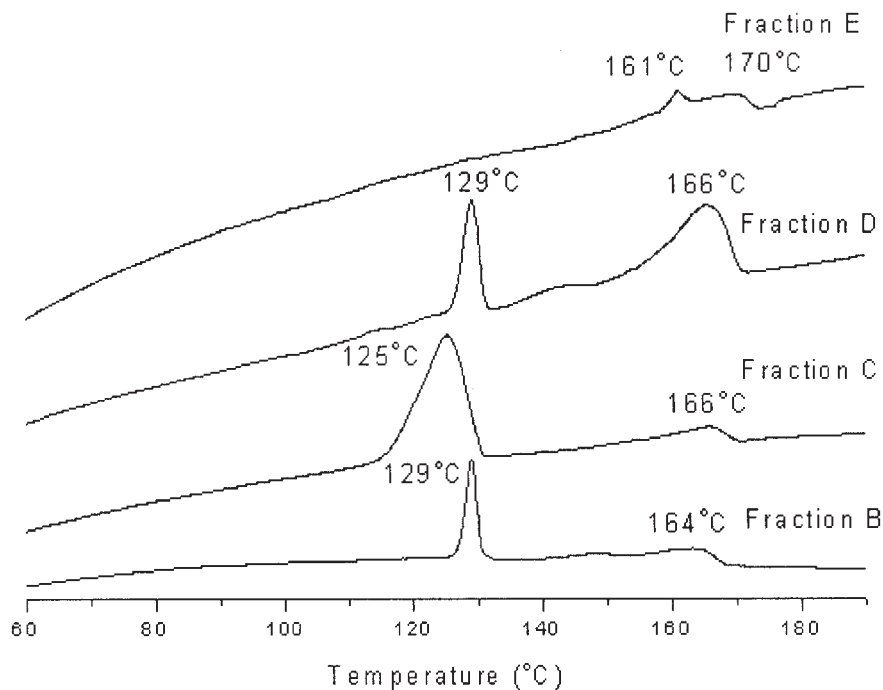


Figure 10 DSC analysis of fractions of the graft copolymer.

and the PP segments are densely grafted by PMMA branches.

CONCLUSIONS

By the free-radical initiated solid-state graft copolymerization process, a high level of MMA (11.5–29.6 wt % based on the grafting product) can be grafted to PE/PP *in situ* alloy spherical particles. This reaction uses no solvent or interfacial agent and can be performed at relatively low temperatures (100–120°C) and at atmospheric pressure.

By studying the effects of the reaction conditions on the grafting degree, we have found that the reaction temperature, the amount of the initiator, the feed ratio of MMA, and the chemical composition of the PE/PP alloy are all key factors influencing the grafting degree. A high initiator amount, a high PP segment content in the alloy, and especially a high reaction temperature are favorable to the grafting reaction. Under favorable conditions, a grafting degree as high as 29.6 wt % can be reached.

The graft copolymer has been fractionated by TGEF into six fractions, and each fraction has been characterized by FTIR and DSC. The graft copolymer is composed mainly of five components: (1) an ungrafted ethylene–propylene random copolymer, (2) an ungrafted ethylene–propylene segmented copolymer, (3) ethylene–propylene block copolymers having PE and PP segments of different lengths and grafted by

PMMA, (4) PP grafted by PMMA, and (5) nearly pure PP. PMMA is predominantly grafted on the propylene segments.

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