Styrene-Assisted Free-Radical Graft Copolymerization of Maleic Anhydride onto Polypropylene in Supercritical Carbon Dioxide

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ABSTRACT: The free-radical graft copolymerization of maleic anhydride (MAH) onto polypropylene (PP) with the assistance of styrene (St) in supercritical carbon dioxide (CO_2) was studied. The effects of the St concentration and initiator concentration on the functionality degree of the grafted PP in supercritical CO_2 were investigated. The addition of St drastically increased the MAH functionality degree, which reached a maximum when the molar ratio of MAH and St was 1:1. St, an electron-donating monomer, could interact with MAH through charge-transfer complexes to form the St–MAH copolymer (SMA), which could then react with PP macroradicals to produce branches by termination between radicals. There was SMA in the grafting reaction system characterized by Fourier transform infrared and differential scanning calorimetry. Furthermore, the highest MAH functionality degree was obtained when the concentration of 2,2'-azobisisobutyronitrile (AIBN) was 0.6 wt % based on PP. The effects of the temperature and pressure of supercritical CO_2 on the functionality degree of the grafted PP were analyzed. An increase in the temperature accelerated the decomposition rate constant of AIBN, thereby promoting the grafting reaction. In addition, an increase in the temperature increased the diffusion of monomers and radicals in the disperse reaction system of supercritical CO_2. The highest degree of functionality was found at 80°C. Also, the functionality degree of grafted PP decreased with an increase in the pressure of supercritical CO_2 within the experimental range. The morphologies of pure PP and grafted PP were significantly different under polarizing optical microscopy. The PP spherulites were about 38 μm in size, and the grafted PP spherulites were significantly reduced because of heterogeneous nucleation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 853–860, 2003

Key words: radical polymerization; poly(propylene) (PP); functionalization of polymers

INTRODUCTION

Polypropylene (PP) has been one of the fastest growing polymers in recent decades because of its intrinsic properties, low cost, and versatility. Its applications have spread to areas formerly restricted to other polymers, such as the automobile market. The use of PP in the automobile industry is due to the growing trend toward PP composites and expanded PP as substitutes for engineering plastics and polyurethane, respectively.

However, the hydrophobic nature and lack of polar sites of PP restrict its applications in systems composed of polar polymers and inorganic fillers.[1,2] The functionalization of PP with polar monomers has been performed so that it can be used as a third component in blends of PP and polar polymers and in composites of PP and inorganic fillers. The free-radical melt grafting of maleic anhydride (MAH) onto PP has become a widely used postpolymerization method for functionalizing the material. MAH has some advantages over other monomers because of the difficulty in homopolymerizing it due to the deficiency of electrons in the double bond.[3,4] However, the radical melt grafting of MAH onto PP in the presence of an initiator is often accompanied by severe degradation of the PP backbone. An analysis of MAH-modified PP has shown that MAH is usually grafted onto the PP chain ends[5] and that the grafted MAH is present as single MAH.[6] Recently, it was shown that the addition of styrene (St) as a second monomer in the melt grafting system assisted in increasing the grafting degree of MAH on PP.[7] Because MAH is not sufficiently reactive toward PP macroradicals, it would be helpful to use a second monomer that can react with them much faster than MAH, and the resulting free radicals could then copolymerize readily with MAH. The comonomer (St) serves as a medium to bridge the gap between the PP macroradicals and the MAH monomer. It has been proposed that, in the aforementioned system, St preferentially reacts with the PP macroradicals to form more stable St macroradicals, which then copolymerize with MAH to form branches.

It has also been well established that a free-radical grafting process starts with the formation of macro-

radicals along the PP chains by a so-called hydrogen abstraction mechanism.[8] These macroradicals may subsequently follow two competing pathways. They can either initiate the grafting of monomers or undergo chain scission, which is the main side reaction at higher temperatures. In a study of the high-temperature grafting of St and MAH onto PP, Gaylord[9] concluded that the predominant graft structure consists of single St–MAH copolymer (SMA) units. It might be anticipated that the length of the polymer side chain would be dependent on the temperature and the concentration of MAH. The ceiling temperature for the polymerization of $5M$ MAH in benzene has been determined to be about 150°C.[10] Long chains could only be formed at relatively low temperatures and with high concentrations of MAH.

The objective of this investigation was to exploit supercritical carbon dioxide (CO_2) as a medium of graft copolymerization of MAH onto PP with the addition of St as a second monomer. Supercritical graft copolymerization is advantageous for several reasons. CO_2 is nontoxic, nonflammable, and inexpensive. The temperature of the graft copolymerization of MAH onto PP can be controlled between 60 and 90°C, much lower than that of melt-grafting technology. Supercritical CO_2 causes considerable polymer swelling and significant depression of the polymer glass-transition temperature. Mass transfer in a supercritical medium is very high. In addition, because of the unique properties of supercritical CO_2, the solvency of the medium can be controlled through changes in the density of the reaction medium through temperature and pressure profiling. This is in contrast to conventional systems for which mixed solvents are used to tune the solvency of the reaction medium.[11] In addition, the application of supercritical CO_2 fluid provides significant economic and social benefits for environmental protection and energy conservation.

EXPERIMENTAL

Materials

The PP powder used in this study was supplied by Shanghai Petrochemical Co., Ltd., with a melt-flow index of 16 g/10 min. The MAH monomer (analytical-grade), St monomer (analytical-grade), and 2,2′-azobisisobutyronitrile (AIBN) initiator (chemical-grade) were commercially available from Shanghai Chemical Co. MAH was finely ground and stored in a sealed container under dry nitrogen. St was washed with a 10% NaOH aqueous solution to remove the inhibitors and then was washed with distilled water. It was then dried over anhydrous $MgSO_4$ and finally distilled under a near-vacuum condition. It was stored at −75°C before use. AIBN was recrystallized twice from ethanol. Commercial xylene and acetone were distilled before use. Analytical-grade CO_2 (99.9%) was obtained from Air Product Co.

Experimental instrumentation

The main part of the experimental unit was a high-pressure, 0.5-L stainless steel reactor with bolt closure. The CJF-05 high reactor, manufactured by Da Lian Tongda Autoclave, Inc., had a maximum working pressure of 40 MPa and a maximum working temperature of 320°C; it was fitted with a rupture disk rated at 20 MPa. The reactor was equipped with an impeller, which was magnetically coupled to an external shaft with a V-belt pulley to provide it with a stable rotational speed and was controlled by an AI-708 intelligence controller. A flexible heating wire tape was wrapped around the reactor to provide it with uniform heat, and it was controlled by the AI-708 intelligence controller. The thermocouple of the controller reached 20 cm down inside the reactor. The reactor was insulated with an insulated blanket. A cold trap was installed at the outlet of the reactor to capture the unreacted monomer in the effluent. A high-pressure metering pump was used to inject CO_2 through a shutoff valve into the reactor. The pump (2JX, Hangzhou Zhijiang Scientific Instrument Co.) was designed to deliver liquid against a pressure of 30 MPa, and it had a flow rate of 12.6 L/h.

Experimental procedure

First, preweighed amounts of the PP, monomer, and initiator were charged into the high-pressure reactor. The reactor was closed and was vacuumed to remove the air inside. CO_2 was pumped into the reactor at 40°C. The impeller was turned on, and the temperature and pressure of the reactor were increased to the desired value.

The reaction time was 4 h. The temperature was varied between 60 and 90°C. The decomposition rate constant of AIBN in supercritical CO_2 had different values depending on the temperature and pressures. The half-life time of the initiator for the experiments was between 10 and 18 h. The reaction pressure was varied from 8 to 14 MPa. The molar concentration ratio of St to MAH was varied from 0 to 1.5. The AIBN concentration was varied from 0.2 to 0.8 wt % based on PP. When the reaction ended, opening the outlet valve depressurized the high-pressure reactor. The effluent was passed through the cold trap to capture the monomer dissolved in CO_2, and the gas was vented into the atmosphere.

Purification and characterization of grafted PP

The reaction product consisted of mixtures of the grafted copolymer [i.e., PP-g-MAH, PP-g-St, and PP-
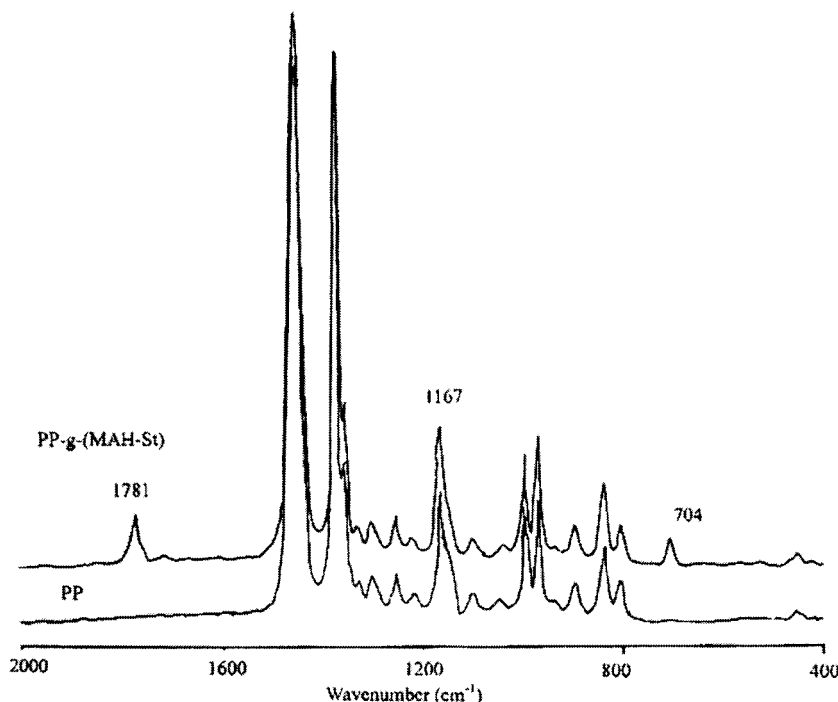
Figure 1 FTIR spectra of PP and PP-*g*-(MAH–St) (functionality degree = 0.92 wt %).

g-(MAH–St)], the ungrafted polymer (PP), the homopolymer of the monomer, the copolymer of MAH and St, and the unreacted monomer. The product was dissolved in refluxing xylene at a concentration of 0.8% (w/v) at 120°C, and excess acetone was then added to precipitate it. Acetone could precipitate only the grafted and ungrafted PP. By this procedure, any homopolymer and copolymer of MAH and St and unreacted monomer were separated. The precipitated samples were filtered, washed, and dried *in vacuo* at 70°C for 48 h. They were subsequently characterized with Fourier transform infrared (FTIR). FTIR spectroscopy was used for qualitative and quantitative identification of grafting onto PP. The measurement was made on an IFS28 FTIR spectrometer system (Bruker Co., Germany). Any given sample was melted into a thin film. The film was then subjected to FTIR measurements. In some cases, the filtrate left after the purification process was also analyzed. Solvents such as acetone and xylene were evaporated from the remaining filtrate until a white powder was obtained, which was then vacuum-heated at 70°C for 24 h. FTIR spectra were recorded from thin flakes compressed with a mixture of the obtained powder and analytical-grade KBr powder. A PerkinElmer Co. Pyris 1 differential scanning calorimetry (DSC) analyzer was used for thermal analysis. The instrument was calibrated with indium. All runs were made in a dry nitrogen atmosphere at a heating rate of 5°C/min from room temperature to 200°C. Polarized hot-stage optical microscopy (PHSOM) was performed. Polymer specimens were cut with a microtome and mounted on

glass slides. The specimens were heated to 200°C for 2 min, cooled to 100°C at 5°C/min, and kept there for 4 h at 100°C. PHSOM was observed with a camera. The PHSOM images were used to study the morphology and nucleation.

FTIR analysis

The FTIR spectra of the pure PP and grafted PP after purification [PP-*g*-(MAH–St)] are shown in Figure 1. The new absorption due to the phenyl group in the grafted St appears at 704 cm^{-1}, and the absorption due to the carbonyl group in the grafted cyclic anhydride appears at 1781 cm^{-1}. The peaks can clearly be seen in a comparison of spectra of the homopolymer PP and PP-*g*-(MAH–St). The absorptions at 1167 cm^{-1} can be assigned to the characteristic absorption of CH_3 groups, proportional to the amount of the PP skeleton. The absorbance ratio of the areas of the bands at 1781 (A_1) and 1167 cm^{-1} (A_2; internal reference) shows the relative degree of functionalization.

Determination of the MAH functionality degree of grafted PP

The amount of grafted MAH was determined by the titration of the acid groups after the complete hydrolysis of the anhydride groups. In a typical procedure, 0.5 g of purified and functionalized PP was dissolved in 80 mL of water-saturated xylene at 100°C. The system was kept refluxing for 1 h, and then it was hot-titrated with 0.02N ethanolic KOH with phenolphthalein as an indicator.
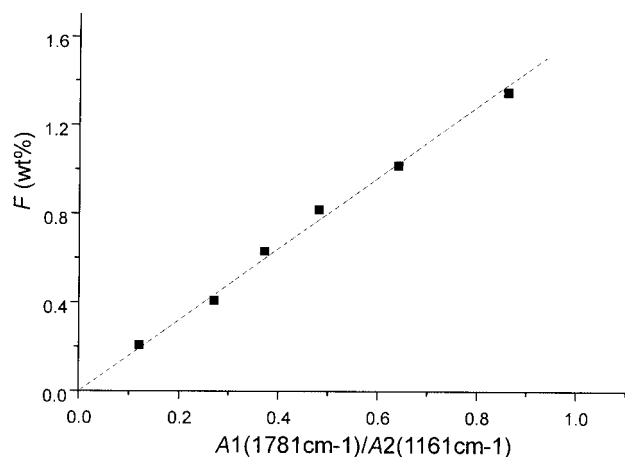
Figure 2 Calibration curve for absolute functionality degree (F) determination (relevant coefficient = 0.9974).

The plot of the functionality (wt %, obtained by titration) against A_1/A_2 (absorbance ratios from FTIR) shows a linear relation (Fig. 2). This graph has been used as a product calibration curve to determine the absolute functionality degree. The functionality degree reported in this article was obtained by the interpolation of the FTIR ratio (A_1/A_2) in the plot.

RESULTS AND DISCUSSION

Effect of the St concentration on the functionality degree of grafted PP in supercritical CO_2
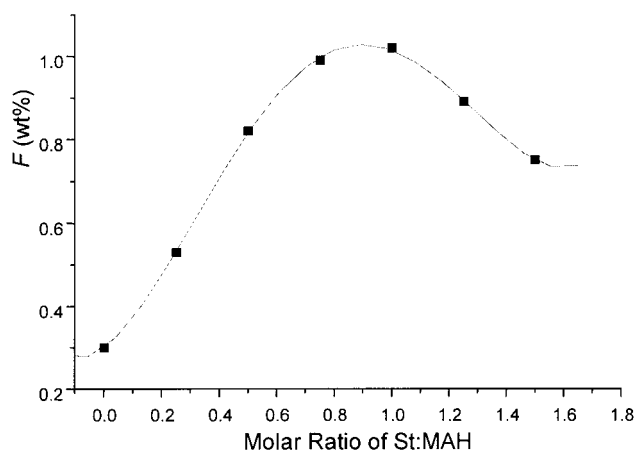
Figure 3 shows the effect of the St concentration on the functionality degree of the grafted PP. When the MAH and AIBN concentrations were fixed at 10 and 0.6 wt %, respectively (based on PP), the supercritical reaction time was 4 h, the reaction temperature was 80°C, and the pressure remained at 8 MPa. The MAH grafting degree of the resulting polymer was drastically higher in the presence of St than in the absence of St. It reached a maximum when the molar ratio of MAH and St was about 1:1 and then decreased when the concentration of St was higher than that of MAH.

Mechanism of the St-assisted free-radical grafting of MAH onto PP in supercritical CO_2

For the free-radical grafting system of MAH with PP in supercritical CO_2 in the absence of St, the grafting degree of MAH is very low because of the low free-radical reactivity of MAH toward radical reactions. This is inherently due to its structural symmetry and deficiency of electron density around the double bond.[12] Much of the MAH monomer added is grafted onto PP chain ends after PP undergoes chain scission.[5] It is conceivable that the presence of a monomer capable of donating electrons could activate MAH by rendering its structure unsymmetrical and its bond of

radical–anion character. St is an electron-donating monomer; it can interact with MAH through charge-transfer complexes (CTCs) and copolymerize with MAH alternatively under certain conditions.[13] It can be proved from Figure 3 that the MAH functionality degree of the 1:1 MAH/St series was the highest (because the molecular weight of St was 105 and the molecular weight of MAH was 98, it was assumed that the molar concentration ratio was equal to the weight concentration ratio of MAH and St). When equimolar amounts of MAH and St were added to the grafting system, St and MAH could interact with each other to form a CTC, which could then react with PP macro-radicals, producing branches by termination between the radicals. Therefore, the functionality degree of MAH could be improved significantly. When the St concentration was less than the MAH concentration (e.g., for the 1:0.5 MAH/St series), the amount of the resulting MAH–St copolymer was less, so the functionality degree of MAH was also less than that for the 1:1 MAH/St series. When more St than MAH was added to the grafting system, part of the St monomer reacted with MAH to form the SMA copolymer. Other St monomers could preferentially react with PP chain macroradicals to produce relatively stable styryl macroradicals, thereby partially depressing PP degradation. Because of the stability of the latter macroradicals, their further reaction with the SMA copolymer would be difficult. As a result, the MAH functionality degree of the resulting material was lower than that of the 1:1 MAH/St series.

If the aforementioned mechanism is true for the system of MAH–St grafting onto PP, there should be some ungrafted SMA copolymer remaining in the extruded PP. The SMA copolymer can be dissolved by acetone during the purification process mentioned in

Figure 3 Effect of the St concentration on the functionality degree (F) of grafted PP in supercritical CO_2 (10 wt % MAH and 0.6 wt % AIBN based on PP; supercritical reaction time = 4 h; reaction temperature = 80°C; supercritical CO_2 pressure = 8 MPa).
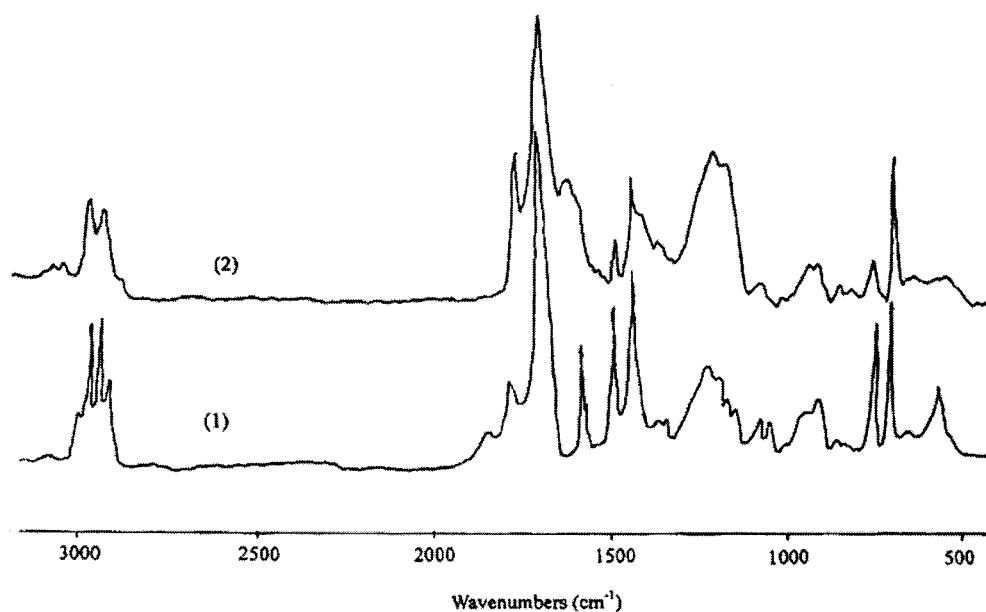
Figure 4 FTIR spectra of (1) SMA and (2) white powder obtained from the filtrate of the 1:1 MAH/St series.

the Experimental section; therefore, it should stay in the filtrate. We analyzed the filtrate left from the purification process of the functionalized PP (for the 1:1 MAH/St system) to determine whether there was any SMA copolymer. After the solvents were evaporated from the filtrate, some white powder was obtained, which was then vacuum-heated for the removal of any unreacted MAH monomer. Figure 4 shows the FTIR spectrum of the obtained powder and that of SMA, which was obtained by radical copolymerization. Both spectra showed the strong characteristic absorptions of the benzene ring and the carbonyl groups of cyclic anhydride. The difference in the two spectra was due to the different MAH contents of the two substances. Polystyrene and poly(maleic anhydride) could also be present in the aforementioned filtrate, and the white powder gave rise to the absorption bands of the benzene ring and the carbonyl groups, respectively. For that reason, we cannot only use the FTIR spectra as proof of the presence of the SMA copolymer. The DSC curve of the white powder showed thermal transitions at about 60 and 158°C (see Fig. 5), which corresponded to the glass transitions of polystyrene (60°C) and SMA (158°C) separately, as reported in the literature.[14] No glass transition for poly(maleic anhydride) was detected. Therefore, we have concluded that the SMA copolymer is formed during the grafting of MAH–St onto PP in supercritical CO_2.

Effect of the reaction temperature on the functionality degree of grafted PP in supercritical CO_2

The effect of the reaction temperature on the grafting degree was studied. The other reaction parameters—

the time (4 h), the PP/MAH/St/AIBN weight ratio (100/10/10/0.6), and the pressure (8 MPa)—were kept constant. It can be seen in Figure 6 that grafting increases with temperature (60–80°C). An increase in the temperature accelerates the decomposition rate of AIBN, thereby promoting the grafting reaction. In addition, an increase in the temperature increases the diffusion of the monomers and initiator in the disperse reaction system in supercritical CO_2. At temperatures higher than 80°C, the grafting degree decreases. Gaylord[9] concluded that the predominant graft structure consists of single SMA units. It might be anticipated that the length of the polymer side chain would mainly be dependent on temperature. Long chains can only be formed at relatively low temperatures. A few parts of polystyrene are agglomerated. Therefore, there is an increasing tendency toward homopolymerization of the St monomer.

Effect of the reaction pressure on the functionality degree of PP in supercritical CO_2

The experimental results for the dependence of the pressure (8–14 MPa) on the functionality degree are shown in Figure 7. The reaction time was kept at 4 h, and the temperature was fixed at 80°C; the weight ratio of PP/MAH/St/AIBN was 100/10/10/0.6. The grafting degree decreases with pressure. An increase in pressure increases the specific density of supercritical CO_2, thereby promoting the dissolvability of St in supercritical CO_2. MAH is a polar monomer, the dissolvability of which in supercritical CO_2 is lower. Therefore, the sorption of St in the PP phase decreases with an increase in pressure. A few parts of the prod-
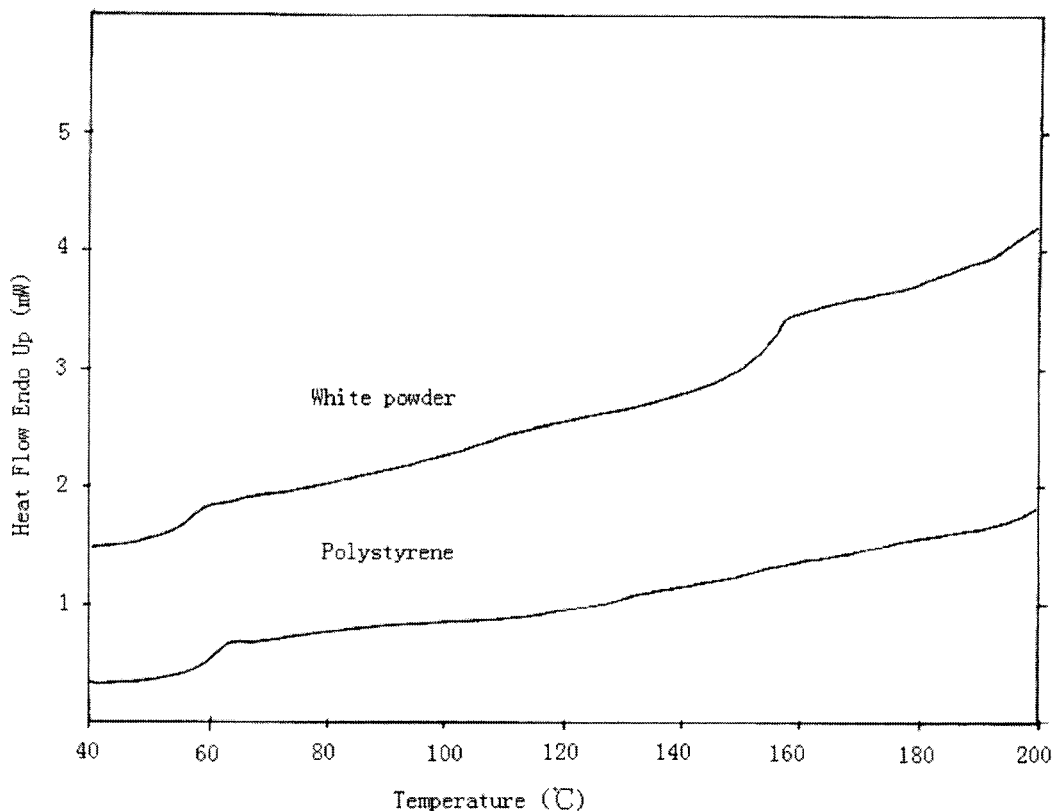
Figure 5 DSC thermograms of white powder obtained from the filtrate of the 1:1 MAH/St series and polystyrene.

ucts are agglomerated because the homopolymerization of St is favored in the phase of supercritical CO_2 by an increase in pressure.

Effect of the initiator concentration on the functionality degree of grafted PP in supercritical CO_2

The effect of the initiator concentration on the functionality degree of MAH was studied; (shown in Fig.

8) the MAH and St concentrations were fixed at 10 and 10 wt %, respectively (based on PP); the supercritical reaction time was 4 h; the reaction temperature was 80°C; and the pressure was kept at 8 MPa. The MAH grafting degree first increased and then decreased with an increasing AIBN concentration. The highest MAH grafting degree was obtained when the AIBN concentration was 0.6 wt % (based on PP). This means that when the molar concentration ratio of MAH and
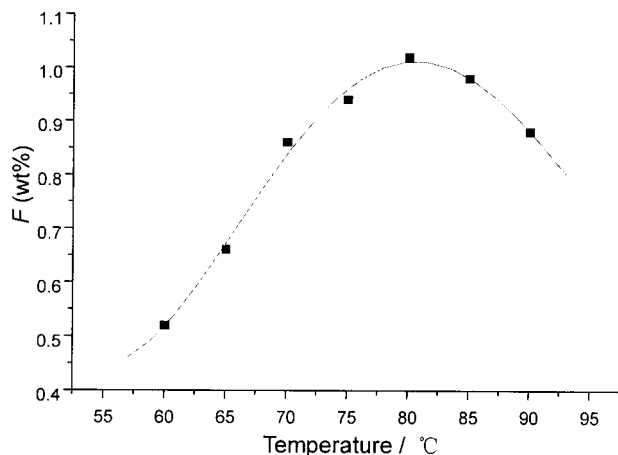

Figure 6 Effect of the reaction temperature on the functionality degree (*F*) of grafted PP in supercritical CO_2 (supercritical reaction time = 4 h; PP/MAH/St/AIBN = 100/10/10/0.6; pressure = 8 MPa).
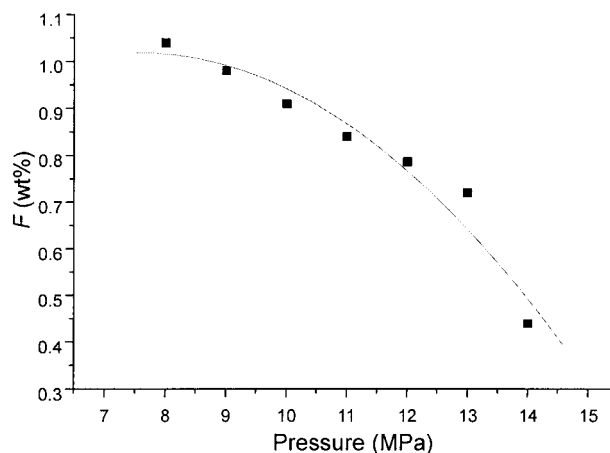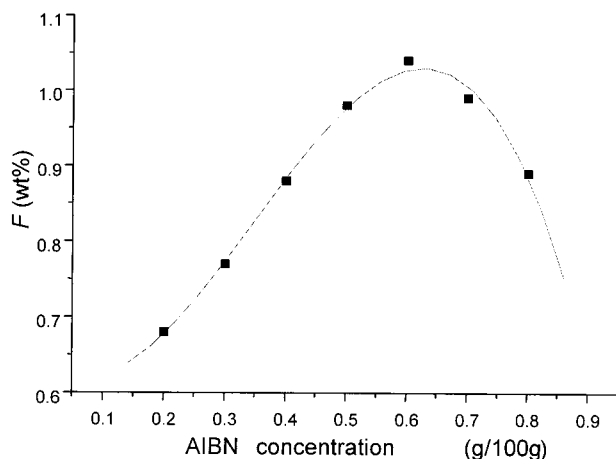

Figure 7 Effect of the reaction pressure on the functionality degree (*F*) of grafted PP in supercritical CO_2 (supercritical reaction time = 4 h; reaction temperature = 80°C; PP/MAH/St/AIBN = 100/10/10/0.6 w/w/w/w).

Figure 8 Effect of the initiator concentration on the functionality degree (*F*) of grafted PP in supercritical CO_2 (supercritical reaction time = 4 h; reaction temperature = 80°C; pressure = 8 MPa; 10 wt % MAH and 10 wt % St based on PP).

St was about 1:1, increasing the initiator concentration within certain limits was effective for improving the grafting degree of MAH. However, when the initiator was used excessively, the functionality degree decreased because of severe chain degradation of the PP backbone. In addition, when the initiator concentration was excessive, more PP macroradicals were produced. Some of the St monomer could then react with these macroradicals and form styryl macroradicals, that is, stable macroradicals, and a further reaction with the SMA copolymer would be difficult. As a result, the functionality degree decreased.
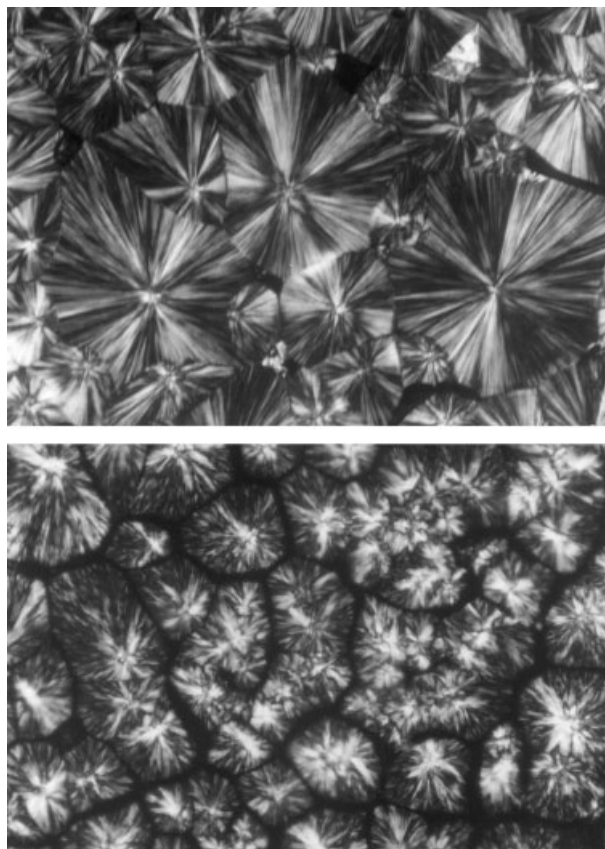
Morphologies of pure PP and PP-*g*-(MAH–St)

Figure 9 shows the morphologies of pure PP and PP-*g*-(MAH–St) under polarizing optical microscopy. The morphologies of pure PP and PP-*g*-(MAH–St) are significantly different. The PP spherulites are about 38 μm in size, and the PP-*g*-(MAH–St) spherulites are reduced in size. This is proposed to be due to the MAH–St side chain of the grafting polymer, which helps to bring about heterogeneous nucleation in the grafting polymer. The density of the nuclei increases, so the growing space of the nuclei becomes smaller. The spherulites impact one another in a short time. A large number of small spherulites appear.

CONCLUSIONS

1. The FTIR spectra of grafted PP show that the functionality degree of grafted PP is implemented through the free-radical graft copolymerization of MAH onto PP in supercritical CO_2.
2. The MAH grafting degree of the resulting polymer is drastically higher in the presence of St than in the absence of St. It reaches a maximum when the molar ratio of MAH and St is about 1:1.
3. The FTIR and DSC characterization of the products shows that there is SMA in the grafting reaction system when the molar ratio of MAH to St is about 1:1. When equimolar amounts of MAH and St are added to the grafting system, St and MAH can interact with each other to form a CTC, which may then react with PP macroradicals, producing branches by termination between the radicals.
4. An increase in the temperature of supercritical CO_2 accelerates the decomposition rate of AIBN, thereby promoting the grafting reaction. In addition, an increase in the temperature increases the diffusion of monomers and radicals in the disperse reaction system in supercritical CO_2. Furthermore, at a temperature higher than 80°C, the grafting degree decreases.
5. Within the experimental range, the functionality degree of grafted PP decreases with an increase in pressure of supercritical CO_2.
6. The highest functionality degree of grafted PP can be obtained when the AIBN concentration is 0.6 wt % (based on PP).

Figure 9 Morphologies of pure PP (top) and PP-*g*-(MAH–St) (bottom) under polarizing microscopy (original magnification, 280×).

7. The morphologies of pure PP and grafted PP are significantly different. The PP spherulites are about 38 μm in size, and the grafted PP spherulites are significantly reduced in size because of heterogeneous nucleation.

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