

Free-Radical Grafting of Acrylic Acid onto Isotactic Polypropylene Using Styrene as a Comonomer in Supercritical Carbon Dioxide

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ABSTRACT: Free-radical grafting of acrylic acid (AAc) onto isotactic polypropylene (iPP) using styrene (St) as a comonomer in supercritical carbon dioxide (SCCO₂) medium was studied. The effects of temperature and pressure of reaction on functionalization degree (grafting degree of AAc) of the products were analyzed. The increase of reaction temperature increases the diffusion of monomers and radicals in the disperse reaction system of SCCO₂. In addition, the increase of temperature accelerates the decomposition rate of 2,2'-azobisisobutyronitrile (AIBN), thus promoting grafting reaction. It was also observed that functionalization degree of the products decreases with the increase of pressure of SCCO₂ in the range of experiment. The effects of comonomer St on the functionalization degree of the products were investigated. The AAc graft degree of the resulting polymer was drastically higher in the present of St. It reached a maximum when the mass ratio of St and AAc was about 0.7 : 1. Because AAc is not sufficiently reactive toward iPP macroradicals, it would be helpful to use a second monomer that can react with them much faster than AAc. St preferentially reacts with the iPP macroradicals to form more stable styrene macroradicals, which then copolymerize with AAc to form branches. The highest functionalization degree was obtained when the AIBN was 0.75 wt %. When the initiator was used excessively, the functionalization degree decreased because of severe chain degradation of the

iPP backbone. The morphologies of pure iPP and grafted iPP are different under the polarizing optical microscope. The diameter of the pure iPP spherulites is 20–38 μ and that of the grafted iPP spherulites is reduced with the increase of the functionalization degree of the products. This is proposed to be because the polar grafts formed during the reaction would have a tendency to associate in the hydrophobic PP environment. This might preserve some of the local crystalline order that existed during the reaction in the swollen iPP phase. It can be proven by a DSC cooling investigation that the crystallization temperature increased as the functionalization degree increased. This is proposed to be because the side-chain of grafting polymer helps to bring about the heterogeneous nucleation in grafting polymer. Therefore, a large number of nuclei can emerge to a lesser supercooling degree. It can be also proven that the percent crystallization decreased as the functionalization degree increased, probably due to the grafted branches, which disrupted the regularity of the chain structure and increased the spacing between the chains. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2203–2210, 2004

Key words: free-radical grafting copolymerization; isotactic poly(propylene) (iPP); acrylic acid (AAc); supercritical carbon dioxide (SCCO₂)

INTRODUCTION

Isotactic polypropylene (iPP) has been one of the fastest growing major thermoplastics in recent decades. The current worldwide production of this resin is well over 10 billion kilograms, and the growth rate is greater than those of many other commodity polymers. Polypropylene is readily available at a relatively low cost and yet possesses many unique properties that are suitable for a wide variety of industrial products. It has expanded its applications to areas formerly restricted to other polymers, such as the automobile market. Utilization of polypropylene in the automo-

bile industry is due to the growing trend toward using polypropylene composites and expanded polypropylene as substitutes for engineering plastics and polyurethane, respectively. However, the hydrophobic nature and lack of polar sites of polypropylene restrict its application.^{1,2} In this way, grafting of polypropylene with unsaturated polar monomer, such as acrylic acid or maleic anhydride, has been performed to use it as an additive component in blends of iPP and polar polymers or in composites of iPP and inorganic fillers.^{3–6}

Conventional techniques for grafting use excessive amounts of toxic liquid solvents to dissolve the polymer, which in turn requires an expensive solvent recovery scheme in the process. Supercritical grafting processing exploits nontoxic, nonflammable, and inexpensive carbon dioxide as a solvent, which can be completely removed from the product by simply de-

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pressurizing the system. Volatile components, such as residual monomer and solution used in the grafting, are effectively removed with SCCO₂. SCCO₂ is rapidly becoming a viable alternative solvent for polymerization.⁷⁻¹⁴ SCCO₂ is known to reduce the T_g for many glassy polymers, and the polymer-free volume can easily be tuned by changing the pressure and temperature of the SCCO₂ system.¹⁵ Supercritical CO₂ causes the polymer considerable swelling. Furthermore, it is possible to change the degree of swelling simply by changing the system pressure. This is in contrast to conventional systems where mixed solvents are used to tune the solvency of the reaction medium.¹⁶ Thus, it seems feasible that the SCCO₂ system could significantly influence mass transfer properties in the process of grafting.

In this investigation, a new graft copolymerization of acrylic acid (AAc) onto polypropylene under addition of styrene (St) as a second monomer in SCCO₂ media has been developed. The functionalization degree was higher than that of products in absence of St as a second monomer in SCCO₂. Because AAc is not sufficiently reactive toward iPP macroradicals, it would be helpful to use a second monomer that can react with iPP macroradicals much faster than AAc, and the resulting free radicals can then copolymerize readily with AAc. The comonomer St serves as a medium to bridge the gap between the iPP macroradicals and the AAc monomer. It is proposed that, in the above system, St preferentially reacts with the iPP macroradicals to form styrene macroradicals, which then copolymerize with AAc to form branches. Recently, it was also shown that the addition of St as a second monomer in the melt grafting system assisted in increasing the graft degree of maleic anhydride on iPP.¹⁸

It has been well established that a free-radical grafting process starts with the formation of macroradicals along the iPP chains by a so-called hydrogen abstraction mechanism.¹⁹ These macroradicals may subsequently follow two competing pathways. They can either initiate grafting of monomers or undergo chain scission, which is the main side reaction under higher temperatures.

The temperature of graft copolymerization in SCCO₂ was controlled between 60 and 90 °C, which is much lower than that of melt-grafting technology. Therefore, the side reaction of chain scission decreased. In addition, the application of the supercritical CO₂ fluid as a kind of green solution is of momentous current significance for protecting environment.

EXPERIMENTAL

Materials

The polypropylene powder used in this study was supplied by Shanghai Petrochemical Co. Ltd. with a

melt-flow index (MFI) of 16 g/10 min. The AAc monomer (analytical grade), St monomer (analytical grade), and initiator 2,2'-azobisisobutyronitrile (AIBN) (analytical grade) were commercially available from the Shanghai Chemical Company. AAc and St were purged to remove the hydroquinone and monomethyl ether hydroquinone inhibitors using an inhibitor remover disposable column (Aldrich Chemical). The pure AAc and St were stored at -25 °C before use. AIBN was recrystallized twice from ethanol. Commercial methanol, xylene, and cyclohexane were distilled prior to use. Analytical grade CO₂ (99.9%) was obtained from Air Product Company.

Experimental instruments

The main part of the experimental unit was a high-pressure 0.5-L stainless-steel reactor with bolt closure (CJF-05, Da Lian Tongda Autoclave Inc.), which has a maximum working pressure of 40 MPa and a maximum working temperature of 320 °C and was fitted with a rupture disk rated at 30 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 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 even heat and was also controlled by the AI-708 intelligence controller. The thermocouple of the controller reached 20 cm down inside the reactor. The reactor was insulated using an insulating blanket. A cold trap was installed at the outlet of reactor to capture the unreacted monomer in the effluent. A high-pressure metering pump was used to inject CO₂ through the shutoff valve into the reactor. The pump (2JX, Hangzhou Zhijiang Scientific Instrument Company) was designed to deliver liquid against a pressure of 30 MPa and had a flow range of 12.6 L/h.

Experimental procedures

First, preweighed amounts of polypropylene (5 g), monomer, and initiator were charged into the high-pressure reactor. The reactor was closed and vacuumed to remove the air inside. CO₂ was pumped into the reactor at 40 °C. The impeller was switched on and the temperature and pressure of the reactor were increased to the desired values.

The temperatures examined varied between 60 and 90 °C. The decomposition rate constant (k_d) of AIBN in supercritical CO₂ has differing values depending on the temperature and pressures. The half-life time of the initiator for the condition of experiment was between 10 and 18 h. The reaction pressure was varied from 8 to 14 MPa. The mass ratio of St : AAc was varied from 0 : 1 to 1 : 1. The AIBN concentration was

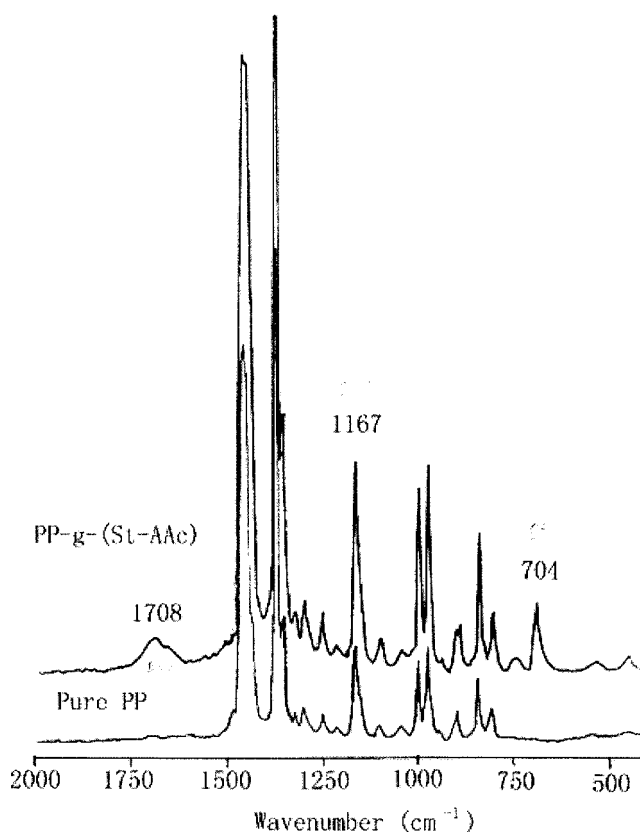


Figure 1 FTIR spectra of pure iPP and grafted polymer (functionalization degree: 3.2 wt %)

varied from 0.25 to 1.0% (wt) based on iPP. The reaction time was varied from 1 to 6 h. When the reaction was ended, opening the outlet valve depressurized the high-pressure reactor. The effluent was passed through the cold trap to capture the monomer dissolved in the CO₂ and the gas was vented to the atmosphere.

Characterization of grafted products

The reaction product consisted of mixtures of grafted copolymer [i.e., iPP-g-AAc, iPP-g-St, and iPP-g-(St-AAc)], ungrafted polymer (iPP), homopolymer of monomer, copolymer of AAc and St, and the unreacted monomer. For avoiding the interference of determination of functionalization degree, the product was extracted in a soxhlet extractor for 4 h using methanol and cyclohexane separately to remove any homo- and copolymer of AAc and St and unreacted monomer. The extracted sample including grafted copolymer and ungrafted iPP was washed with distilled water, dried under vacuum at 70°C for 24 h, and subsequently characterized with FTIR. FTIR spectroscopy was used for qualitative as well as quantitative identification of grafting onto polypropylene. The measurement was made on the IFS28 FTIR spectrom-

eter system (BRUKER Company, Germany). Any given sample was melted into a thin film. The film was then subjected to FTIR measurement.

The FTIR spectra of the pure iPP and the extracted sample are shown in Figure 1. The new absorption due to the phenyl group in the grafted styrene appears at 704 cm⁻¹ and the absorption due to the carbonyl group in the grafted AAc appears at 1,708 cm⁻¹. The peaks are clearly seen by comparison of a spectrum of the pure iPP with that of the extracted sample. The absorptions at 1,167 cm⁻¹ can be assigned to the characteristic absorption of CH₃ groups, proportional to the amount of iPP skeleton. The absorbance area ratio of the bands at 1,708 (A₁) and 1,167 cm⁻¹ (A₂-internal reference) shows the relative degree of functionalization of AAc.

The absolute degree of functionalization and amount of grafted AAc was determined by titrating the acid groups. In a typical procedure, 0.5 g of the extracted sample 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 ethanolic KOH 0.02N, using phenolphthalein as an indicator.

The plot of functionalization degree (obtained by titration) against A₁/A₂ (absorbance ratios from FTIR) shows a linear relation, as demonstrated in Figure 2. This graph has been used as a product calibration curve to determine the absolute functionalization degree. The functionalization degree showed in this paper was obtained by interpolating FTIR ratio (A₁/A₂) in the plot.

Functionalization degree ($F_{wt} \%$)

$$= \frac{\text{Weight of grafted AAc in extracted sample}}{\text{Weight of extracted sample}} \times 100\%$$

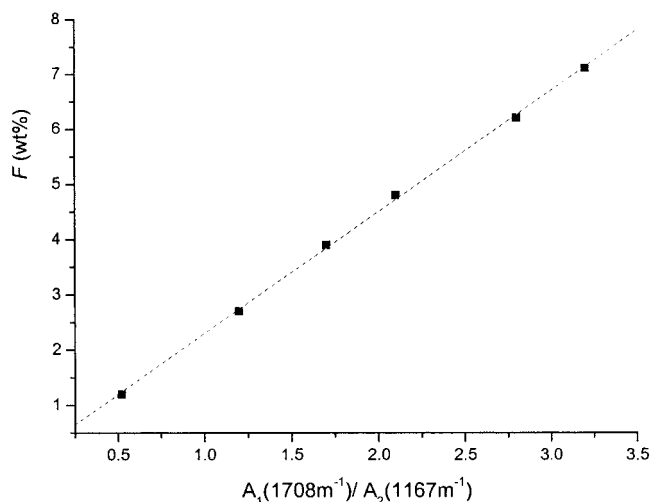


Figure 2 Calibration curve for absolute functionalization degree determination ($R: 0.9974$)

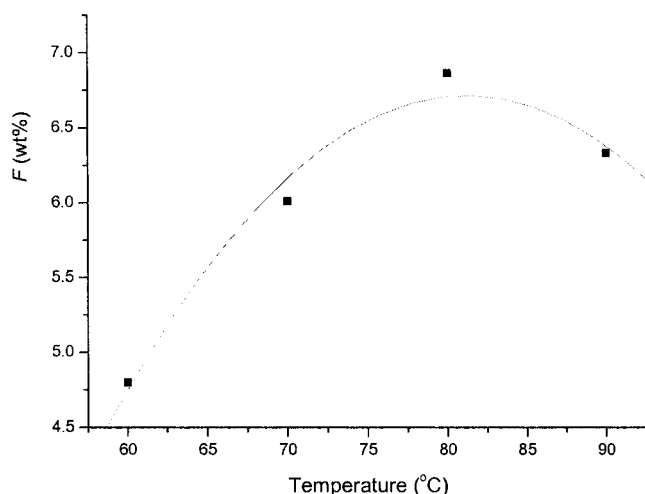


Figure 3 Effect of reaction temperature on functionalization degree of iPP in supercritical CO₂ (reaction time: 4 h; mass ratio of iPP/AAC/St/AIBN: 100/20/14/0.75; pressure: 8 MPa)

Crystal morphology

Polarized hot-stage optical microscopy (PHSOM, $\times 59$, Shanghai Science Instruments Company) was performed. Extracted samples and pure iPP were cut using a microtome and were mounted on glass slides. The specimens were heated to 200°C for 2 min and then cooled to room temperature at rate of 5°C/min. The PHSOM was observed using a camera. The PHSOM images were used to study the crystalline morphology and nucleation.

Differential scanning calorimetry analyzer

A Perkin-Elmer Company Model Pyris-1 differential scanning calorimetry (DSC) analyzer was used to investigate the effects of the functionalization degree of grafting product (after extraction) on its crystallization behavior. The instrument was calibrated using indium. All runs were made in a dry nitrogen atmosphere. Initially, the temperature of the samples was raised from 30 to 200 °C at a rate of 50°C/min and held for 2 min at 200°C to impart a uniform thermal history to all of the samples. The samples then were cooled from 200 to 30°C at rate of -10°C/min and the crystallizing curves were recorded.

RESULTS AND DISCUSSION

Effect of reaction temperature on functionalization degree of grafted products in supercritical CO₂

The effect of reaction temperature on the functionalization degree was studied. The other reaction parameters, i.e., reaction time (4 h), the weight ratio of iPP/AAC/St/AIBN (100/20/14/0.75), and pressure (8

MPa) were kept constant. It can be seen from Figure 3 that the functionalization degree increases with temperature (60–80°C). The increase of temperature accelerates the decomposition rate constant (k_d) of AIBN. In addition, the increase of temperature increases the diffusion of monomers and initiator in the disperse reaction system in supercritical CO₂. It was also observed that, at temperatures higher than 80°C, the functionalization degree decreases and part of the homopolystyrene was agglomerated. Therefore, there is an increasing tendency toward homopolymerization of the AAC monomer.¹⁷ At the same time the grafting of AAC onto iPP decreased.

Effect of reaction pressure on functionalization degree of grafted products in supercritical CO₂

The experimental results for the dependence of pressure (8–14 MPa) on functionalization degree are shown in Figure 4. The reaction time was kept at 4 h and the temperature was fixed at 80°C. The weight ratio of iPP/AAC/St/AIBN was 100/20/14/0.75. It was observed that functionalization degree decreases with pressure increase. The reaction system is a disperse one. Supercritical CO₂ causes the iPP considerable swelling but it is still in the solid phase. The increase of pressure increases the specific density of supercritical CO₂, thus promoting the dissolvability of AAC and St in supercritical CO₂. Therefore, the sorption of AAC and St in the polypropylene phase decreases with the increase of pressure. It was found that a few parts of the products were agglomerated, because homopolymerization of AAC is favored in the phase of supercritical CO₂ by the increase of pressure.¹⁷

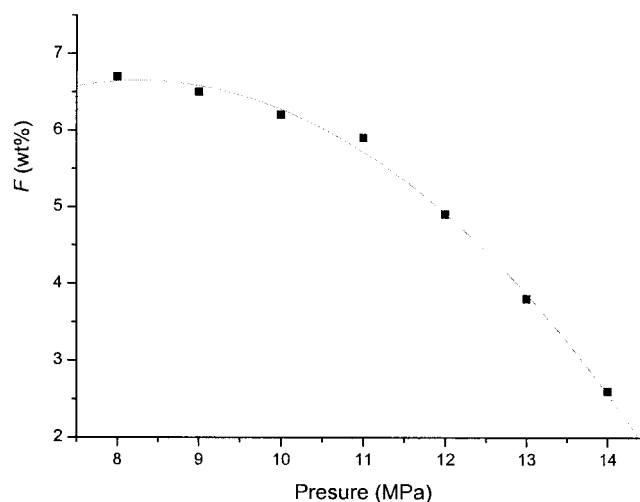


Figure 4 Effect of reaction pressure on functionalization degree of iPP in supercritical CO₂ (reaction time: 4 h; reaction temperature: 80 °C; mass ratio of iPP/AAC/St/AIBN: 100/20/14/0.75)

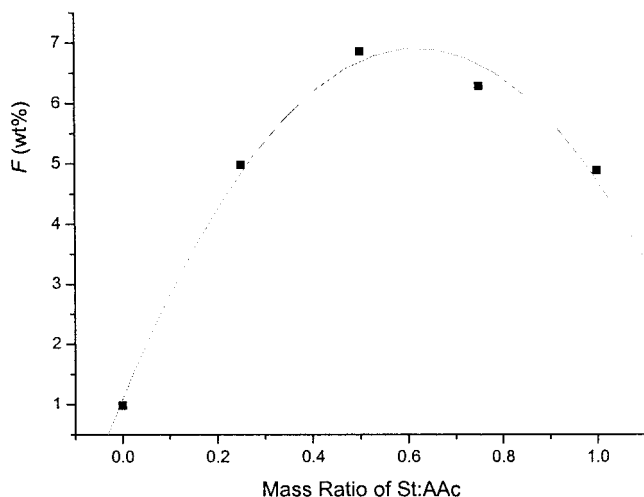


Figure 5 Effect of St concentration on functionalization degree of iPP in supercritical CO₂ (AAc and AIBN concentrations: 20 and 0.75% (wt); reaction time: 4 h; reaction temperature: 80 °C; reaction pressure: 8 MPa)

Effect of St concentration on functionalization degree of grafted products in supercritical CO₂

Figure 5 shows the effect of St concentration on functionalization degree of the grafted products. When the AAc and AIBN concentrations were fixed at 20 and 0.75% (wt) based on iPP, supercritical reaction time was 4 h, reaction temperature was 80 °C, and the pressure remained 8 MPa, respectively. The AAc graft 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 mass ratio of St and AAc was about 0.7 : 1 (molar ratio of St and AAc was about 1 : 1) and then decreased when the concentration of St was higher. In the absence of St, the graft degree of AAc is very low because most of the AAc formed its homopolymer and very little attached itself as side chain grafts to polypropylene. AAc is not sufficiently reactive toward iPP macroradicals. The comonomer (St) serves as a medium to bridge the gap between the iPP macroradicals and the AAc monomer. St preferentially reacts with the iPP macroradicals to form stable styrene macroradicals, which then copolymerize with AAc to form branches. It can be proven from experiments that the AAc graft degree drastically increased when St was used as a second monomer and it was the highest when the mass ratio of St : AAc = 0.7 : 1.

Effect of initiator concentration on functionalization degree of grafted products in supercritical CO₂

The effect of initiator concentration on the functionalization degree of iPP was studied (shown as Fig. 6) when the AAc and St concentrations were fixed at 20

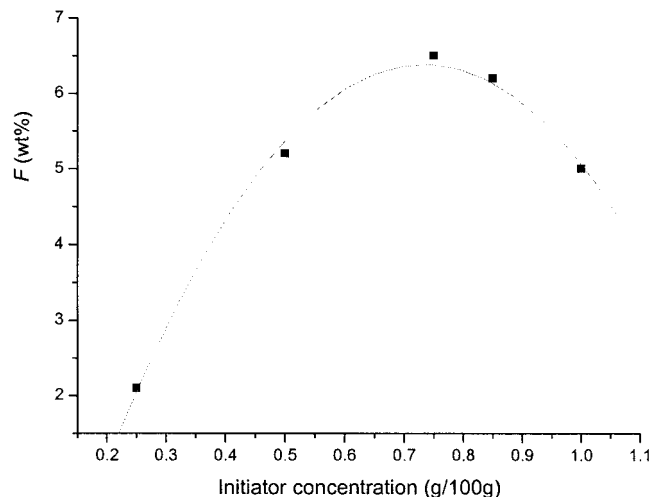


Figure 6 Effect of initiator concentration on functionalization degree of iPP in supercritical CO₂ (AAc and St concentrations: 20 and 14% (wt); reaction time: 4 h; reaction temperature: 80 °C; reaction pressure: 8 MPa)

and 14% (wt) based on iPP, supercritical reaction time was 4 h, reaction temperature was 80 °C, and the pressure remained 8 MPa, respectively. The functionalization degree first increased and then decreased along with increasing AIBN concentration. The highest functionalization degree was obtained when the AIBN was 0.75% (wt) based on iPP. This means that increasing initiator concentration within certain limits is effective for improving the graft degree of AAc. However, the MFI of the products were 18, 20, and 20 when the initiator concentrations were 0.25, 0.5, and 0.75. When initiator was used excessively (AIBN concentration: 1%), the MFI of the grafting product was 30

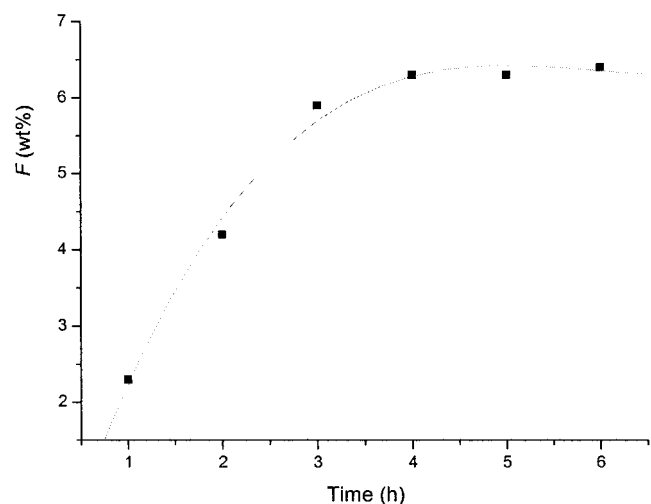


Figure 7 Effect of reaction time on functionalization degree of iPP in supercritical CO₂ (reaction pressure: 8 MPa; reaction temperature: 80 °C; mass ratio of iPP/AAc/St/AIBN: 100/20/14/0.75)

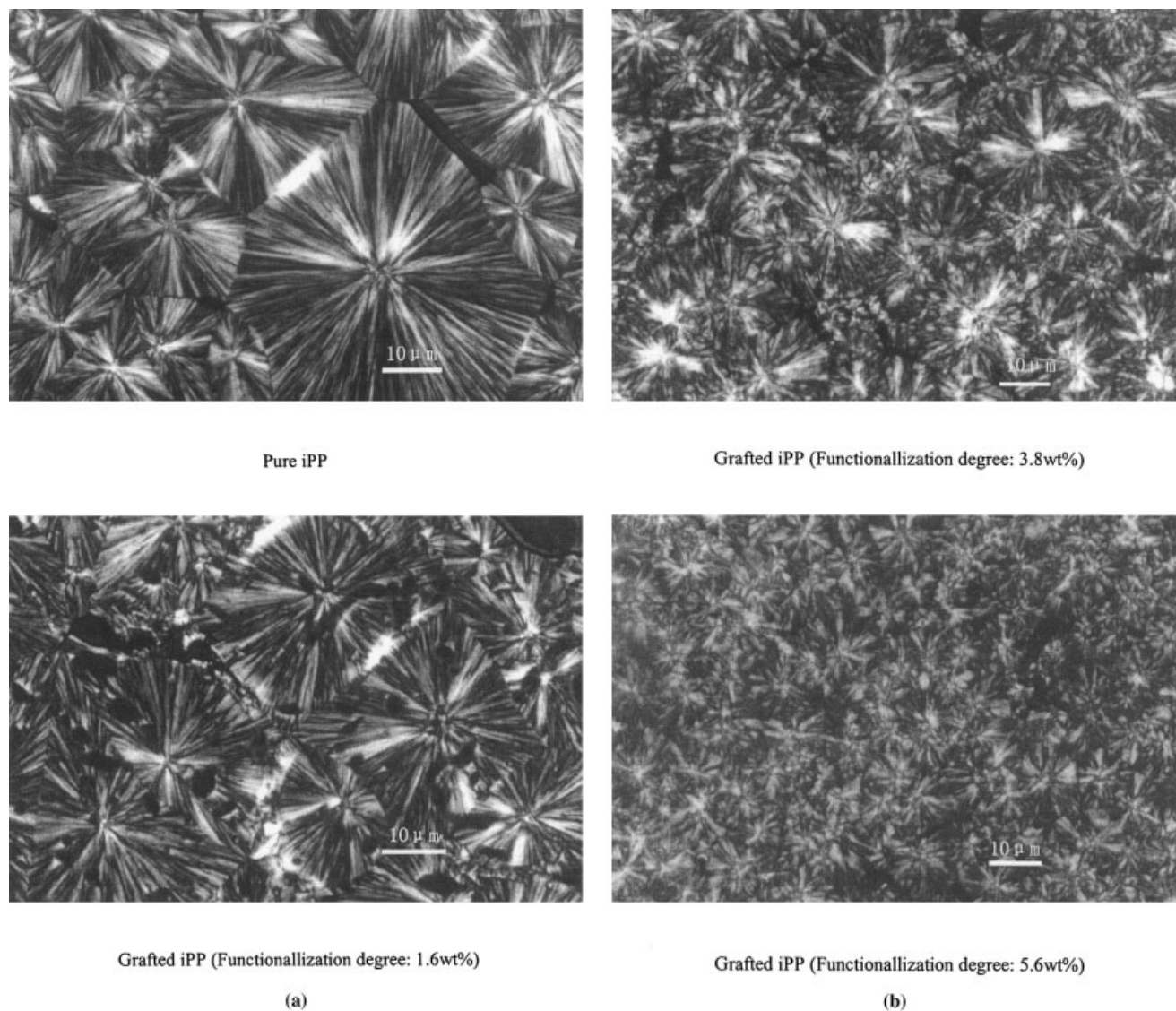


Figure 8 Crystal morphologies of pure iPP and different degrees of functionalization of grafted polymers (F : 1.6 wt %, F : 3.8 wt %, F : 5.6 wt %)

g/10 min because of severe chain degradation of the iPP backbone. In addition, when the initiator concentration was excessive, St and AAc monomer had greater homopolymerization tendencies. As a result, the functionalization degree decreased.

Effect of reaction time on functionalization degree of grafted products in supercritical CO_2

The effect of reaction time on the functionalization degree was studied. The reaction pressure was kept at 8 MPa and the temperature was fixed at 80°C. The mass ratio of iPP/AAc/St/AIBN was 100/20/14/0.75. It was observed from Figure 7 that functionalization degree increases with time and it reaches saturation when the reaction time is longer than 4 h.

Crystal morphologies of pure iPP and grafted product

Figure 8 shows crystal morphologies of pure iPP and grafted product under the polarizing optical microscope. The size of crystal morphologies of pure iPP and grafted product are significantly different. The diameters of the iPP spherulites were about 20–38 μ and the diameters of the grafted iPP spherulites were about 25 μ (F : 1.6 wt %), 20 μ (F : 3.8 wt %), and 10 μ (F : 5.6 wt%), respectively. Their size were reduced with the increase of functionalization degree. This is proposed to be due to the increase in difficulty of polymer chain arrangements as the grafted branch chains prohibited the movements of the polymer segments.²⁰ On the other hand, the side-chain of the grafted polymer helps to bring about the heteroge-

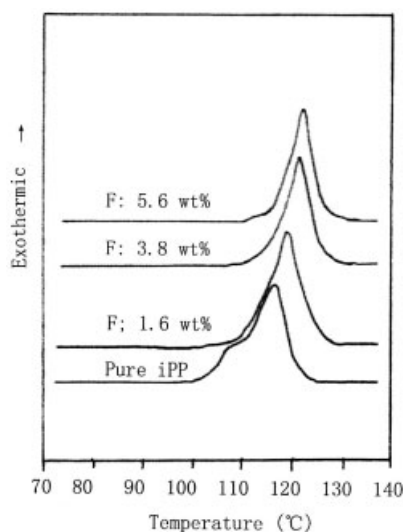


Figure 9 DSC cooling scan curves for pure iPP and different degrees of functionalization of grafted polymers (F : 1.6 wt %, F : 3.8 wt %, F : 5.6 wt %).

neous nucleation in the grafted polymer. The density of nuclei increased so that the growing space of nuclei became smaller. The spherulites impacted each other in a short time. It can be seen that a large number of small spherulites appeared.

DSC cooling scans analysis

Figure 9 shows DSC cooling scans at $10^{\circ}\text{C}/\text{min}$ for pure iPP and grafted product. It can be seen that the iPP crystallization temperature (T_c) was 116°C and the heat of crystallization (ΔH_c) was 103 J/g . A shoulder is observed in the crystallization peak, which is probably due to the formation of imperfect crystallite at a lower temperature when the iPP was subjected to the relatively fast cooling process in this experiment. The crystallization temperatures of grafted polymer were 120 , 122 , and 123°C and their heats of crystallization were 98 , 89 , 84 J/g , respectively. The temperature of crystallization increased and the heat of crystallization decreased with increase of functionalization degree. The heat of crystallization, which indicates the percentage of crystallization of grafted polymer, decreased as the functionalization degree increased. It was probably due to the grafted branches, which disrupted the regularity of the chain structure and increased the spaces between the chains. The temperature of crystallization increased after grafting reactions. This is proven furthermore in that the side-chain of grafting polymer helps to bring about the heterogeneous nucleation in grafting polymer. Therefore, a large number of nuclei can emerge to a lesser supercooling degree. The density of effective nuclei increased so that the crystallization process was completed in a short time at a higher temperature.

CONCLUSION

1. The FTIR spectra of the grafted product show that the functionalization of iPP was implemented through free-radical graft copolymerization of acrylic acid onto polypropylene using styrene as a comonomer in supercritical carbon dioxide.
2. The AAc graft degree of the resulting polymer was drastically higher in the present of St. It reached a maximum when the mass ratio of St and AAc was about $0.7 : 1$.
3. The effect of reaction temperature on the functionalization degree of iPP was studied. The functionalization degree increases with temperature ($60\text{--}80^{\circ}\text{C}$). There is an increasing tendency toward homopolymerization of the St and AAc monomer when the temperature is higher than 80°C . Functionalization degree of iPP decreases with pressure increase. Homopolymerization of AAc and St is favored in the supercritical CO_2 phase by the increase of pressure. The highest functionalization degree was obtained when the AIBN was 0.75% (wt) based on iPP.
4. The morphologies of pure iPP and grafted product are different under the polarizing optical microscope. The diameter of the iPP spherulites was about $20\text{--}38\ \mu$ and the size of the grafted product spherulites was reduced as the functionalization degree of grafted iPP increased. This is proposed to be because the polar grafts formed during the reaction would have a tendency to associate in the hydrophobic PP environment. This might preserve some of the local crystalline order that existed during reaction in the swollen iPP phase.
5. It can be proven that the crystallization temperature increased as the functionalization degree of grafted product increased. This is proposed to be because the side-chain of grafting polymer helps to bring about the heterogeneous nucleation in grafting polymer. A large of nuclei can emerge to a lesser supercooling degree because of the presence of large number of polar grafts in the iPP- CO_2 phase. The density of effective nuclei increased so that the crystallize process was completed in a short time at a higher temperature. It can be also proved that the percentage of crystallization decreased as the functionalization of grafted product increased, which was probably due to the grafted branches, which disrupted the regularity of the chain structure and increased the spacing between the chains.

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