Polymer 43 (2002) 1183–1188

polymer

www.elsevier.com/locate/polymer

# Grafting of methyl methylacrylate onto isotactic polypropylene film using supercritical $CO_2$ as a swelling agent

Zhimin Liu, Liping Song, Xinhua Dai, Guanying Yang, Buxing Han*, Jian Xu

*Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

Received 25 July 2001; received in revised form 28 September 2001; accepted 18 October 2001

**Abstract**

Grafting of methyl methacrylate (MMA) onto isotactic polypropylene (iPP) film was carried out by free radical polymerization using supercritical (SC) carbon dioxide (SC $CO_2$) as a solvent and swelling agent. The iPP film was first impregnated with the monomer MMA and initiator benzoyl peroxide (BPO) using SC $CO_2$ at 308.15 K. After releasing $CO_2$, the MMA molecules in the film were grafted onto the iPP at a higher reaction temperature. Using this method, the grafting level and the morphology can be controlled by the soaking time, pressure and concentrations of MMA and BPO in the fluid phase. The products were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and wide angle X-ray diffraction (WAXD). © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Benzoyl peroxide; Methyl methacrylate; Polymerization

## 1. Introduction

The modification of nonpolar polymeric materials is important for various applications, such as the dyeability of textiles, the improvement of adhesion for packaging industry, and the elaboration of membranes with specific properties. Because of its growing commercial applications, isotactic polypropylene (iPP) film has attracted particular attention. However, its drawbacks, such as low surface energy, lack of chemical functionalities, and poor compatibility with synthetic polar polymers, have restricted the use of iPP. Graft copolymerization by hydrogen abstraction from tertiary carbon offers an effective approach to introduce some desirable properties into the polymer and thus expands its application without adversely affecting the architecture of the iPP backbone. Grafting of polar compounds onto iPP using conventional methods have been studied by different techniques, such as ultraviolet radiation [1], cobalt-60 gamma radiation method [2], and liquid solvent method [3,4]. Conventional methods of grafting of polar monomers on iPP suffer from several drawbacks. For example, the solvent must be removed from the final product and that creates additional waste streams. The other common method of grafting iPP involves melt extrusion in which polar monomer and initiator is co-extruded with the polymer, thermally initiating the free radical reaction.

Supercritical fluids (SCFs), especially supercritical carbon dioxide (SC $CO_2$), have many unique properties [5,6]. Supercritical (SC) technique opens a bright way for polymer science, and recently some excellent work has been done for different purposes, such as synthesis of various polymers [7–11], preparing polymer composites [12–15] and incorporation of additives into polymers [16–19]. SC $CO_2$ can swell many polymers, so it has been used as a swelling agent to produce polymer blends [12–15]. Recently, Hayes and McCarthy [20] grafted maleic anhydride onto poly (4-methyl-1-pentene) using SC $CO_2$ as a solvent and swelling agent. The density of SC $CO_2$, and thus its solvent strength, is continuously tunable from gas-like to liquid-like by changing temperature or pressure. This provides the ability to control the degree of swelling of polymers as well as the partitioning of small molecules between the swollen polymer phase and the fluid phase. The low viscosity and zero surface tension of SCFs allow for fast mass transfer of penetrates into a swollen polymer. Moreover, since $CO_2$ is a gas at ambient conditions, removal of the solvent from the final product is extremely facile. All these are favorable to modification of polymers using SC $CO_2$ as a swelling agent.

In this work, we studied the free radical grafting of methyl methacrylate (MMA) onto iPP film using SC $CO_2$

---

* Corresponding author. Tel.: +86-010-6256-2821; fax: +86-010-6255-9373.

*E-mail address:* hanbx@pplas.icas.ac.cn (B. Han).

PII: S0032-3861(01)00703-0

as a solvent and swelling agent. The effect of various factors, such as the soaking time, pressure of $CO_2$, monomer and initiator concentrations and reaction time on the graft level were studied. The morphology and structure of grafted and un-grafted substrates were determined using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and wide angle X-ray diffraction (WAXD).

## 2. Experimental section

*Materials*. iPP film used in this work was 30 μm in thickness, supplied by Beijing Yanshan Petrochemicals Company, and soxhlet-extracted from acetone for 24 h and dried in a vacuum oven at 80 °C. MMA produced by Tianjin Chemical Reagent Center (A.R. grade) was washed successively with 5% aqueous NaOH and deionized water, dried over anhydrous $Na_2SO_4$ overnight, and then distilled under reduced pressure. Benzoyl peroxide (BPO) purchased from Beijing Jinlong Chemical Reagent Company was used after recrystallization in chloroform. Acetone (A.R. grade) received from Beijing Chemical Factory was used without further purification. Carbon dioxide with purity of 99.95% was provided by Beijing Analytical Instrument Factory and used as received.

*Grafting procedures*. Grafting procedures consisted of two steps: soaking process and grafting reaction. During the soaking process, iPP film was impregnated with MMA and BPO (initiator) at 308.15 K using SC $CO_2$ as a solvent and swelling agent. Then $CO_2$ was released and MMA was grafted onto the iPP matrix at a higher temperature. Before impregnating the iPP films with MMA and BPO with the aid of SC $CO_2$, we first studied the phase behavior of $CO_2$/MMA/BPO mixture using an optical cell, which allowed us to select suitable conditions at which the mixture was homogeneous. In a typical experiment, the iPP films (0.5 g) and MMA–BPO solution were loaded in a stainless steel vessel of 32 ml, and the air in the vessel was removed. After the system had reached thermal equilibrium, $CO_2$ was charged by a syringe pump (Model SB-2, Beijing Xiantong Scientific Instrument Co.) until the desired pressure was reached. During this process, the iPP films were swollen and some of the MMA + BPO infused into the films. After a desired soaking time, the fluid in the system was released. The impregnated films were transferred into another stainless steel vessel and the air in the vessel was replaced by $N_2$. The grafting reaction was carried out at 120 °C for 4 h. At the end of the reaction, the vessel was quenched with water. The samples were then Soxhlet-extracted using hot acetone for 24 h to remove the unreacted monomer and homopolymer. Then a portion of sample was put in *o*-dichlorobeneze and heated to 90 °C. The sample was dissolved completely and the solution was obtained, which indicated the MMA or PMMA grafted onto iPP film. The percent of grafting was calculated by the following equation:

$$\%\ \text{Grafting}(G) = \frac{W_t - W_0}{W_0} 100 \tag{1}$$

where $W_0$ is the initial weight of iPP and $W_t$ is the weight of grafted iPP.

*Characterization*. FTIR (Perkin–Elmer 180) was used to characterize the grafting of polymer. The morphology of various samples was observed with Hitachi S-530 SEM in the normal secondary electron imaging (SEI) mode. The surface was coated with gold to avoid charging under an electron beam. The thermal behavior of films was analyzed by means of DSC with a Mettler TA 2910 equipped with a control and programming unit. The apparent melting temperature, $T_m$, was determined following this procedure: the samples (≈10 mg) were heated from room temperature to 200 °C at a rate of 10 °C/min and the heat evolved during the scanning process was recorded as a function of temperature. The observed $T_m$ and the apparent enthalpies of melting ($\Delta H^*$) were obtained from the maxima and the area of the melting peak, respectively. The apparent crystallinity, $C_a$, of the iPP and the grafted iPP were calculated by the following equation:

$$C_a(\%) = \Delta H^*/\Delta H^0 \times 100 \tag{2}$$

where $\Delta H^0$ is the heat of fusion per gram of 100% crystalline iPP. Brandrup and Immergut [21] reported that $\Delta H^0$ was 209 J/g for iPP. Because crystallization of the grafted iPP occurs in the iPP portion, the crystallinity of iPP in the grafted copolymer, $C$, can be expressed as the following:

$$C = C_a/W_{iPP} \tag{3}$$

where $W_{iPP}$ is the weight fraction of iPP in the grafted copolymer.

WAXD study of iPP and the grafted iPP was performed by means of a Japan D/MAX.RB diffractometer with Cu Kλ radiation ($\lambda = 0.154$ nm) at a generator voltage of 40 kV and a generator current of 100 mA. The scanning speed and the step were 2°/min and 0.02°, respectively. The initial $2\theta$ value was 10°.

## 3. Results and discussion

### 3.1. Grafting reaction

In this work, the soaking experiments were conducted under conditions at which $CO_2$, MMA, and BPO exist as a single phase. To optimize the operation conditions, effects of the soaking time, the pressure of SC $CO_2$, monomer and initiator concentrations, and reaction time on the graft level were studied, and the results were shown in Figs. 1–5.

The soaking time was varied from 2 to 15 h at 35 °C and 120 bar. The dependence of grafting percentage on soaking time is shown in Fig. 1, which indicates that equilibrium can be reached after a soaking period of 5 h.

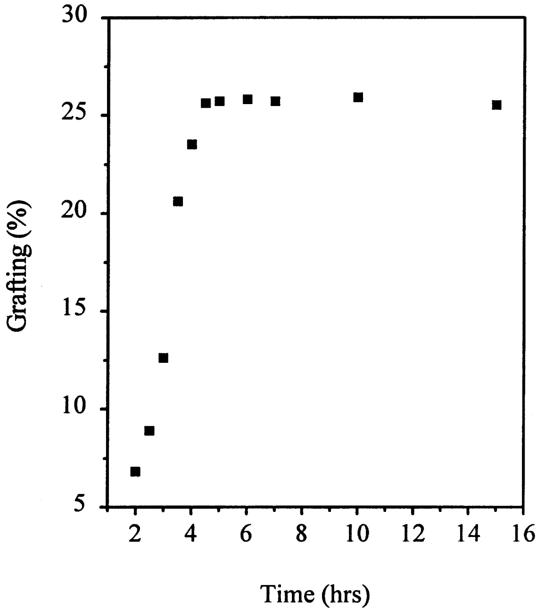


Fig. 1. Grafting level of iPP films as a function of the soaking time at 35 °C and 120 bar. The concentration of MMA with 0.3 mol% is 0.828 mol/l.

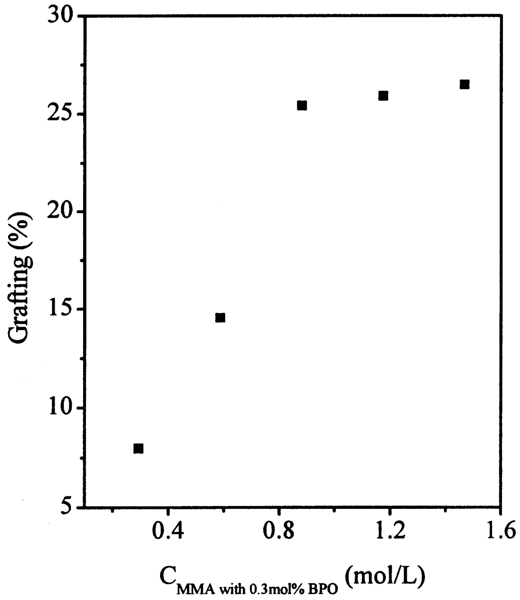


Fig. 3. Effect of the concentration of MMA with 0.3 mol% BPO on grafting level at soaking condition of 35 °C and 14 MPa bar (reaction at 120 °C for 4 h).

Fig. 2 shows the effect of pressure on the grafting percentage in the pressure range from 10 to 20 MPa. It is clear that the grafting percentage reaches a maximum at 14 MPa. We explain this phenomenon as following: there are two opposite factors to affect the soaking amount of MMA. First, an increase in pressure results in increased solvent power of $CO_2$, which is not favorable to partitioning of MMA in the iPP matrix. At the same time, increasing the pressure of $CO_2$ induces an increase in swelling of iPP substrate, which is favorable to increase the adsorption of MMA. The resulting maximum at 14 MPa indicates a balance of these competing effects.

Fig. 3 shows the effect of monomer (MMA) concentration on the percentage of grafting of MMA on iPP. It can be seen that the grafting percentage increases initially with increasing of monomer concentration, and then decreases with monomer concentration. The main reason is that most of the monomer is utilized by the available free radical sites on the iPP backbone at the lower monomer concentrations, and thus the extent of homopolymerization of the monomer

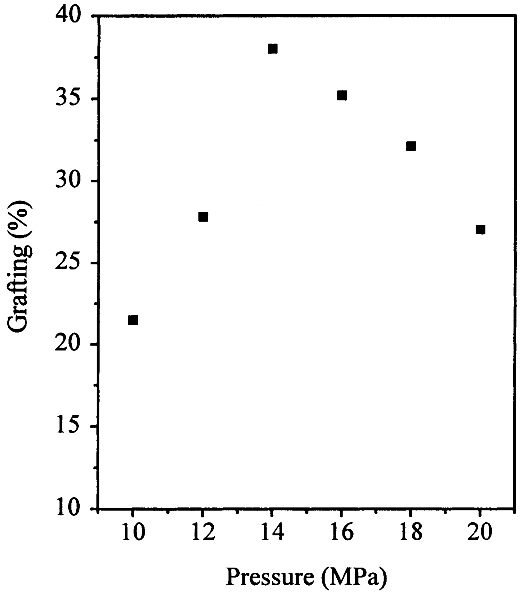


Fig. 2. Grafting level of iPP films as a function of pressure at 35 °C with soaking time of 6 h. The concentration of MMA with 0.3 mol% is 0.828 mol/l.

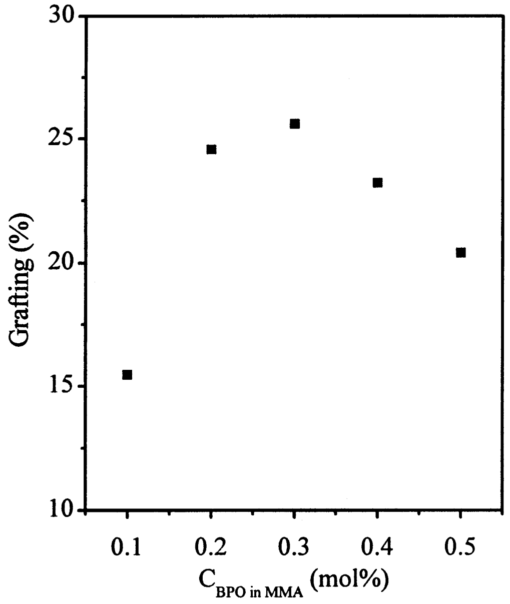


Fig. 4. Effect of the concentration of initiator in 0.828 mol/l MMA solution on grafting level at soaking condition of 35 °C and 14 MPa (reaction at 120 °C for 4 h).

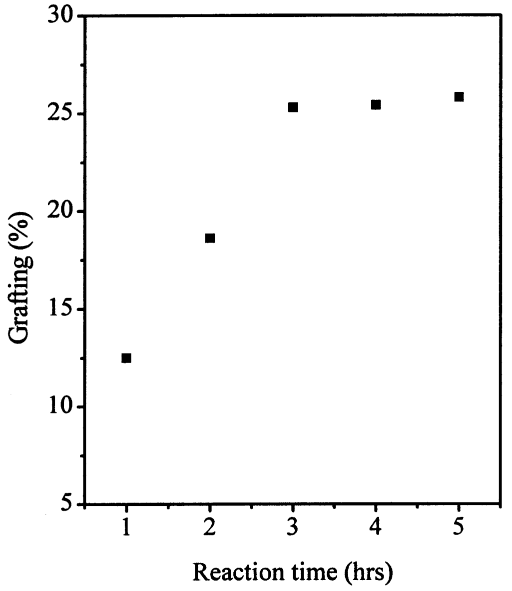


Fig. 5. Effect of reaction time on grafting level at soaking condition of 35 °C and 14 MPa. The concentration of MMA with 0.3 mol% is 0.828 mol/l (reaction at 120 °C).

is smaller. At the higher monomer concentrations, however, the number of free radical sites available on the iPP backbone becomes a limiting factor. At the same time, the free radicals generated in the solution come into contact, with each other easily. As a result, the degree of homopolymerization increases and the grafting percentage decreases.

The effect of BPO concentration on the basis of MMA on the grafting percentage is shown in Fig. 4. It was observed that with increasing concentration of BPO, the percentage of grafting initially increases and passes through a maximum. The initial increase in the grafting level is caused by the increased availability of free radicals for grafting of the monomers. When the concentration of the initiator, exceeds a value, increased free radical concentration results in serious homopolymerization. These opposite factors result in the appearance of the maximum shown in Fig. 4.

After iPP films were infused with MMA/BPO, the grafting reaction were carried out at 120 °C, because at this temperature BPO can decompose rapidly. The effect of reaction time on the percentage of grafting was investigated. It can be seen from Fig. 5 the grafting level increases initially with reaction time and reaches a plateau in 4 h. With an increase in reaction time, the free radicals have more time for reaction and therefore result in a higher level of grafting. After some time, all the initiator and monomer are used up. Thus, no further change in grafting level was observed with increasing reaction time.

### 3.2. Characterization

*Infrared spectroscopy measurement.* The presence of grafting of MMA onto iPP film was confirmed through FTIR analysis. Fig. 6 shows the IR spectra of virgin iPP, iPP processed by SC $CO_2$ (without the monomer and initiator) at 308.15 K and 120 bar, and MMA-grafted iPP (90/10) obtained in this work.

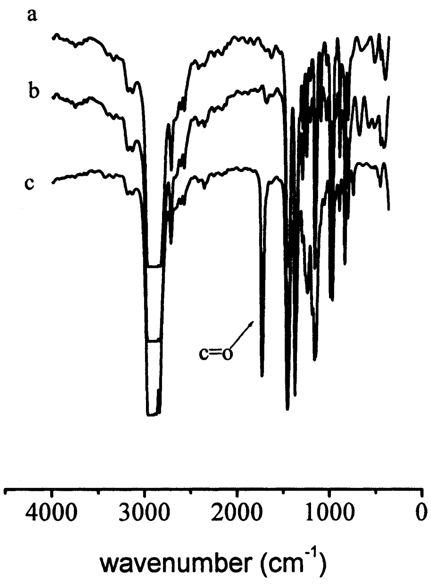


Fig. 6. (a) FTIR spectra of pure iPP, (b) SC $CO_2$ processed iPP and (c) iPP-*g*-2-MMA (90/10).

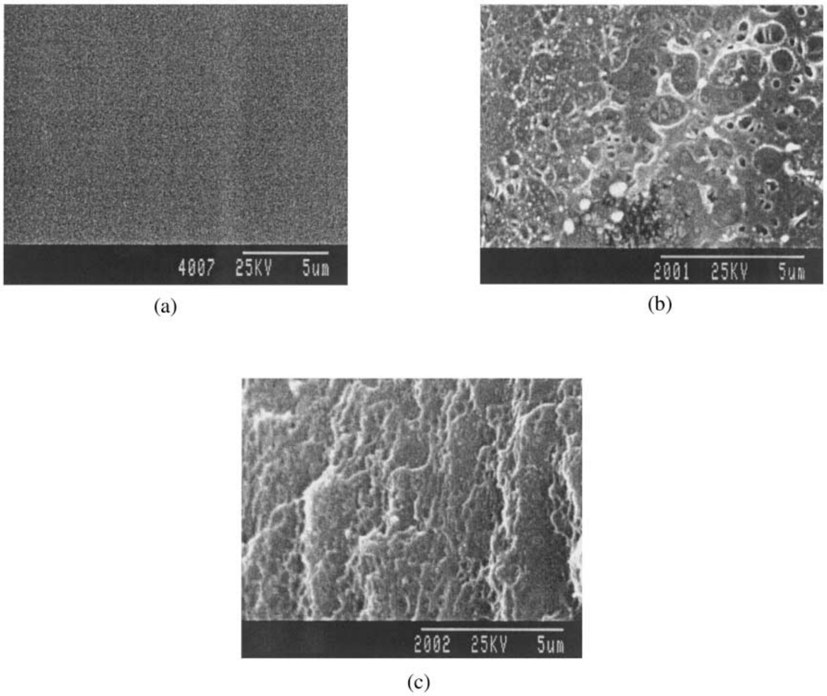
As expected, the spectra of virgin iPP and iPP processed by SC $CO_2$ are almost identical because SC $CO_2$ cannot change the chemical structure of iPP in the course of swelling. The spectra of iPP-*g*-MMA shows stretching bands at 1730 cm$^{-1}$ for the carbonyl group (–C=O) and ether carbon bands at 1130–1160 cm$^{-1}$, indicating that MMA has been grafted onto iPP.

*SEM measurements.* The surfaces of the virginal iPP, $CO_2$-processed iPP and the grafted iPP films were examined by SEM, and the results are shown in Fig. 7.

After processed by SC $CO_2$ at 308.15 K and 12 MPa for 4 h, the morphology of iPP is different significantly from that of virgin iPP, as can be known by comparing Fig. 7(a) and (b). After treating with SC $CO_2$, cell structure was formed on the surface of iPP, which was caused by phase separation in the course of decompression. The phase separation leads to the formation of spherical domain of SC $CO_2$, which, in turn, leads to the formation of cell. The grafted surface shows a markedly bumpy texture. The bumpy surface of grafted layers can be explained by different initiation rates at amorphous and crystalline sites, partly arising from different swelling rates in amorphous and crystalline regions of iPP.

*DSC measurement.* DSC measurements were performed for virgin iPP, iPP processed by SC $CO_2$ at 308.15 K and 120 bar for 4 h, and the iPP-*g*-MMA samples with graft percentage of 27%. The melting and crystallization behaviors of the samples are shown in Figs. 8 and 9.

It is clear from the melting behavior that the iPP-*g*-MMA copolymer shows a double melting peak, the first being broader and lower than the second one. This indicates that



(a) (b)

(c)

Fig. 7. (a) Scanning electron micrographs of virgin iPP film, (b) SC $CO_2$ processed iPP film and (c) iPP-*g*-2-MMA (90/10) film.

the copolymer obtained in this paper is composed of iPP-*g*-MMA and iPP components.

The $T_m$, corresponding to the maxima of the peaks in the heating DSC diagrams, and the $T_c$, corresponding to the maxima of the peaks in the cooling DSC diagrams, are listed in Table 1 together with the crystallinity of iPP and the graft copolymer.

It is known from data in Table 1 that the properties of the SC $CO_2$-treated and untreated iPP film are nearly the same. However, the grafting results in considerable changes in these properties. Grafting of MMA onto iPP film reduces the heat of fusion, and the larger the grafting percentage, the larger the effect. The heat of fusion is proportional to the amount of crystalline iPP in the sample. Thus, crystallinity decreases with an increase in grafting percentage. The reason for the decrease in heat of fusion is that the weight fraction of crystalline iPP in copolymer decreases due to incorporation of MMA. However, the crystallinity in iPP

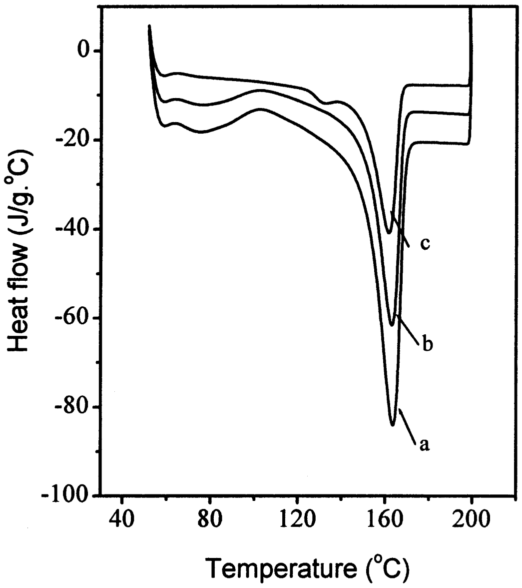


Fig. 8. (a) DSC thermographs for pure iPP, (b) SC $CO_2$ processed iPP and (c) iPP-*g*-2-MMA (90/10) specimens (heating).

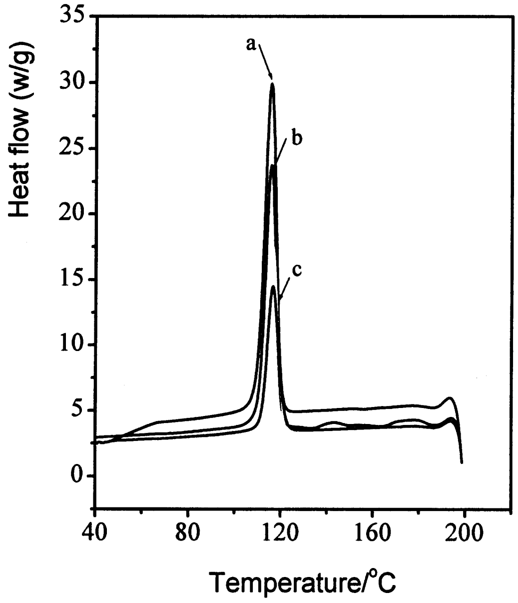


Fig. 9. (a) DSC thermographs for pure iPP, (b) SC $CO_2$ processed iPP and (c) iPP-*g*-2-MMA (90/10) specimens (cooling).

Table 1
Related parameters of iPP and iPP-*g*-MMA

| Samples | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_m$ (J g$^{-1}$) | $\Delta H_c$ (J g$^{-1}$) | $C_a$ (%) | $C$ (%) |
|---|---|---|---|---|---|---|
| iPP | 163.5 | 115.7 | 77.02 | 91.06 | 36.9 | 36.9 |
| iPP $CO_2$ processed | 163.0 | 115.8 | 75.31 | 90.89 | 36.0 | 36.0 |
| iPP-*g*-MMA (9%) | 161.5 | 116.5 | 70.27 | 81.63 | 33.7 | 37.0 |
| iPP-*g*-MMA (27%) | 160.0 | 116.4 | 59.69 | 63.84 | 28.6 | 39.4 |
| iPP-*g*-MMA (38%) | 159.5 | 117.4 | 57.70 | 55.73 | 26.7 | 43.2 |

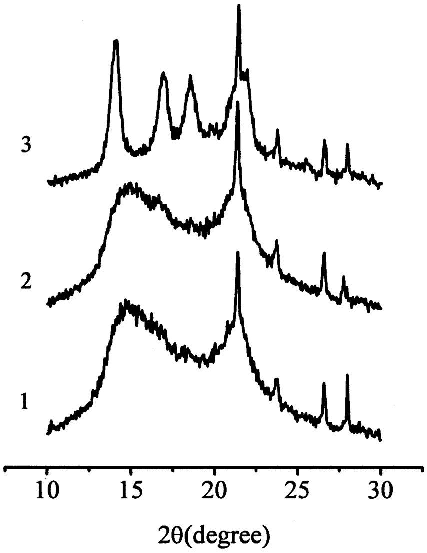


Fig. 10. (a) WAXD diffractiongraphs for pure iPP, (b) SC $CO_2$ processed iPP and (c) iPP-*g*-2-MMA (90/10) specimens.

portion increases with the percentage of grafting, mainly because the MMA acts as a nucleation agent.

*WAXD*. In order to investigate the crystallization behavior of the grafted iPP obtained using SC $CO_2$ as solvent and swelling agent, WAXD study was performed. Typical WAXS diffractograms of plain iPP, iPP processed by SC $CO_2$, and iPP-*g*-MMA films are shown in Fig. 10. As shown in Fig. 10, the plain iPP and SC $CO_2$ processed iPP films show the similar diagrams. Two diffraction peaks appearing at $2\theta = 14$ and 21°, which indicates β-form crystallines. This also suggests that treating with SC $CO_2$ cannot change the crystalline form of iPP noticeably. However, the grafted iPP films shows five diffraction peaks, and the angles corresponding to the diffraction peaks are characteristic of the crystal structure of the α form of polypropylene. So grafting MMA onto iPP results in the transformation of crystalline from β to α form. Fang et al. [2] also found this phenomenon in their study on grafting 2-hydroxyethyl methacrylate onto polypropylene membrane.

## 4. Conclusion

The iPP-*g*-MMA graft copolymer could be prepared by free radical polymer in the swollen iPP matrix with the aid of SC $CO_2$ as solvent for MMA and BPO and swelling agent for iPP matrix. FTIR spectra of virgin iPP, SC $CO_2$ processed iPP, and grafted iPP confirm that MMA indeed grafted onto iPP. DSC measurements show that the melting temperature of the grafted copolymer is lower than that of virgin iPP, and the effect of grafting on the crystallization temperature is not noticeable. SEM studies allow assessing the effect of grafting on morphology. WAXD study indicates that the crystallinity of the grafted iPP decreases with increasing degree of grafting.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (50173030) and the Project of the Chinese Academy of Sciences KGCX2-202. The authors are grateful to Prof. Lianghe Shi who read the paper carefully and proposed helpful opinion.

## References

[1] Shukla SR, Athalye AR. J Appl Polym Sci 1993;49:2019.
[2] Fang Y, Lu XB, Cheng Q. J Appl Polym Sci 1998;68:83.
[3] Patel AC, Brahmbhatt RB, Jain RC, Devi S. J Appl Polym Sci 1998;69:2107.
[4] Sathe SN, Rao S, Devi S. J Appl Polym Sci 1994;53:239.
[5] Eckert CA, Knutson BL, Debenedetti PG. Nature 1996;383:313.
[6] McHugh MA, Krukonis VJ. Supercritical fluids extraction: principle and practice. 2nd ed. Boston: Butterworth-Heinemann, 1994.
[7] Canelus DA, DeSimone JM. Macromolecules 1997;30:5673.
[8] Xu Q, Han BX, Yan HK. Engng Chem Metall (China) 1999;20:313.
[9] Yates MZ, Li G, Shim JJ, Maniar S, Johnston KP, Lim KT, Webber S. Macromolecules 1999;32:1018.
[10] Huang ZH, Shi CM, Xu JH, Kikic S, Enick RM, Beckman EJ. Macromolecules 2000;33:5437.
[11] Long DP, Blackburn JM, Watkins JJ. Adv Mater 2000;12:913.
[12] Watkins JJ, McCarthy TJ. Macromolecules 1994;27:4845.
[13] Watkins JJ, McCarthy TJ. Macromolecules 1995;28:4067.
[14] Li D, Han BX. Macromolecules 2000;33:4550.
[15] Li D, Han BX. Ind Engng Chem Res 2000;39:4509.
[16] Kazarian SG, Vincent MF, West BL, Eckert CA. J Supercrit Fluids 1998;13:107.
[17] Vincent MF, Kazarian SG, Eckert CA. AIChE J 1997;43:1838.
[18] Berens AR, Huvard GS, Korsmeyer RW, Kunig FW. J Appl Polym Sci 1992;46:231.
[19] Li D, Yang GY, Han BX, Yan HK, Gao XS. Engng Chem Metall (China) 1999;20:305.
[20] Hayes HJ, McCarthy TJ. Macromolecules 1998;31:4813.
[21] Brandrup S, Immergut EM. Polymer handbook, vol. 5. New York: Interscience, 1975.