Polym. Bull. (2009) 63:341–354
DOI 10.1007/s00289-009-0091-6

ORIGINAL PAPER

In situ chlorinating-graft copolymerization on isotactic polypropylene in gas–solid phase

Li Zhang · Yingying Sun · Yanqing Ma · Jiruo Zhao · Ying Feng · Jinghua Yin

Received: 2 January 2009 / Revised: 20 April 2009 / Accepted: 21 April 2009 /

Abstract A novel method in situ chlorinating-graft copolymerization (ISCGC) of grafting maleic anhydride (MAH) on isotactic polypropylene (iPP) in gas–solid phase was investigated in this paper. Chlorine (Cl_2) was used as initiator, chlorinating agent and termination agent at the same time during the reaction. The iPP was chlorinated as well as grafted with MAH in the reaction process. The product with chlorine and MAH in the same molecule was named as PP-*cg*-MAH. Existence of PP-*cg*-MAH was identified by Fourier transform infrared. Thermal behavior and crystallinity of PP-*cg*-MAH were analyzed by differential scanning calorimetry, X-ray diffraction and polarizing microscope. Influencing factors for the value of graft degree were also discussed. Compared with conventional peroxide initiated graft method, ISCGC revealed higher MAH graft efficiency (33%), and particularly alleviated degradation of iPP. iPP could be grafted successfully and without changing physical properties dramatically through this method.

Keywords In situ chlorinating-graft copolymerization · Isotactic polypropylene · Gas–solid phase

---

L. Zhang · Y. Sun · Y. Ma · J. Zhao (✉) · Y. Feng
Key Laboratory of Rubber-Plastics, Ministry of Education,
Qingdao University of Science and Technology,
266042 Qingdao, People's Republic of China
e-mail: jiruozhao@qust.edu.cn

J. Zhao · J. Yin
State Key Laboratory of Polymer Physics and Chemistry,
Changchun Institute of Applied Chemistry, Chinese Academy of Science,
130022 Changchun, People's Republic of China

Introduction

Commodity isotactic polypropylene (iPP) [1, 2] has outstanding mechanical properties, chemical stability, and low cost, so it was used widely in daily life and industry. However, iPP is limited [3] in its applications in some important technological fields because of its lack of chemical functionalities, low surface energy, poor hygroscopicity, low impact strength, and poor compatibility with other polymers. In order to improve the polarity of iPP, a great deal of work has been carried out. Chemical modification such as grafting maleic anhydride (MAH) onto iPP is one of the effective methods. The history of graft modification of PP with MAH can date back to the mid-1960s [4] when a method was developed for reacting MAH on particulate isotactic PP below its melting point. From then on, the functionalization of iPP through grafting MAH [5–16] in the presence of organic peroxide as initiator has received much attention and studied extensively through various approaches. Solution [5], molten [6–8] and solid-state processes [9–11] have been successfully built for the preparation of functionalized PP.

Molten process, due to its economic and operational advantages, has been widely used in industry. But some undesirable side reactions, such as degradation of iPP molecular weight caused by β-scission or chain transfer reaction can not negligible in this method. Chung and coworkers [6–8, 12] have been made great efforts toward reducing iPP chain scission during the molten grafted process. Solid-state process, due to its easy operation, lower reaction temperature and free from the need for solvent recovery, has been used widely in recent years. Supercritical carbon dioxide ($scCO_2$) has been the most attractive benign solvent and swelling agent in the process of grafting polar monomers onto PP in the solid state due to its ability to swell and plasticize amorphous domains of macromolecular materials and reduce diffusion resistance. The results [13, 14] showed that $scCO_2$-assisted solid-state grafting process of MAH onto iPP has some scientifically interesting and industrially relevant advantages over the classical solid-state or molten process. But the biggest disadvantage of this method was the complexity for operation.

A novel and convenient method [17, 18] named in situ chlorinating-graft copolymerization (ISCGC) using chlorine (Cl_2) as initiator grafting MAH onto iPP in gas–solid phase is introduced in this paper. There are three advantages over this method. Firstly, it is a one step reaction, chlorinated and grafted MAH onto iPP finished at the same time. Secondly, new polymers with improved properties are easy to obtain by introducing various functional monomers. Thirdly, it is an environmental-friendly process without releasing residual Cl_2 into the air and solvent recovery process. When applying this method to industry field, the unreacted Cl_2 can be recycled and used again. As to the byproduct, hydrochloride is absorbed by water to produce hydrochloric acid with the concentration up to 30%. It can be utilized to avoid draining of the acid solution. These have been reported in the paper [17].

ISCGC have been applied to the graft modification of HDPE and PVC with different monomers [18, 19]. There was no cross-linking or degradation reaction in HDPE and PVC modified copolymers. Graft degree (GD) of MAH grafting on HDPE could reach 2.6 wt% when chlorine content was about 35% [20]. The reason is that although stabilized macroradicals can not be formed in this reaction system, the quick termination reaction of iPP macroradical by chlorine can block β-scission or chain transfer reaction efficiently.

The target of this paper is to investigate the feasibility of the method on modifying iPP and explore the influencing factors on grafting degree. A series of experiments were addressed on iPP to obtain PP-*cg*-MAH copolymer with higher graft degree, lower degradation and lower cross-linking. Molecular structure, thermal properties and crystallinity of PP-*cg*-MAH were identified by FTIR, DSC and XRD.

Experimental

Materials

Commercial PP with 0.25 mm and 0.83 mm particle diameter, melt flow rate (MFR) 5.6 g 10 min^{-1} supplied by Sinopec Qilu Company Ltd (People's Republic of China) was used as matrix polymer; chlorine gas supplied by Qingdao Sinoplase (People's Republic of China) was used as initiator; commercial maleic anhydride without further purification was used as modified monomer supplied by Tianjin dibo chemical Ltd. Xylene, methonal, *N*-*N* dimethyl formamide and decahydronaphthalene et al. were reagent-grade.

Preparation of PP-*cg*-MAH copolymer

The experiment apparatus was shown in Fig. 1. A quantity of 50 g iPP powder and 1.5 g grinded MAH powder were put into a round-bottom three-neck flask (2) equipped with a thermometer (3), a vane stirrer (4) and gas delivery tube. The total weight of them (2, 3, 4 and 5) was marked as W_0. Every apparatus was sealed well to form a sealed system to prevent the release of Cl_2. The contents in the flask (2)

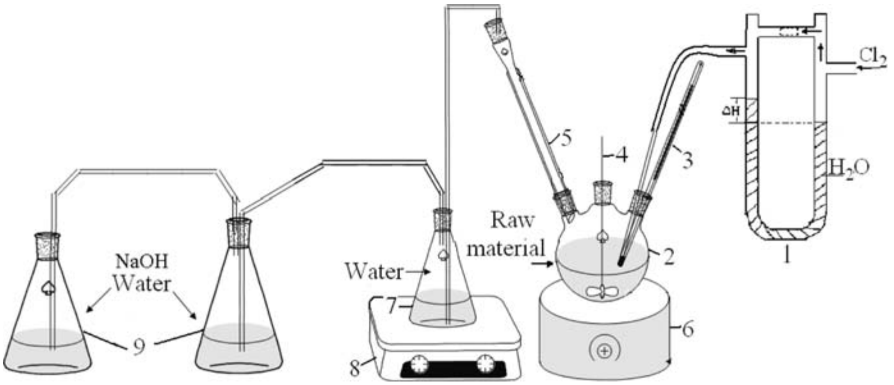


Fig. 1 Schematic representation of the experimental apparatus. *1* U flow meter, *2* three-necked flask, *3* thermometer, *4* vane stirrer, *5* buffer tube, *6* temperature controller, *7* water bottle, *8* balance, *9* NaOH solution bottle

were stirred and heated to 60 °C for 30 min to disperse MAH well in iPP. Then heat was stopped and certain amount of separant SiO_2 was added into the flask (2) to inhibit the agglomeration of iPP at high temperature. After that, nitrogen (N_2) was introduced into the reactor system at about 40 °C for 15 min to eliminate the oxygen (O_2). And then, chlorine was introduced to initiate the reaction. Reaction temperature was controlled by temperature controller.

The extent of reaction was indicated by the amount of hydrogen chloride (HCl) released from the reaction system. The amount of HCl was calculated by checking the weight changing of the water bottle (7) by the balance (8) in Fig. 1. When precalculated HCl weight was reached, Cl_2 and the heat were stopped and the reaction was terminated. The whole reaction took about 1 h after chlorine gas was introduced. After the system was cooled down to room temperature, residual chlorine gas in the flask (2) was cleared completely by vacuum pumping. Checking the weight of the 2, 3, 4, and 5, the result was marked as $W_{t.}$ The chlorine content of the reaction products is as follows:

$$\mathrm{Cl}\,\% = \frac{\frac{\Delta W}{34.5} + \Delta W}{m(\mathrm{MAH}) + m(\mathrm{iPP}) + \Delta W} \tag{1}$$

where m(MAH) is the initial mass of MAH, m(iPP) is the initial mass of iPP, $\Delta \mathrm{W} = W_t - W_{o.}$

Chlorinated iPP (CPP) was prepared through the above process without monomer in the flask (2).

Purification of the products

PP-*cg*-MAH was purified by reprecipitation. The modified iPP was dissolved in xylene at an elevated temperature (130 °C), and subsequently precipitated by methanol ($V_{\mathrm{xylene}} : V_{\mathrm{methanol}} = 1{:}2$–$3$) to remove the residual unreacted or chlorinated MAH. Then the precipitate was filtered and dried in an oven at 60 °C for 2 h. The process was repeated three times and the final product was dried in a vacuum oven at 50–60 °C until the final product reached constant weight.

Characterization

Fourier transform infrared (FTIR) spectra of the purified copolymer (KBr pellet) were recorded on a VERTEX-70 FTIR spectrometer (Germany) with the wave number 4,000–400 cm^{-1} to character molecular structure of polymers.

Graft degree (GD) of PP-*cg*-MAH was determined by standard titration method by calculating the carboxylic acid number in graft copolymer. About 0.5 g purified PP-*cg*-MAH was weighed accurately and put into a beaker, and then 60 mL xylene was put into it. After the mixture boiled for about an hour, three drops water and three drops dimethyl formamide which was to accelerate maleic anhydride hydrolysis were dropped into the beaker at about 80 °C. Then the mixture was heated for another half an hour. Phenolphthalein/methanol solution was used as tracer agent. Titration was held at high temperature with KOH/methanol solution

(0.008 mol L^{-1}). After titration end-point reached, more 2 mL KOH/methanol was added into the beaker, and then the system was back titration by HCl/isopropanol solution (0.029 mol L^{-1}). There was no deposition formed during the titration process. The Eq. (2) [21] was applied to calculate the graft degree:

$$\mathrm{GD}\ \% = \frac{C_{\mathrm{KOH}} V_{\mathrm{KOH}} - C_{\mathrm{HCl}} V_{\mathrm{HCl}}}{2m} \times 98.06 \tag{2}$$

where C_{KOH} and V_{KOH} are the concentration (mol L^{-1}) and volume (mL) of the titrant KOH/methanol solution, C_{HCl} and V_{HCl} are the concentration (mol L^{-1}) and volume (mL) of HCl/isopropanol solution, m (mg) is the weight of the polymer sample. 2 in Eq. (2) represents that one maleic anhydride can form two carboxylic acid after entire hydrolyzation.

Graft efficiency (GE) of MAH is calculated as follows:

$$\mathrm{GE} = \frac{\text{weight of grafted MAH}}{\text{initial concentration of MAH}} \times 100\% \tag{3}$$

Thermal characteristics of the grafted copolymers, including melting point temperature (T_{m}) and degree of crystallinity (χ_{c}), were determined by first scanning DSC. The thermal behavior of the copolymers was assessed with a DSC (204F1, Germany) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The area under the melting peak was taken to be the melting enthalpy. The crystallinity of the graft copolymers was determined by Eq. (4) [21]:

$$x_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100\% \tag{4}$$

where ΔH_f(J g^{-1}) is the melting enthalpy of copolymers, and ΔH_f^0 is the enthalpy of 100% crystalline PP (ΔH_f^0= 209 J g^{-1}).

The crystallinity of the graft copolymer was determined by X-ray diffraction (XRD) analysis using D/MAX-RB powder diffractometer (Japan) employing Cu Kα ($\lambda = 1.54059$ Å) radiation over the range $5° \le 2\theta \le 40°$. The crystallinity of the graft copolymers was calculated using the following equations [22]:

$$x_c = \frac{I_c}{I_c + 1.25 I_A} \times 100\% \tag{5}$$

I_c and I_A are intensities of X-ray scattering from crystalline and amorphous regions, respectively;

$$I_c = I_{110} + 1.63 I_{040} + 2.14 I_{130} + 3.51 I_{111}^{044} \tag{6}$$

$I_{110}, I_{040}, I_{130}, I_{111}^{044}$ are X-ray scattering intensity from 2θ: 14.16°, 17.08°, 18.60°, 21.20°, respectively.

Spherulite morphology of iPP and PP-*cg*-MAH were observed by Olympus-BX 51 Polarizing Microscope, Nikon-E200 camera system (Japan). The samples were given a uniform thermal treatment prior to taking the microgram. They were heated to 180 °C from ambient temperature at a rate of 10 °C min^{-1}, and then cooled down to room temperature in ambient atmosphere.

The intrinsic viscosities of polymers were measured in decahydronaphthalene dilute solution at 135 °C with an Ubbelohde viscometer [23]. The viscosity molecular weight was calculated by the Mark–Houwink equation: $[\eta] = KM^{\alpha}$, where $K = 1.1 \times 10^{-5}$ and $\alpha = 0.80$ [24]. Both CPP and PP-*cg*-MAH used the same K and α value as iPP due to the low chlorine content of CPP, low graft degree about 1 wt% and chlorine content of PP-*cg*-MAH.

Gel content (GC) was measured by putting 0.5 g PP-*cg*-MAH into a nickel screen (mesh size: 120) pack, and then boiled in 150 mL xylene solution for 12 h. After that, samples were dried in a vacuum oven at 50–60 °C until to the constant weight. The value of GC was calculated with the following equation:

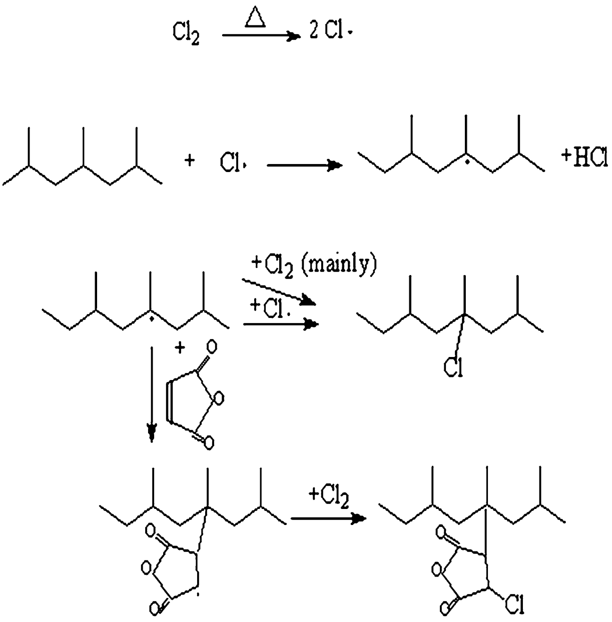
$$\mathrm{GC}\ \% = \frac{W_t}{W_0} \times 100\% \tag{7}$$

where W_t is the constant weight of copolymer after boiled; W_0 is the initial weight of copolymer before boiled.

Results and discussion

Feasibility of in situ chlorinating-graft copolymerization grafting MAH on PP

According to the chlorine free-radical substitution reaction mechanism [25], the chlorinated and MAH grafted process is shown in Scheme 1. A chlorine molecule can split into two chlorine radicals when heated. Chlorine radical can abstract H



Scheme 1 Mechanism of chlorinated and graft reaction process

Table 1 $\overline{M_\eta}$ and GC Comparison of PP, CPP, PP-*cg*-MAH

	MAH portion (g 100 g^{-1} iPP)	$\overline{M_\eta} \times 10^{-3}$ (g mol^{-1})	GD (wt%)	GC (wt%)	Temperature (°C)
PP		201	0	0	
CPP	0	200	0	0	110
PP-*cg*-MAH 1	3	154	0.2	0	80
PP-*cg*-MAH 2	3	147	0.96	0	90
PP-*cg*-MAH 3	3	104	1.02	0	100

atom from iPP backbone to produce iPP macroradical. Then chlorine and sometimes chlorine radical have the chance to terminate macroradical forming chlorinated polypropylene (CPP). In the process of gas–solid phase chlorination, abundant of chlorine molecules and chlorine radicals always exist with chlorine entering the reaction system continuously, which ensure the terminate reaction rate of iPP macroradicals. High producing and terminating rate of macroradicals can hardly provide any chance for radical transfer or coupling termination of polymer backbone. So the CPP molecular weight can maintain as that of iPP. Table 1 showed the GC and $\overline{M_\eta}$ of iPP and CPP. CPP had no GC and almost the same $\overline{M_\eta}$ compared with iPP. So there was almost no cross-linking or degradation of iPP during the chlorinated reaction process in this system.

According to the above paragraph, it is presumed that PP-*cg*-MAH copolymer gained via in situ chlorinating-graft copolymerization also has lower degradation and almost no cross-linking. $\overline{M_\eta}$, GC of PP-*cg*-MAH 1, PP-*cg*-MAH 2 and PP-*cg*-MAH 3 prepared under 100 °C were shown in Table 1. There was no GC in the three graft copolymers, which indicated the nonexistence of cross-linking. The values of $\overline{M_\eta}$ which decreased from 204,000 (iPP) to 104,000 (PP-*cg*-MAH3) indicated that ISCGC could limit degradation of iPP compared with conventional method using DCP as initiator [6], $\overline{M_\eta}$ of which decreased from 161,000 (iPP) to 78,000 (PP-*g*-MAH). GD of the copolymer could reach 1 wt% with only 5% chlorine content after reacted for an hour, showed that ISCGC was an efficient method for the modification of iPP. Further efforts will focus on obtaining copolymer with higher graft degree and lower degradation by forming stabilized macroradicals.

Identification of graft copolymer PP-*cg*-MAH

The presence of the MAH units grafted onto iPP was analyzed by FTIR. In Fig. 2, three spectra were shown, they referred to virgin iPP (spectrum a), chlorinated PP (spectrum b), purified MAH grafted PP (spectrum c), respectively. In spectrum b, additional bands appeared in comparison with spectrum a. They were in the range of wave numbers where characteristic bonds of chlorine (under 800 cm^{-1} shown in Table 2). Additional peaks were located at 1,712, 1,380, 960 cm^{-1} in spectrum c compared with spectrum b. The three bands corresponded to the results of hydrolyzation or alcoholysis of the grafted maleic anhydride during the purification

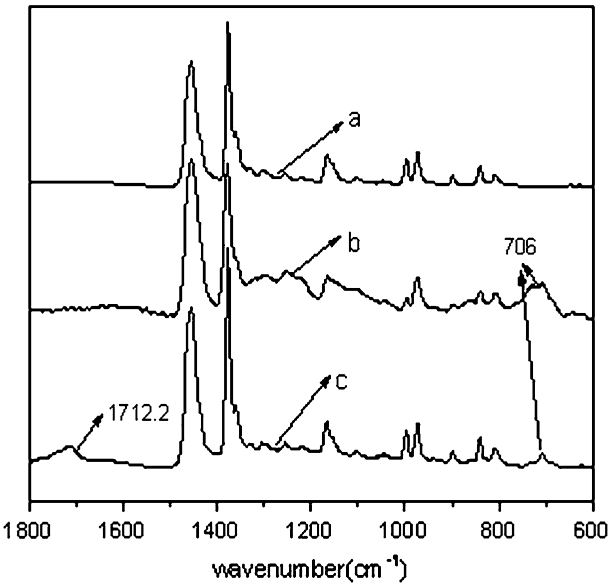


Fig. 2 FTIR spectra of iPP and CPP, PP-*cg*-MAH. *a* iPP, *b* CPP, *c* PP-*cg*-MAH

Table 2 Attribute of characteristic chemical group in FTIR spectra

Chemical group	$-CH_3$ and $-CH_2-$	C–Cl	−C=O	−COOH
Wave-number (cm^{-1})	3,000–2,800	800–600	1,850–1,600	1,725–1,700

of the graft copolymer [26]. And they identified the existence of the graft copolymer PP-*cg*-MAH. There were characteristic bands of helical conformation in PP crystal at 1,165, 998, 895 and 840 cm^{-1} in all the spectra, which illustrated that chlorination and graft have little effect on the regularity of iPP.

Crystal and thermal behavior of PP, PP-*cg*-MAH

Melting temperature of iPP, CPP, PP-*cg*-MAH was 165.1, 154.7 and 151.6 °C, respectively, shown in Fig. 3. T_m of PP-*cg*-MAH was lower than that of virgin iPP. Endothermal peak area of PP-*cg*-MAH was smaller than that of virgin PP, which might be attributed to the crystalline region breakage of iPP by the introduction of MAH. And the average spherulite size in PP-*cg*-MAH was smaller than that of iPP [27]. Crystallinity of iPP, CPP, PP-*cg*-MAH was 31.35%, 32.23% and 29.10%, respectively, shown in Table 3, which indicated that chlorinated and grafted reaction has little influence on crystallity of iPP.

From XRD curves a and b in Fig. 4, the four most intense reflections at $2\theta = 14.1°$, 16.9°, 18.6° and 21.8° were indexed with Miller indices 110, 040, 130, and 131,111. The results indicated that there was α phase crystal in iPP and

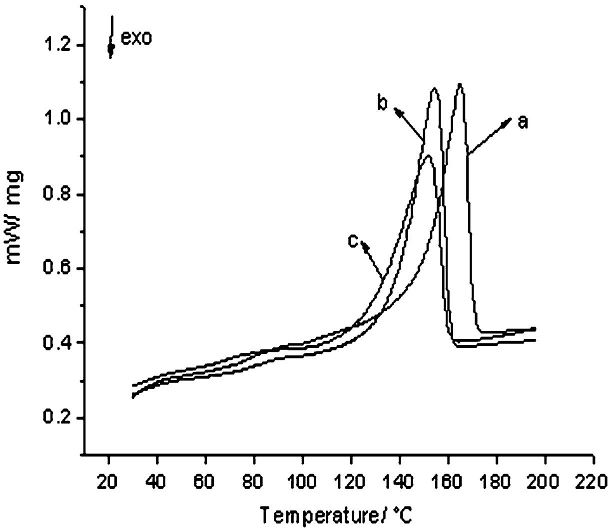


Fig. 3 DSC curves of PP, CPP and PP-*cg*-MAH. *a* PP, *b* CPP, *c* PP-*cg*-MAH

Table 3 Thermal analysis of PP, CPP and PP-*cg*-MAH

	T_m (°C)	H_f (J g^{-1})	X_c (%)
PP	165.1	65.52	31.35
CPP	154.7	67.37	32.23
PP-*cg*-MAH	151.6	60.83	29.10

PP-*cg*-MAH. There was no new crystalline phase [14] formed in the copolymer. The crystallinity of virgin PP was 38.9% and PP-*cg*-MAH was 39.5%. Crystallinity measured by XRD has little difference compared with the result of DSC. It might belong to the error of measurement. The result showed that crystallinity of iPP could maintain after modification.

The crystalline morphology of iPP and PP-*cg*-MAH were given in Fig. 5 by polarizing microscope. Crystalline structure of PP-*cg*-MAH was not as perfect as iPP. PP-*cg*-MAH had smaller spherulite size but more crystalline nucleation compared with iPP, which might be attributed to the leading of MAH into the copolymer, and the presence of carbonyl groups in PP-*cg*-MAH was believed to promote heterogeneous nucleation [28].

Influencing factors on grafting degree

In order to gain PP-*cg*-MAH with higher GD value, we explored many factors which might affect the value of it. Various influencing factors such as concentration of MAH, temperature and chlorine flux were discussed in the following paragraphs.

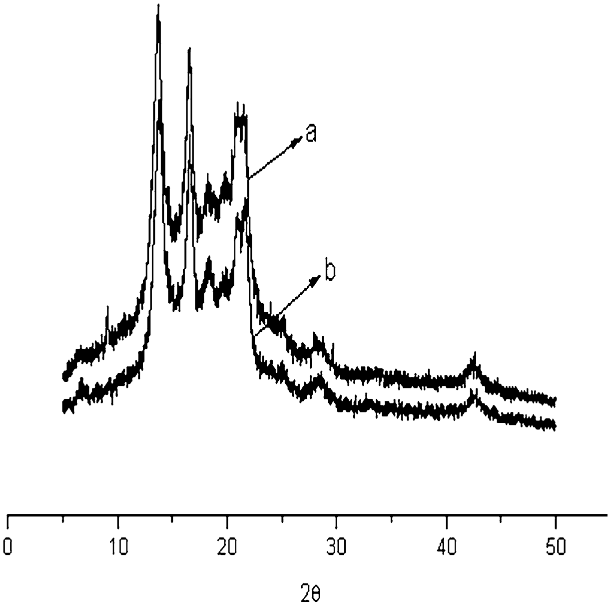


Fig. 4 X-ray diffraction diagrams of PP and PP-*cg*-MAH. *a* PP, *b* PP-*cg*-MAH

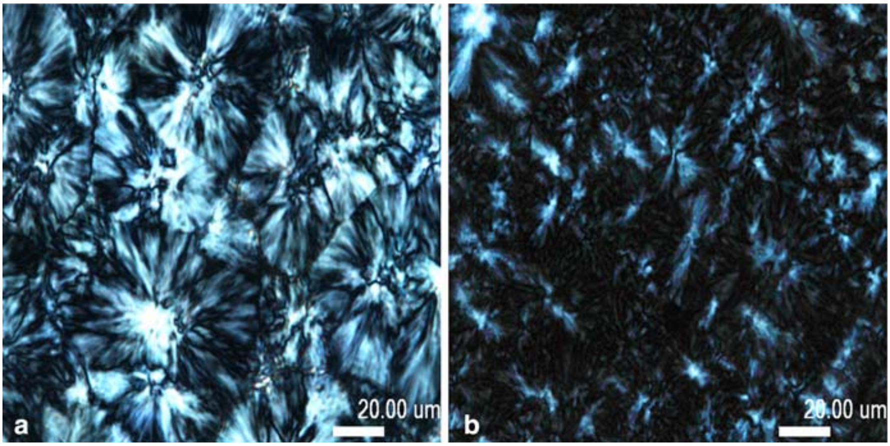


Fig. 5 Polarizing microgram of iPP and PP-*cg*-MAH. **a** iPP, **b** PP-*cg*-MAH

Influence of initial concentration of maleic anhydride

A set of experiments were addressed to investigate the influence of the initial concentration of MAH on grafting degree. Figure 6 showed the value of GD increased with increasing initial concentration of MAH until the initial MAH content was three parts, and the maximum GD was about 1.3 wt%. After that point, graft degree decreased. GE curve showed almost the same tendency as GD curve,

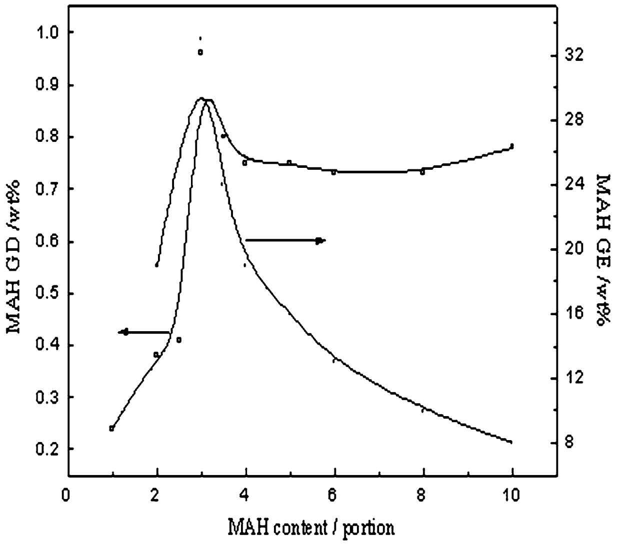


Fig. 6 Effect of initial concentration of MAH on GD and GE

and the maximum value of GE was 33%. Higher GE values of MAH than this have rarely been reported by other papers. After initial MAH content was three parts, GE decreased with initial MAH content increasing. This behavior has already been observed in the maleation of polyolefin in $scCO_2$ system [29]. It could be explained by taking into account the free radicals generated from the chlorine decomposition and MAH diffusion in the reaction system. When a high concentration of anhydride was presented in the system, consumption of chlorine radicals by MAH was favored, and a lower concentration of polymer macroradical was generated. These resulted in a decline of grafting degree, despite the higher MAH concentration in polymer matrix. Otherwise, as conventional solid-phase process, the graft reaction in this system was controlled by the diffusion of monomer in the bulk polymer. With increasing MAH concentration, MAH particle began to aggregate, which reduced the contact area between MAH and iPP matrix and resulted in decline of GD.

Influence of reaction temperature and PP particle diameter

GD first increased and then decreased with increasing reaction temperature shown in Fig. 7. The optimum temperature of the copolymerization were at about 110 °C for both curve a and b. The three competitive reactions: chlorination of MAH, chlorination of iPP backbone, and MAH grafted reaction occurred at the same time in the reaction system. Under low temperature (lower than 90 °C), a low concentration of polymer macroradicals were generated due to low reaction activity of chlorine, MAH chlorinated reaction was inclined to occur and the opportunity for MAH grafting reaction was reduced. Then concentration of macroradicals increased

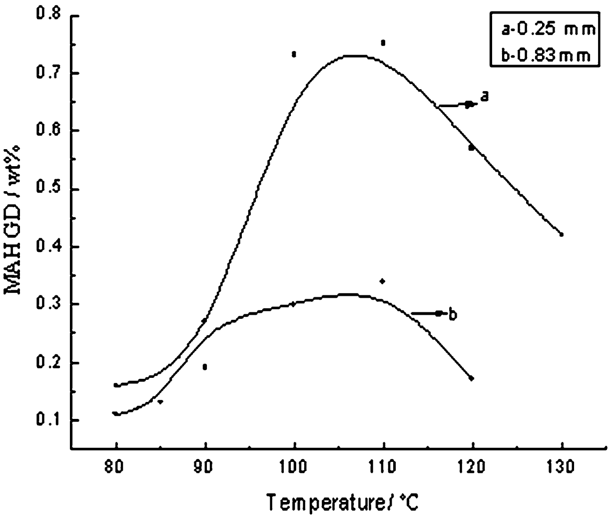


Fig. 7 Effect of temperature on GD with different iPP particle diameter. **a** iPP particle diameter 0.25 mm, **b** iPP particle diameter 0.83 mm

with temperature increasing, the chance for MAH to react with microradicals enhanced, which resulted in the increasing of GD.

Figure 7 also indicated that decreasing iPP particle diameter was in favor of the increase of GD. The particle diameter of iPP was one of the controlling factors in gas–solid reaction system. Decreasing iPP particle diameter would increase contact area between iPP and MAH, and resulted in a higher value of GD.

Influence of chlorine flux

Chlorine acted as initiator in MAH grafted reaction and termination agent in in situ chlorinating graft copolymerization system. The effect of chlorine flux was actually the effect of initiator and termination agent concentration. When the chlorine flux at 16.8 mmol min^{-1}, the value of graft degree was higher compared with chlorine flux at 14.4 mmol min^{-1} at 80 °C; while at 110 °C, the value of graft degree decreased with increasing chlorine flux. The phenomena obtained from Table 4 were interesting. Ability of chlorine decomposing into chlorine radical was weak at

Table 4 Effect of chlorine flux on grafting degree

	Temperature (°C)	Chlorine flux (mmol min^{-1})	GD (wt%)
1	80	14.4	0.19
2	80	16.8	0.42
3	110	14.4	1.3
4	110	16.8	0.61
5	110	30.7	0.2

low temperature (below 90 °C), low concentration of chlorine radical resulted in low concentration of PP macroradicals and limited the opportunity for MAH grafted onto iPP. So a higher chlorine flux might increase the chlorine radical concentration and resulted in a higher value of GD compared with low chlorine flux at low temperature. Value of GD decreased with increasing chlorine gas flux at 110 °C was due to prone tendency of chlorine decomposing into chlorine radicals at higher temperature (higher than 100 °C). When the chlorine flux was small, chlorination of iPP and chlorination of MAH was limited efficiently, so GD reached the maximum under this reaction condition. With increasing chlorine gas flow, the concentration of iPP macroradicals increased, while the opportunity for the termination of iPP macroradicals by chlorine and MAH chlorinated reaction were also easy to occur, they both were competitive reaction with MAH grafted reaction. So after certain primary chlorine radical concentration reached, increasing chlorine flux, the reaction condition would be favorable for chlorination of iPP, therefore, the graft reaction would be restrained and value of GD decreased.

The results from Table 4 indicated that different chlorine gas flux was needed at different reaction temperature in order to attain a higher graft degree. The chlorine gas flux could be changed conveniently in this reaction system according to the necessary.

Conclusions

Feasibility of modifying iPP via in situ chlorinating graft copolymerization was identified in this paper. The results of FTIR confirmed the grafting of MAH onto iPP. T_m of the graft copolymer decreased compared with iPP characterized by DSC. There was no new crystalline phase formed in PP-*cg*-MAH copolymer, crystallinity could maintain mostly compared with iPP and grafted MAH onto iPP could decrease the spherulite size of iPP from XRD and Polarizing Microscope analysis. With varying experiment conditions, the maximum value of grafting degree and graft efficiency could reach 1.3 wt% and 33% respectively. Under low temperatures in this reaction system, such as below 100 °C, side reactions like degradation and cross-linking of iPP could be controlled efficiently, and PP-*cg*-MAH had similar molecular weight compared with iPP. In ISCGC reaction system, the initiator concentration could be changed conveniently when needed; GD could reach 1.3 wt% in an hour; graft copolymer with controlled degradation and cross-linking could be obtained. So it was a feasible, simple and efficient method for the modification of iPP.

Acknowledgment The authors acknowledge financial support from National Natural Science Foundation of China (50373042, 50390090).

References

1. Saule M, Moine L, Castaing MD (2005) Chemical modification of polypropylene by decomposition of unsaturated peroxides. Macromolecules 38:77–85
2. Naqvi MK, Choudhary MS (1996) Chemically modified polyolefins and their blends. Polym Rev 36:601–629

3. Guldogan Y, Egri S, Zakir MO (2004) Comparison of maleic anhydride grafting onto powder and granular polypropylene in the melt by reactive extrusion. J Appl Polym Sci 92:3675–3684
4. Reid DE, Spurlin HM (1968) Modification of crystalline propylene polymers. US Patent 3414551
5. Minoura Y, Ueda M, Mizunuma S (1969) The reaction of polypropylene with maleic anhydride. J Appl Polym Sci 13:1625–1640
6. Coiai S, Passaglia E (2004) Control of degradation reactions during radical functionalization of polypropylene in the melt. Macromolecules 37:8414–8423
7. Lu B, Chung TC (1998) Maleic anhydride modified polypropylene with controllable molecular structure: new synthetic route via borane-terminated polypropylene. Macromolecules 31:5943–5946
8. Wang Z, Hong H, Chung TC (2005) Synthesis of maleic anhydride grafted polypropylene with high molecular weight using borane/O_2 radical initiator and commercial PP polymers. Macromolecules 38:8966–8970
9. Rengarajan R, Parameswaran VR, Lee S (1990) Peroxide-catalyzed swell grafting of maleic anhydride onto polypropylene. Polymer 31:1703–1706
10. Ko TM, Ning P (2000) Peroxide-catalyzed swell grafting of maleic anhydride onto polypropylene. Polym Eng Sci 40:1589–1595
11. Patel AC, Brahmbhatt RB, Rao PC (2000) Solid phase grafting of various monomers on hydroperoxidized polypropylene. Eur Polym J 36:2477–2484
12. Shi D, Li R, Zhu Y (2006) Nano-reactors for controlling the selectivity of the free radical grafting of maleic anhydride onto polypropylene in the melt. Polym Eng Sci 46:1443–1454
13. Galia A, Gregorio RD, Spadaro G (2004) Grafting of maleic anhydride onto isotactic polypropylene in the presence of supercritical carbon dioxide as a solvent and swelling fluid. Macromolecules 37:4580–4589
14. Liu T, Hu G (2005) Supercritical carbon dioxide assisted solid-state grafting process of maleic anhydride onto polypropylene. Ind Eng Chem Res 44:4292–4299
15. Flaris V, John DM (2001) High melt flow, highly-grafted polypropylene. US Patent 6228948
16. Häusler L, Gerecke J (2007) Method for producing polypropylenes modified by maleic acid anhydride. EP Patent EP1389302
17. Zhao JR, Li JY, Feng Y (2007) A novel approach to synthesis of functional CPVC and CPE or graft copolymers-in situ chlorinating graft. Polym Adv Technol 18:822–828
18. Zhao JR, Feng Y, Chen X (2003) Graft-modified HCPE with methyl methacrylate by the mechanical chemistry reaction. I. Synthesis and characterization. J Appl Polym Sci 89:811–816
19. Zhao JR, Feng Y, Chen X (2004) Graft-modified HCPE with methyl methacrylate by the mechanochemistry reaction? The physical-mechanical properties and processability. J Appl Polym Sci 91:282–287
20. Lin YS, Li LL, Zhao JR (2005) In-situ chlorinating and MAH grafting on molecular chains of high density poly-ethylene. Chin J Appl Chem 22:1282–1286
21. Gaylord NG, Mishra MK (1983) Nondegradative reaction of maleic anhydride and molten polypropylene in the presence of peroxides. J Polym Sci: Polym Lett Ed 21:23–30
22. Yin JH, Mo ZS (2001) Contemporary polymer physics. Chemical Industry Press, Beijing
23. ISO1628 13-1991(E)
24. Brandrup J, Immergut EH (1989) Polymer handbook, 3rd edn. Wiley-Interscience, New York
25. March J (1992) Advanced organic chemistry, 4th edn. Wiley-Interscience, New York
26. Wang ZX (1989) Polymer FTIR analysis. Sichuan University Publication, Chengdu
27. Gaceva GB, Mahngovska B, Mahder E (2000) Crystallization kinetics of maleic anhydride—modified iP studied by POM. J Appl Polym Sci 77:3107–3118
28. Sathe S, Rao G, Revi S (1994) Grafting of maleic anhydride onto polypropylene: synthesis and characterization. J Appl Ploym Sci 53:239–245
29. Dong Z, Liu Z, Han B (2002) Modification of isotactic polypropylene film by grafting of acrylic acid using supercritical CO_2 as a swelling agent. J Mater Chem 12:3565–3569