

Preparation of Epoxy Functionalized PP with Unique Structure and Its Post-Ring Open Reaction

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ABSTRACT: This article discusses a convenient chemical approach named *in situ* chlorination graft copolymerization (ISCGC) to prepare epoxy functionalized isotactic polypropylene (iPP) with a unique structure. This method was carried out in the gas-solid state, and chlorine was used as radical initiator as well as terminate agent. The effect of influence factors on the structure of the functionalized PP was investigated, and it was determined by levels of grafted GMA moieties. The results showed that PP modified with GMA could obtain higher grafting level. Crystallinity and mechanical properties of the functionalized PP were also investigated. For the purpose of researching the reactivity of epoxy groups located at the grafted side chains, trichloroacetic acid and hydroxyl-terminated butadiene-acrylonitrile rubber (HTBN) were used

as models to explore the ring open reaction of the epoxy groups of the functionalized PP. The structure and property of the modified PP that has undergone post-ring open reaction was characterized by FTIR, dynamic property analysis. The results indicated that epoxy groups of the graft side chains have successfully undergone ring open reaction in the presence of carbonyl and hydroxyl groups. Additionally, the compatibilization of PP with HTBN is enhanced after PP was modified by GMA. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4827–4837, 2012

Key words: functionalization of polymers; poly(propylene) (PP); grafting; post-ring open reaction; structure-property relations

INTRODUCTION

Isotactic polypropylene (iPP) is a very interesting polyolefin because of its excellent mechanical property and chemical stability; additionally, it can be obtained from inexpensive feed stocks. Therefore, it was used in a variety of applications. However, it suffers from lacking of reactivity and polarity leading to low adhesive and compatibility with other polar polymers, metals, and ceramics.¹ To expand its application, modification of polypropylenes by introducing the functional groups is an efficient strategy to generate new materials with enhanced chemical or physical properties, including terminal functionalized PP,^{2–4} radical grafting reaction,^{5,6} and anion grafting reaction.⁷ Among these modification approaches, a great deal of work has been carried out in radical grafting reaction due to its economic and operational advantages. Grafting monomers including maleic anhydride (MAH),^{8–10} acrylic acid (AA),¹¹ and glycidyl methacrylate (GMA)^{12–14} have

been largely reported. Among these grafted monomers, PP modified by GMA has been intensively studied over the past decades due to the advantages of GMA that is a bifunctional monomer containing an unsaturated group suitable for free-radical grafting and an epoxy group capable of interacting with numerous reactive groups such as hydroxyl, carbonyl, and amine.¹⁵ So GMA-modified polyolefin has been widely used as an effective compatibilizer in PP/PBT,¹⁶ PP/PET blends.^{17,18} Moreover, other functional groups could be introduced into polymer by a post-ring open reaction involving epoxy rings in GMA. For example, the phosphonation or the sulfonation of the PGMA graft side chains would result in the graft side chains containing phosphoric acid groups or sulfonate groups, the prepared post-functionalized polymer can be used as ion-exchange materials.^{19,20}

Grafting of GMA onto PP can be successfully performed in the melt, solution, and solid state. However, both the melt and solution suffers from major problems, the former suffers from the PP chain β scission due to the higher operating temperature, which will compromise the good mechanical properties of PP; the later faces the difficulty in removing the organic solvent from the functionalized polymer. While modifying PP in the solid state is an attractive approach to functionalize PP at a relatively lower

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temperature and solvent free system.²¹ Additionally, new initiator has been applied to pursue functionalized PP with higher GMA grafting level as well as unaltered molecular structure of PP.²²

In this article, a novel chemical approach named *in situ* chlorination graft copolymerization (ISCGC) would be used to prepare epoxy functionalized PP with higher grafting level and grafting efficiency, which was carried out in the gas–solid state.

Our laboratory has been interested in polyolefins modified by ISCGC for many years.^{23–26} In fact, this chemical approach has taken advantage of the high chemical reactivity of the chlorine. Chlorine plays multi roles in grafting, in which it can be served as free radical initiator as well as radical termination agent. Chlorine is led into the reaction system continuously; and radical can be regenerated and terminated constantly due to the high reactivity of chlorine. Thus, some side reactions including chain transfer reactions or macroradicals combination can be largely limited because these radicals can be terminated by chlorine timely. We attempt to apply this chemical approach in PP modification for the purpose of obtaining modified PP with higher grafting level and limited PP chain degradation. Some preliminary research has got some progress.^{24–26}

Multi functionalization PP with both epoxy groups and C=C double bonds located at the graft side chains has been gained by ISCGC.²⁶ The goal of this study is to obtain functionalized PP with higher grafted GMA levels by exploring the preparation conditions, such as GMA initial concentration, chlorine concentration, reaction temperature, and the addition of a second comonomer. It can be concluded that grafting degree of the functionalized PP can reach 1.34%. Subsequently, the reactivity of epoxy groups with carboxyl and hydroxy was discussed in the final section of the article. On the basis of FTIR and dynamic property analysis (DMA) analysis, it indicated that epoxy functionalized PP can successfully undergo post-ring open reaction in the presence of carbonyl and hydroxyl groups. What's more, PP-*cg*-GMA maintained the mechanical properties of PP and with a higher polarity. Because the epoxy functionalized PP is actually the PP grafted polymer, for the purpose of clarity, the original epoxy functionalized PP is denoted as PP-*cg*-GMA.

EXPERIMENTAL

Materials

Isotactic polypropylene powder (iPP number average molecular weight (M_n) = 32,480 g/mol, polydispersity index: PDI = 5.89) was purchased from Shandong Fufeng Chemical Co. (China). Chlorine was supplied by Hygain Chemical Group Co.

(China). Glycidyl methacrylate (GMA, purity $\geq 98.0\%$) was purchased from Shanghai Yuanji Chemical Co. (China), and it was used without further purification. Hydroxyl-terminated butadiene–acrylonitrile rubber (HTBN, $M_n \geq 2500$) was supplied by Zibo Qilong Chemical Industry Co. (China). Trichloroacetic acid (analytical reagents) was purchased from Tianjin Kamel Chemical Reagent Co. (China). Solvents, involving toluene, xylene, acetone, and methanol were all analytical reagents and it was purchased from Yantai Sanhe Chemical Reagent Co. (China).

Preparation and purification of PP-*cg*-GMA

Preparation

A round-bottom three-neck flask was charged with PP powders (50 g), and then a known quantity of GMA was added into the PP matrix in multiple times, using a vane stirrer to stir the mixture continuously to make GMA monomers disperse well in the PP matrix. The additional amount of GMA was varied from 1 to 8% (v/wt %). Then the flask was equipped with a thermometer, a vane stirrer and gas delivery tubes were sealed well to form a sealed system to prevent the release of Cl_2 . After that, the flask was purged with chlorine for 15 min to remove the oxygen. The system was then heated to the desired reaction temperature (from 90 to $135 \pm 2^\circ\text{C}$) that was controlled by a temperature controller. The addition of further chlorine and the heating were stopped when the expected chlorine content of the product was reached. Chlorine content of the grafted copolymer 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 by a balance. Finally, residual chlorine gas in the flask was removed by vacuum pumping after the temperature was cooled down to room temperature. During this process, the flask was evacuated and backfilled with atmosphere three times to completely clear the residual chlorine. The schematic diagram of ISCGC reaction system is depicted in detail in our previously published work.²⁴ The chlorine content of PP-*cg*-GMA prepared was controlled at about 3–4 wt %, and its calculated method can consult reference.²⁶

Purification

Crude PP-*cg*-GMA sample was purified by precipitation. PP-*cg*-GMA (1.5 g) was dissolved in xylene (40 mL) and the solution was refluxed at its boiling temperature for about 1/2 h, and subsequently precipitated by cold acetone (80 mL) to remove the residual un-reacted GMA monomer and homopolymer of GMA (PGMA). Then the precipitate was filtered

using a vacuum pumping, and the sample “cake” can be obtained and dried in an oven at 50–60 °C for 2 h. The aforementioned process was repeated three times and the final sample cake was crushed into small pieces, and subsequently dried in a vacuum oven at 50–60°C until a constant weight was reached.

Characterization

Determination of grafting degree (GD) and grafting efficiency (GE)

The grafting degree (GD) of GMA in PP-*cg*-GMA is defined as the weight percentage of GMA. A nonaqueous back titration was employed to determine GD of PP-*cg*-GMA, and performed by the following procedures: about 0.3 g purified sample was dissolved in 60-mL toluene, subsequently 1-mL CCl_3COOH /xylene (concentration: $0.3239 \text{ mol L}^{-1}$) was added into the mixture, and stirred for 20 min. The solution was kept at 110–115°C and refluxed for about 2 h. Then, the hot solution was titrated immediately with the $0.0469 \text{ mol L}^{-1}$ KOH/CH₃OH and phenolphthalein/methanol solution was used as an indicator. Titration was stopped when the coloration remained for 30 s, and there was no precipitate formed during titration. The following equation is used for calculating the grafting degree (GD) of PP-*cg*-GMA:

$$\text{GD} = \frac{(C_1V_1 - C_2V_2) \times 142.15}{1000W} \times 100\% \quad (1)$$

where C_1 and V_1 are the concentration (mol L^{-1}) and addition volume (mL) of the CCl_3COOH /xylene solution, C_2 and V_2 are the concentration (mol L^{-1}) and consumed volume (mL) of KOH/CH₃OH solution respectively, “142.15 g mol^{-1} ” is the molecular weight of GMA, and W (g) is the weight of the grafted polymer.

To determine GE of the product, GMA homopolymer yield is necessary to be determined by a soxhlet extraction. Crude grafted samples were dissolved in hot xylene at refluxing temperature ($m_{\text{polymer}}/V_{\text{xylene}}$ is 4 g/100 mL); subsequently, it was poured into excess amount of cold methanol (300–400 mL) and the mixture was being stirred at the same time. After that, the polymer precipitate was filtered by vacuum pumping to remove the solvent. Finally, the sample cake obtained was dried under vacuum at 50–60°C until a constant weight was reached. In the aforementioned process, the residue GMA monomer would be removed from the polymer, and the grafted polymer and homopolymer would be deposited as the sample cake. Later, the dried sample cake was hot pressed into thin sheet and cut into small pieces, then weighted accurately and denoted as W_0 .

Subsequently, it was extracted in a Soxhlet extractor using acetone for 20 h, and after that, the extracted samples were dried under vacuum at 50–60°C until a constant weight was reached. The dried samples were accurately weighted and denoted as W_1 . The homopolymer would dissolve in the refluxing acetone during the extraction, and GMA homopolymer content was calculated as $W_0 - W_1$. Herein, grafting efficiency (GE) was defined as the quotient of monomer graft content divided by GMA homopolymer content; it was described as the following relationships:

$$\text{GE} = \frac{m_{\text{graft}}}{m_{\text{homopolymer}}} = \frac{W_0 \times \text{GD}}{W_0 - W_1} \quad (2)$$

Viscosity average molecular weight (M_v)

M_v of the functionalized PP were measured according to ISO 1628-3: 1991 in dilute decahydronaphthalene solution at 135°C using an Ubbelohde viscometer and were calculated according to the Mark–Houwink equation $[\eta] = KM_v^\alpha$. For PP polymer measured in decahydronaphthalene solution, the $K = 1.1 \times 10^{-2} \text{ mL g}^{-1}$ and $\alpha = 0.80$,²⁷ K , α value of functionalized PP was same as PP due to the low-chlorine content (about 3%) and GMA grafting level (about 1%) .

FTIR analysis

The spectra of the purified functionalized polymer were recorded on a BIO-RAD FTS-135 IR spectrometer (USA). Its measurement scope was 400–4000 cm^{-1} . Samples should be hot compressed into transparent film before testing. A KBr slice was used for FTIR spectrum of HTBN.

X-ray analysis

The crystallinity and crystal form of the functionalized PP was determined by wide angle X-ray diffraction (WAXD) analysis. The samples for measurements need to be held on a hot stage at 190°C for 5 min to remove thermal history, and then cooling at a rate of 7°C min^{-1} to the room temperature before testing. WAXD measurements were performed using a Rigaku D-MAX 2500/PC diffractometer (Japan) with a RINT2000 vertical goniometer operating at 100 mA and 40 kV. X-ray radiation CuK^α ($\lambda = 0.15418 \text{ nm}$) was used and the scan scope was 5–60°. The crystallinity of the polymer was calculated according to computational multiphase resolution method.

Post-ring open reaction of PP-*cg*-GMA

Post-ring open reaction of PP-*cg*-GMA under the effect of CCl_3COOH

About 1-g purified PP-*cg*-GMA was resolved in hot toluene (50 mL). CCl_3COOH /xylene (2 mL) was

added into the solution, and it was kept at 110–115°C for 2 h. Subsequently, the solution was precipitated by an excess amount of acetone (150 mL); the obtained deposit was filtered by a vacuum pumping. Finally, the deposit was dried in a vacuum oven at 50–60°C until a constant weight was reached.

Post-ring open reaction of PP-cg-GMA under the effect of HTBN and its purification

About 50 g PP-cg-GMA (GD: 1 wt %) and 12.5 g HTBN was resolved in 500 mL toluene. Then 0.011 mol *N,N*-dimethylbenzylamine was added into the mixture to be used as a catalyst. The mixture was then kept at 115–120°C and stirred constantly for 2 h. The reaction product was finally precipitate by ethanol/cyclohexane ($V : V = 1 : 1$). The deposit was dried in a vacuum oven for 48 h. The obtained reactive blend was named as PP-cg-GMA/HTBN, and the purification was as follows: little amount of the crude product was hot pressed in to transparent film. Subsequently, the film was extracted in a Soxhlet extractor using cyclohexane for 48 h. Unreacted HTBN, GMA monomers and PGMA would be removed in this process. Then the film was dried in a vacuum oven at 50–60°C until a constant weight was reached. The purified sample was named as PP-cg-GMA-re-HTBN, and it was put in a desiccator prepared for FTIR measurement.

Mechanical property

DMA analysis

The dynamic mechanical properties of functionalized PP were examined by using a dynamic mechanical analyzer (NETZSCH-DMA242, Germany) operated in a bending mode. The samples used for testing were rectangular in shape and about 2 mm in thickness, 20 mm in length, and 4 mm in width. The samples were subjected to the temperature sweeps. Temperature sweep measurements were carried out from –50 to 100°C and at a heating rate of 3°C min⁻¹. The test frequency was fixed at 1 Hz, and stress is 5 N with a displacement 30 μm.

Static mechanical property testing

The tensile test was carried out with a GOTECH AI-7000M Universal Testing Machine (China). The tensile rate was 10 mm min⁻¹ at 23°C. Reported values were the average values of five individual measurements. The notched impact strength of the samples was determined according Charpy impact strength measurements at 23°C. The size of the rectangular specimens was 80 × 10 × 4 mm³ and the notch depth was 0.8 mm. Reported values were

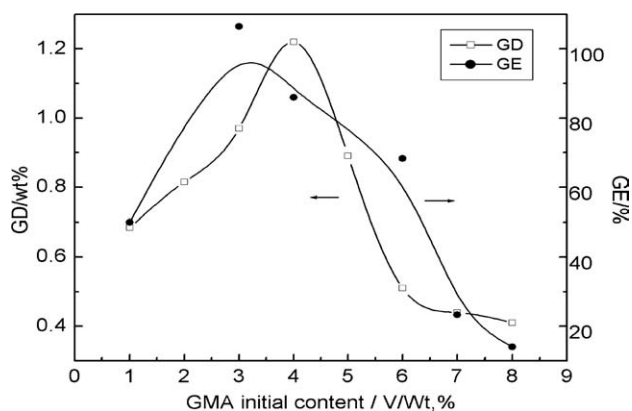


Figure 1 Influence of GMA monomer concentration on grafting degree (GD) and grafting efficiency (GE). Reaction temperature was 120°C; chlorine flux was 21 mmol min⁻¹; v/wt % represents the addition of volume of GMA per 100 g PP.

the average values of 10 individual measurements. Hardness was determined by a Shore Hardness Tester (TH210 Shanghai Precision Instruments Co., China).

RESULTS AND DISCUSSION

The influential factors of grafting degree (GD)

Effect of GMA initial concentration

The plots of GD and GE of PP-cg-GMA as a function of GMA initial concentration are given in Figure 1. GD is increased with the increasing of GMA concentration when GMA initial concentration is lower than 4%, and while further increasing the GMA initial concentration it lead to a decrease in GD conversely. The reason was ascribed as follows: the chlorine radicals formed by chlorine homolysis, picking up hydrogen from PP to produce PP macroradicals. When GMA initial concentration is lower, GMA be available to react with PP macroradicals would be increased with the increasing of the concentration of GMA, which lead to an increase in GD of PP-cg-GMA. Chlorine radical either abstract hydrogen from PP backbone or initiate GMA double bonds undergoing homopolymerization. The homopolymerization and grafting reaction of GMA are two competitive reactions. Further increasing the GMA initial concentration result in a poor dispersion of GMA in PP matrix, and more GMA would undergo homopolymerization as the result of chlorine radicals trapped by a high local concentration of the GMA. Consequently, GMA homopolymerization would predominant over GMA grafting reaction and GD is decreased. GD increases up to a maximum value and then it would be decreased with the further increasing of GMA initial concentration.

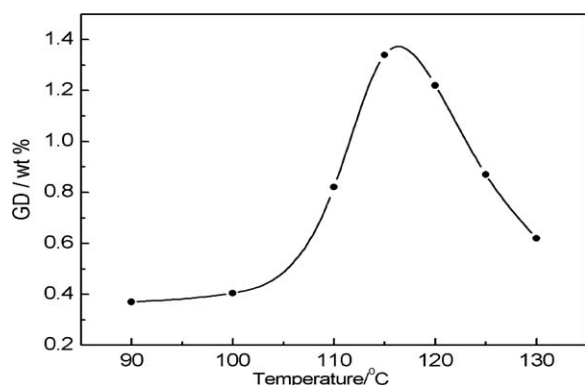


Figure 2 Influence of reaction temperature on grafting degree (GD) of PP-cg-GMA. GMA initial concentration was 4.0% (v/wt %); chlorine flux was 21 mmol min⁻¹.

Herein, GE is also investigated to further confirm the above explanation, as shown in Figure 1. GE is decreased with the further increasing of GMA initial concentration when the addition amount of the monomer exceeded 3%. The maximum value of GE and GD almost appear at the same time. This illustrates that both the GMA grafting reaction and GMA homopolymerization exist during ISCGC, and GMA homopolymerization would become the main reaction at a relatively higher GMA initial concentration, which would lead to a decrease in GE as well as GD. The maximum value of GD is 1.22% when the GMA initial concentration is 4%, and the GE is 81%.

Effect of reaction temperature

To prevent PP powder from agglomeration, the reaction temperature of grafting modification was carried out in the solid state is usually lower than 140°C. The influence of reaction temperature on GD is also an object of investigation and the result is given in Figure 2. GD is increased and then decreased with the increasing of the reaction temperature; the optimized reaction temperature is at the range of 115–120°C. PP-cg-GMA with higher GD (1.34%) could be gained at 115°C. PP *in situ* chlorination grafting GMA is a free radical process. To obtain PP-cg-GMA with higher GMA grafting percentage, the concentration of PP macroradicals should be proportionate to the concentration of GMA monomer. PP macroradicals is generated by the hydrogen abstraction of the chlorine radicals. According to Arrhenius equation $K = Ae^{\frac{-AE}{RT}}$, primary chlorine radicals cannot be largely generated because the decomposition rate of chlorine would be slower at lower reaction temperature, which result in creating less PP macroradicals. Accordingly, less PP macroradicals can be available to react with GMA monomers, thus the obtained PP-cg-GMA with lower

GD. The generation rate of primary chlorine radicals is gradually faster owing to the quickly decomposition of chlorine at higher reaction temperature. As a result, there would be a large scale of PP macroradicals can be available to react with GMA monomer and the GD would be accordingly increased. However, GD is decreased sharply on the account of the termination reaction, chain transfer reaction, and chain degradation when the reaction temperature surpasses 120°C. All these side reactions are the competitive reactions of the grafting reaction, and these side reactions might prohibit the desired grafting reaction in some extent, thus lead to a decrease in GD.

Co-effect of the GMA concentration and reaction temperature

GD of PP-cg-GMA is gradually decreased when the reaction temperature is surpassing 120°C on the basis of the above discussion. The influence of GMA monomer concentration on GD at different reaction temperature (lower than 120°C) is further discussed to confirm the above conclusion and have a better understanding of the reactivity of chlorine related to GD. The GD change trends with GMA initial concentration at different reaction temperature are given in Figure 3. It can be obviously seen that GD is increased with the increasing of reaction temperature (90–120°C). This behavior further confirms that the thermal decomposition of chlorine obeys the Arrhenius equation. The increasing in temperature cause a increase of the decomposition of chlorine, which lead to more primary chlorine radicals involving in PP hydrogen abstraction to form PP macroradicals. Subsequently, the macroradicals initiate GMA monomers undergoing grafting reaction, and that would bring about an increase in GD. Besides that, it also can be seen that there is almost a maximum value in each curve (Fig. 3). It is reasonable to propose that the

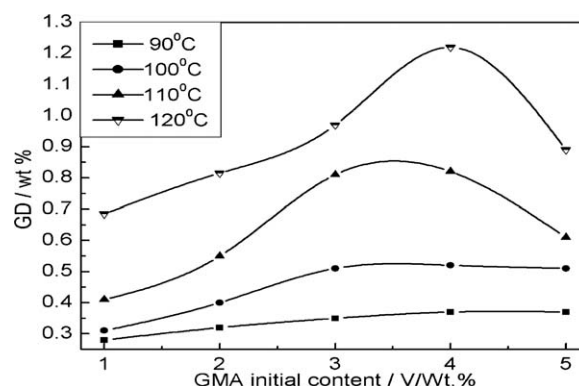


Figure 3 Influence of GMA initial concentration on grafting degree (GD) at different reaction temperature. Chlorine flux was 21 mmol min⁻¹.

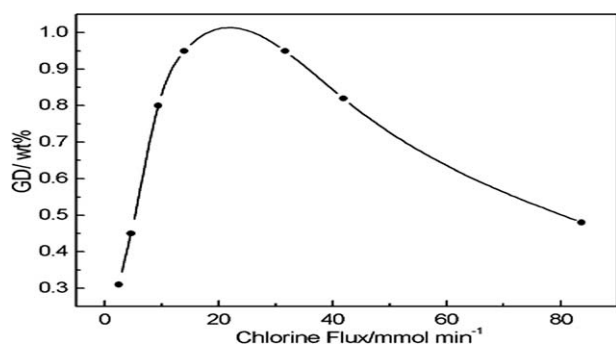


Figure 4 Influence of chlorine flux on grafting degree (GD). GMA initial concentration was 3.0% (v/wt %); reaction temperature was 110°C.

GMA grafting reaction and GMA homopolymerization are two competitive reactions, and GD would be decreased when the GMA homopolymerization become the mainly reactions. The result obtained here is correlated very well with the plots of the GD varied with GMA initial concentration and that of the GD varied with reaction temperature.

Effect of chlorine concentration

High-reactivity chlorine is served as free radical initiator during ISCGC. The influence of chlorine concentration as one of the most important parameters would affect the GD of PP-*cg*-GMA. Chlorine concentration is represented by chlorine flux in this article. GD varied with chlorine flux is given in Figure 4. It can be seen that the GD is increased with increasing chlorine flux up to 21 mmol min⁻¹. With a further increase in chlorine concentration beyond this value, it causes a decrease in GD. It might be that chlorine radicals which are available to involve in PP hydrogen abstraction are relatively less at lower chlorine concentration, resulting in less PP macroradicals initiating GMA monomers undergoing grafting reaction, and it lead to a decrease in GD. Chlorine radicals generated by chlorine thermal decomposition is increased with increasing chlorine concentration, thus there would be an increase in PP macroradicals. The augment in grafting reactive sites along the PP backbones results in an increase in GD. Just as what was aforementioned previously, chlorine is not only served as initiator but also served as terminated agent, and the terminated reaction can be deemed as chlorinated reaction. Further increasing the chlorine concentration up to a relatively higher concentration, chlorinated reaction would predominate over grafting reaction to become the main reaction during ISCGC, accordingly, a decrease in GD would happen.

Effect of the addition of styrene

The main problem exist in PP grafting modification is the PP chain β scission. Functionalized PP with

higher grafting degree and controlled degradation is actively pursued. Herein, the addition of a co-monomer has been shown to promote monomer grafting level as well as control the PP chain degradation. PP modified with co-monomer was denoted as PP-*cg*-St-co-GMA. To indicate the GMA and St have been successfully grafted onto the PP backbones. The FTIR spectra of the purified PP-*cg*-St-co-GMA and PP-*cg*-GMA are given in Figure 5. The absorptions at 1720 cm⁻¹ corresponding to the carbonyl stretch vibration and absorptions at 1640 cm⁻¹ corresponding to C=C stretching vibration, respectively, which indicate both epoxy groups and C=C double bonds are located at the grafted side chains of PP-*cg*-St-co-GMA as well as PP-*cg*-GMA and the reasons are discussed in detail in Ref. 26. Besides that, in comparison with the spectrum of PP-*cg*-GMA, additional peaks in the region of 692 and 771 cm⁻¹, which belong to the out-of-plane bending mode of the aromatic C-H are observed in the spectrum of PP-*cg*-St-co-GMA (spectrum b in Fig. 5), indicating that St has been grafted onto PP successfully.

The effect of the addition of a co-monomer [styrene (St)] on structure (GD_{GMA} , M_v) of the functionalized PP would be explored. GD_{GMA} is the GMA grafting level of PP-*cg*-St-co-GMA. The effect of the addition of St on GMA grafting level (GD_{GMA}) is shown in Figure 6. As seen in Figure 6, GD_{GMA} of PP-*cg*-St-co-GMA is higher than that of PP-*cg*-GMA. A possible explanation would be that St is a nonpolar monomer; and it can be dispersed well and more easily absorbed by nonpolar PP matrix. When PP macroradicals would be formed after PP hydrogen was abstracted by chlorine radicals, St could react with PP macroradicals much faster than GMA and the resulting styryl macroradicals can readily copolymerize with GMA monomer. According to the literature report,²⁷ Q value (conjugation effect) of GMA is 0.96; e value (polar effect) of GMA

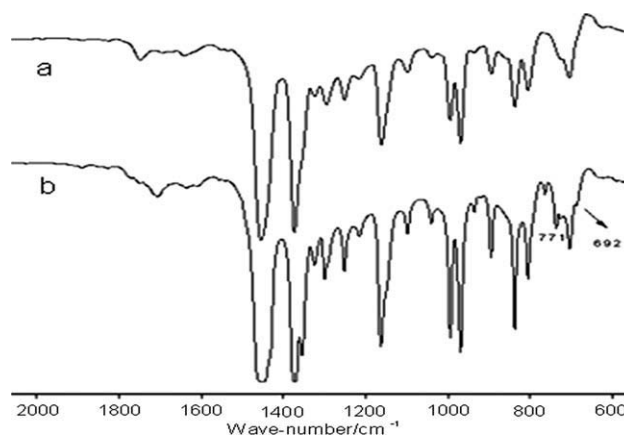


Figure 5 FTIR spectra of PP-*cg*-GMA (a) and PP-*cg*-St-co-GMA (b).

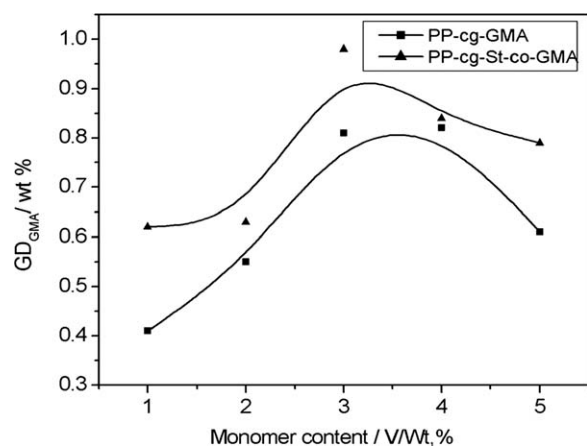


Figure 6 Influence of St on GMA grafting degree (GD_{GMA}) of PP-cg-St-co-GMA.

is 0.2; Q value of St is 1; e value of St is -0.8 . Because the two monomers possess very close values of Q , they are inclined to undergo copolymerization. On the basis of Alfrey-Price semiempirical formula, the reactivity ratios (r) of the two monomers is r_{GMA} is 0.79 and r_{St} is 0.45. Both the r values are less than 1, so the copolymerization is favored compared to the homopolymerization. St is served as a mediator to bridge the gap between the PP macroradicals and GMA monomer, and can rapidly react with PP macroradicals lead to the formation of the more stable styryl radicals. GMA monomer is more easily to react with more stable styryl radicals compared to PP macroradicals, and then the styryl radicals would copolymerize with GMA. All these explanations mentioned above can be used to illustrate the addition of St causing an increase in GD_{GMA} of the PP-cg-St-co-GMA.

To further discern the underlying reasons behind the phenomenon previously discussed, viscosity average molecular weight measurements were undertaken and the results are given in Figure 7. M_v of PP-

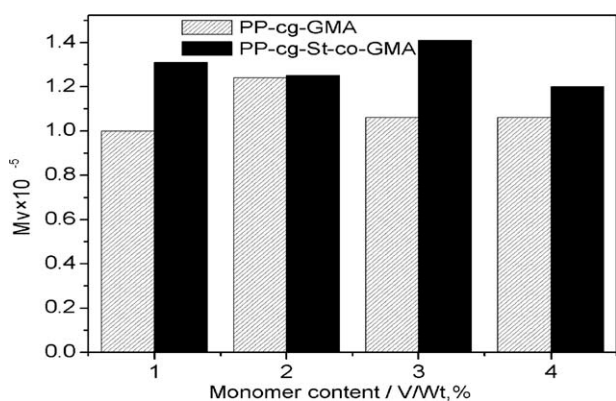


Figure 7 Viscosimetric average molecular weight (M_v) of PP-cg-GMA and PP-cg-St-co-GMA. For PP-cg-St-co-GMA, St/GMA = 1/1(volume ratio); reaction temperature was 120°C ; chlorine flux was 21 mmol min^{-1} .

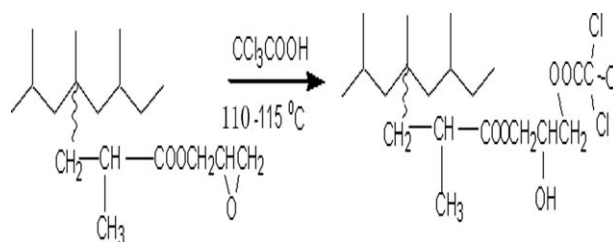


Figure 8 Schematic of epoxy groups reacting with trichloroacetic acid.

cg-St-co-GMA is higher than that of PP-cg-GMA, it shows that the PP chain scission is effectively controlled after the addition of St. It further illustrate that St can disperse well in PP matrix owing to the polar effect, and the St can react with PP tertiary radical more timely compared to GMA. Accordingly, PP tertiary macroradicals react with St monomer to form more stable styryl radicals before PP chain β scission, which is the main reason for the PP-cg-St-co-GMA with controlled degradation. The M_v results once again confirm that the St would be served as a mediator to bridge the gap between the PP macroradicals and GMA monomer, and St is more readily to react with PP macroradicals to form the stable styryl radicals.

Reaction between epoxy group and carboxyl group

Trichloroacetic acid was used as a model to explore the reactivity of epoxy groups with carboxyl groups, and the ring-open reaction of epoxy is depicted in Figure 8.

The purified products yielded by the reaction between the PP-cg-GMA and trichloroacetic acid were named as PP-cg-GMA-re- CCl_3COOH . FTIR spectrum of the purified PP-cg-GMA-re- CCl_3COOH is given in Figure 9. It can be clearly seen that the stretching vibration absorption of hydroxyl ($-\text{OH}$)

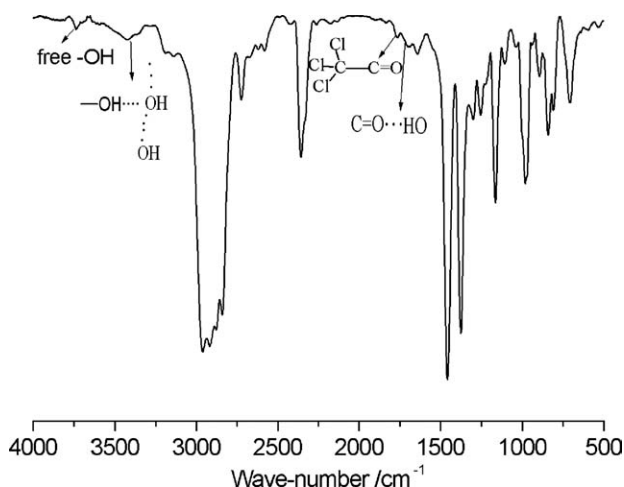


Figure 9 FTIR spectrum of PP-cg-GMA-re- CCl_3COOH .

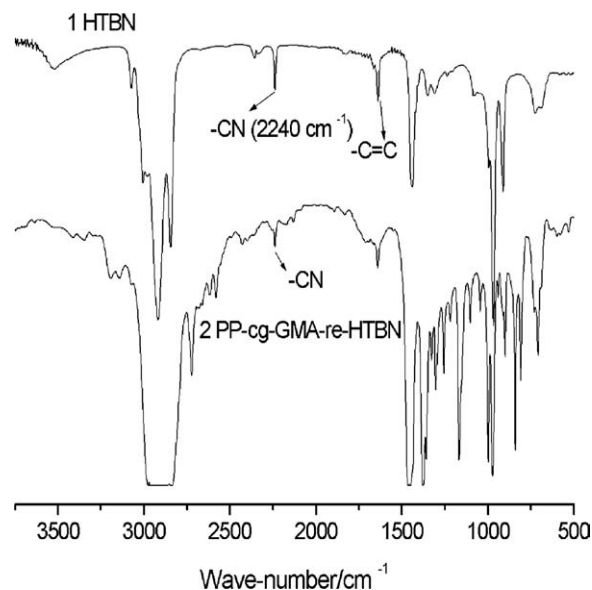


Figure 10 FTIR spectra of PP-*cg*-GMA-re-HTBN and HTBN.

appeared at 3126–3735 cm^{-1} ; 3735–3557 cm^{-1} corresponding to the free $-\text{OH}$ and 3345–3500 cm^{-1} corresponding to $-\text{OH}$ that are held together by hydrogen bonds. Stretching vibration absorption of carbonyl ($-\text{C}=\text{O}$) appeared at 1684–1767 cm^{-1} . Thereinto, absorption bands at 1767 cm^{-1} are corresponding to the $-\text{C}=\text{O}$ of $-\text{OCCCl}_3$, the absorption bands shift into higher wave number owing to the presence of $-\text{CCl}_3$ that exert an electron receptor effect. Absorption bands at 1684 cm^{-1} are corresponding to $-\text{C}=\text{O}$ that are held together with $-\text{OH}$ by hydrogen bonds, which lead to the wave number shifting into lower field and make the absorption band wider. Results of FTIR confirm that epoxy group of PP-*cg*-GMA has successfully undergone ring-open reaction in the presence of trichloroacetic acid. Additionally, according to the publication reports, trichloroacetic acid is commonly used to determine the GMA grafting percentage, but none of these works have confirmed the feasibility of this method.²⁸ Herein, the results from Figure 9 can also verify the feasibility of using trichloroacetic acid to determine the GMA grafting level.

Reaction between epoxy group and hydroxyl group

HTBN rubber was used as a model polymer to investigate the reactivity of epoxy of PP-*cg*-GMA with hydroxyl. FTIR spectrum of the purified product yield by the reaction between PP-*cg*-GMA and HTBN is given in Figure 10, and the reaction product is denoted as PP-*cg*-GMA-re-HTBN. FTIR spectrum of HTBN is also given. As shown in the FTIR spectrum of PP-*cg*-GMA-re-HTBN, absorptions at 3600 cm^{-1} and 3345–3500 cm^{-1} are corresponding to

the stretching vibration of the free $-\text{OH}$, $-\text{OH}$ that are held together by hydrogen bonds, respectively. Absorptions at 2240 cm^{-1} are corresponding to the stretching vibration of $-\text{CN}$. These phenomena demonstrate that epoxy group has undergone ring-open reaction in the presence of hydroxyl of HTBN, and the HTBN molecules have been introduced onto PP backbones.

DMA analysis of PP-*cg*-GMA/HTBN reactive blend

The crude reactive blend yielded by the reaction between PP-*cg*-GMA and HTBN is named as PP-*cg*-GMA/HTBN. E'' plots of PP-*cg*-GMA and PP-*cg*-GMA/HTBN are given in Figure 11. E'' peak temperature was defined as glass transition temperature (T_g) according to ISO standard. There are two peaks appeared at -48.4°C and 12.2°C in E'' plots of PP-*cg*-GMA/HTBN, which are respectively corresponding to T_g of HTBN and that of PP-*cg*-GMA. Compared to PP-*cg*-GMA, T_g of PP-*cg*-GMA in the blends is lower and has a wider glass transition scope. What's the reason behind this behavior? Based on the FTIR results, it is confirmed that HTBN has been grafted onto PP backbones to form PP-*cg*-GMA-re-HTBN. The formed PP-*cg*-GMA-re-HTBN can be located at the interface between PP-*cg*-GMA and HTBN, which making the physical entanglement with neighbor chains stronger, accordingly, increasing the compatibility between PP and HTBN. What's more, the introduction of PGMA side chains and chlorine atoms increasing the polarity of PP which also can increase the compatibility of these two polymers. Thus, T_g of PP-*cg*-GMA and HTBN in the blends is more closely with each other and the glass transition scope would also become wider. T_g (12.2°C) of PP-*cg*-GMA in the blends is lower than that of pure PP-*cg*-GMA (16.2°C).

E' plots of PP-*cg*-GMA and PP-*cg*-GMA/HTBN are given in Figure 12. E' of PP-*cg*-GMA/HTBN is largely lower than that of PP-*cg*-GMA when the

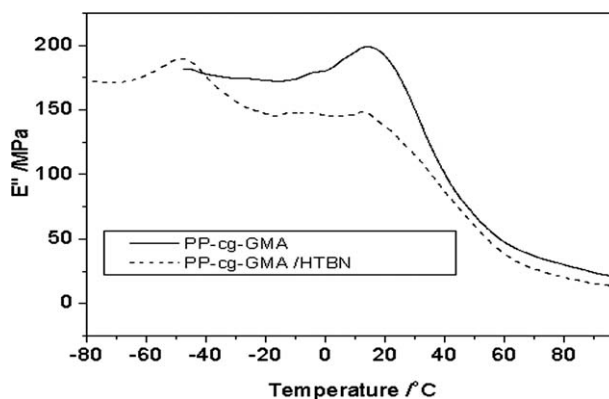


Figure 11 The dependence of loss modulus (E'') on temperature for PP-*cg*-GMA and PP-*cg*-GMA/HTBN.

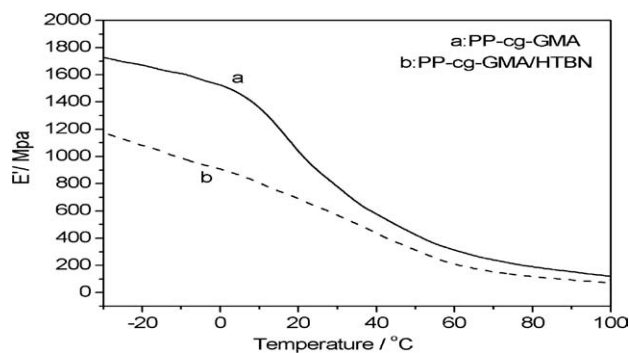


Figure 12 The dependence of elastic modulus (E') on temperature for PP-cg-GMA and PP-cg-GMA/HTBN.

temperature is lower than the T_g of PP-cg-GMA; however, the discrepancy between plots a and b is gradually lower with the increasing of temperature. This probably because that the movement of HTBN chain segments result in a decrease of E' of PP-cg-GMA/HTBN at relatively low temperature. While E' is largely depending on the crystallinity of the polymer when temperature is above T_g of PP-cg-GMA. It can be also concluded that the toughness of PP-cg-GMA/HTBN would be higher than that of PP-cg-GMA because of the lower E' of PP-cg-GMA/HTBN.

Crystallinity and crystal forms of PP-cg-GMA

To investigate the influence of the graft side chains on the crystallinity and crystal forms of PP-cg-GMA. Wide-angle X-ray analysis was carried out to determine the crystallization of polymer. X-ray diffraction patterns of PP-cg-GMA and its compared polymer PP are given in Figure 13.

The relatively intense diffraction peaks for all polymer appeared at 14.1, 16.9, 18.5, 21.2, and 22, respectively, which exhibit five strong characteristic diffractions of (100), (040), (130), (111), and (130)

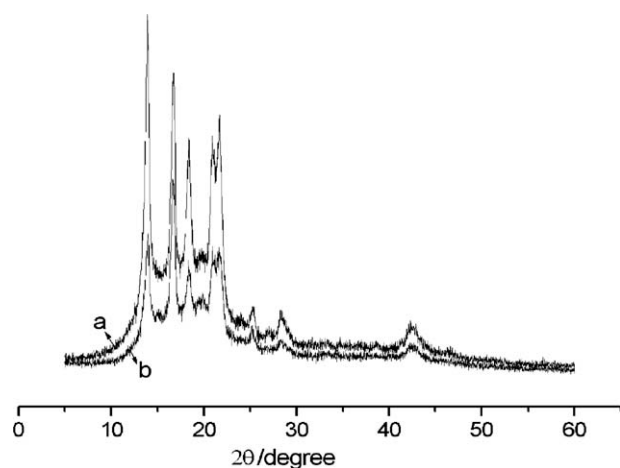


Figure 13 X-ray diffraction patterns of PP (a) and PP-cg-GMA (b).

crystal face of the α phase of PP. No new peak appeared in the diffraction pattern of PP-cg-GMA compared to that of PP, indicating that the graft side chains of PGMA have no effect on the crystal form of PP. However, the crystallinity of PP, PP-cg-GMA is 67.63%, 56.52% respectively according to the calculating method that was proposed in the experiment part. It illustrates that the introduction of the grafted side chains have influence on the crystallinity of PP, that is the introduction of grafted GMA and chlorine atoms have an negative effect on the regularity of PP chains and limit the movement of PP molecule chains. These make the regular packing of PP macromolecular chains and perfect crystallization more difficult. The result of X-ray analysis is almost the same with the DSC and POM results, which has been reported in our another report.²⁶

Mechanical property of PP-cg-GMA

Dynamic mechanical analysis (DMA)

The mechanical property of polymer is closely related to the molecular structure and crystallinity of PP, and the more detailed structure characterization of polymer have been discussed in our previous report,²⁶ while the effect of graft side chains on the mechanical property of PP would be investigated in this work.

Figure 14 shows the loss modulus (E'') varied with temperature. T_g of PP-cg-GMA and PP is 16.2°C, 4.6°C, respectively. In comparison with PP, T_g of PP-cg-GMA is improved owing to the introduction of the polar GMA as well as the little amount of polar chlorine atoms. Both of these polar groups increase the rotary resistance of C—C bond of the PP chains and the induction force between the macromolecular chains, which lead to an augment in T_g for PP-cg-GMA. Besides, the glass transition scope of PP-cg-GMA is obviously wider than that of PP, illustrating that the segments distribution of PP-cg-GMA is

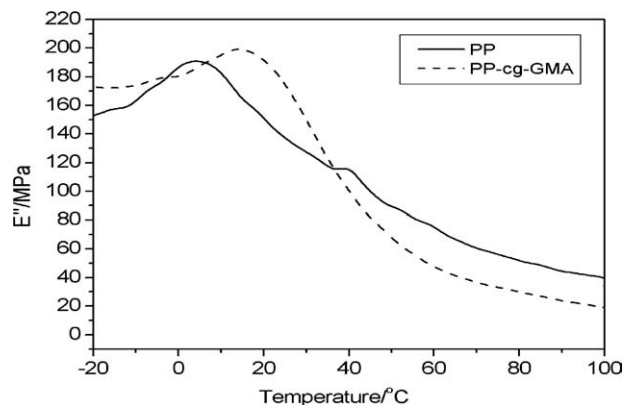


Figure 14 The dependence of loss modulus (E'') on temperature plots for PP-cg-GMA and PP.

broader than that of PP due to the introduction of graft side chains.

The elastic modulus (E') varied with temperature for PP-*cg*-GMA, PP is shown in Figure 15. It was found that there is a large discrepancy of E' between PP-*cg*-GMA and PP when temperature is lower than around 4.6°C (T_g of PP), however, the discrepancy tend to become little with the further increasing of temperature. When the temperature is relatively lower at which the amorphous state of polymer samples is in the glass state. The E' of the polymer largely depends on whether there's a secondary transition of a chemical group at this time. The E' of PP-*cg*-GMA is greatly lower than that of PP at the lower temperature probably because the secondary relaxation of the grafted GMA groups, that is, ester groups in GMA can rotate and wag in the glassy state resulting in a decrease of E' for PP-*cg*-GMA. While the temperature is above T_g , E' of a polymer would largely depend on the crystallinity of PP. The higher the crystallinity is, the higher E' would be. On the basis of XRD analysis, the introduction of GMA groups and chlorine atoms interfering the crystallization process of PP molecular chain, causing an increase in the amorphous regions of PP-*cg*-GMA, thus decreasing the E' value of PP-*cg*-GMA.

Static mechanical properties

Tensile strength, elongation at break, hardness, and impact strength of PP-*cg*-GMA and PP were performed to further determine the dependence of the performance of the polymer on the structure of the polymer, and the results are summarized up in Table I. The tensile strength, impact strength and hardness of PP-*cg*-GMA are slightly lower than PP but with a higher elongation at break. This phenomenon might be attributed to the followings. From what have been discussed previously, the introduction of the grafted GMA and chlorine atoms have

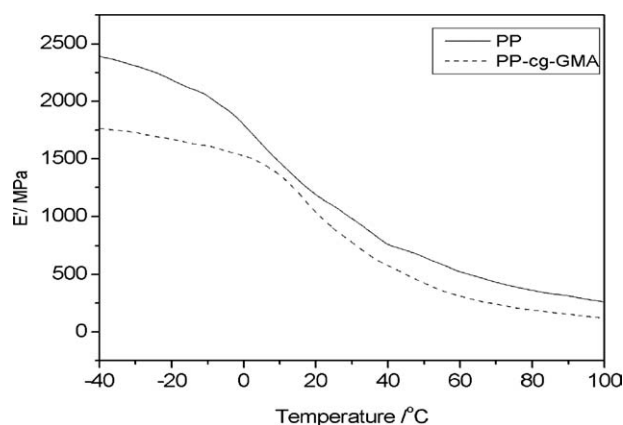


Figure 15 The dependence of elastic modulus (E') on temperature plots for PP-*cg*-GMA and PP.

TABLE I
Static Mechanical Property of PP-*cg*-GMA and PP

Samples	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m ²)	Hardness (Shore D)
PP	29.3	6.1	3.8	78
PP- <i>cg</i> -GMA	25.4	12.6	1.8	70

decreased the crystallinity of PP and increased the amorphous region, which cause a decrease in tensile strength of PP-*cg*-GMA. Amorphous region is prior to undergo deformation compared to the crystallization region. Additionally, according to the POM and DSC analysis,²⁶ the average spherulite size for PP-*cg*-GMA is obviously decreased compared to that of PP. In comparison with large spherulite, the small spherulite is more inclined to slip and undergo deformation, which lead to an increase in the elongation at break. For the hardness of a crystallization polymer, it mostly depend on the crystallinity of the polymer, the decrease of crystallinity of PP-*cg*-GMA also cause the reducing of hardness. However, for the impact strength of a polymer, the most influenced parameter is the temperature. T_g of PP-*cg*-GMA is greatly increased owing to the introduction of grafted side chains on the basis of the aforementioned DMA analysis. The increase of T_g would bring about a decrease in the impact strength. The discrepancy of mechanical prosperities between PP-*cg*-GMA and PP is not too large; it indicates that the mechanical properties of PP-*cg*-GMA are not essentially changed after the introduction of the grafted side chains and chlorine atoms. This might be because the structure of the PP-*cg*-GMA is not greatly changed based on PP structure (crystallinity and molecular weight).

CONCLUSIONS

In situ chlorination graft copolymerization was carried out to graft GMA onto PP backbones. PP-*cg*-GMA with higher GMA grafting degree (1.34%), grafting efficiency (81%) can be obtained by optimizing reaction parameters. The optimum GMA initial concentration is 4%; reaction temperature is 115–120°C; chlorine flux is 21 mmol min⁻¹. The addition of styrene in the grafting system can increase the GMA grafting level as well as decrease the PP chain scission effectively during grafting reaction. Epoxy groups of PP-*cg*-GMA can undergo ring-open reaction with the presence of carboxyl and hydroxyl. The compatibility between PP and HTBN can be enhanced due to the presence of epoxy group. PP-*cg*-GMA presents the same crystal form as PP, however, with a lower crystallinity. The mechanical properties of PP-*cg*-GMA are unessentially changed compared to that of PP.

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