

Styrene-Assisted Melt Free-Radical Grafting of Pentaerythritol Triacrylate onto Polypropylene and Its Crystallization Behavior

Dong Wang,¹ Xu-Ming Xie,¹ Jinder Jow,² Hong-Yu Chen,³ Shih-Yaw Lai⁴

¹Advanced Materials Laboratory, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

²Asia-Pacific Technical Center, Dow Chemical Pacific Private, Ltd., Singapore 638025

³PP&C, Materials Science, Dow Chemical Company, Freeport, Texas 77541

⁴Shanghai R&D Center, Dow Chemical Company, Shanghai, People's Republic of China 200120

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ABSTRACT: The free-radical grafting of the multimonomer system of pentaerythritol triacrylate (PETA) and styrene (St) onto polypropylene (PP) in the melt state was studied by reactive extrusion. The effects of the St and initiator concentrations on the grafting reaction were investigated by means of the melt flow rate, gel permeation chromatography (GPC), and Fourier transform infrared spectroscopy. The results showed that the use of St as a comonomer could effectively depress the degradation of PP and enhance the grafting degree of PETA. Increasing the peroxide level promoted the degradation of PP and reduced the grafting degree of PETA. When the molar ratio of St to PETA was 3 : 1, the GPC data showed that the molecular weight of the grafted PP sample was almost equal to or a little higher than that of virgin PP, suggesting that almost no chain scission

occurred. In the presence of St, the dominant grafting mechanism was that St reacted with the PP macroradicals to form more stable St macroradicals, and thus β scission was limited. Then, St macroradicals reacted with PETA to form PETA-grafted PP. X-ray diffraction results showed that the grafted chains not only had a good nucleating effect on PP crystallization but also might induce the formation of β -form crystals. The presence of ungrafted PETA increased the crystallization and melting temperatures of PP; however, the PETA-grafted samples showed higher crystallization and melting temperatures than physically blended samples. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1737–1743, 2008

Key words: poly(propylene) (PP); crystallization

INTRODUCTION

Polypropylene (PP) is one of the leading and fastest growing versatile polymers in the world. Because of its high melting point, high tensile strength, stiffness, and chemical resistance,^{1,2} PP has found a wide range of applications in packing, automotive industries, and so forth. However, commercial PP is usually prepared by Ziegler–Natta catalysts and has a predominantly linear structure. Although linear PP polymers have many desirable physical properties, they show relatively low melt strength. As a result, conventional PP has been limited in some processes such as thermoforming, foaming, and blow molding.^{2–6}

It is well known that the presence of long grafted chains can dramatically enhance the viscoelastic properties of a polymer, such as the melt strength and

zero-shear viscosity, and improve strain hardening in elongational flow and, as a result, improve the processibility of linear polymers.^{7–9} Therefore, PP with long grafted chains has become one of the major themes in recent PP modification research.^{2–6,8–15} Up to now, several approaches have been developed to prepare branched PP, including high-energy electron-beam irradiation,^{10,12,14} peroxide curing,^{16,17} azide coupling,¹⁸ and in-reactor metallocene copolymerization of propylene with *in situ* generated or externally added macromonomers.^{2,4,6,11,19–25} For example, several research groups^{13,22,26,27} have reported the synthesis of long-chain-branched PP by the copolymerization of propylene and macromonomers, such as atactic PP, polyethylene, or poly(ethylene-*co*-propylene) macromonomers. However, these methods are quiet inconvenient, costly, or complex because of the additional treatment step, the involved reaction mechanism, and the complicated polymer structure produced. More importantly, these methods usually change the PP backbone; thus, the properties of the resulting PP resins are changed.

In comparison with the aforementioned multistep or complicated processes, the relative simplicity and low cost of PP grafted with polyfunctional monomers in a

Correspondence to: X. M. Xie (xxm-dce@mail.tsinghua.edu.cn).

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reactive extrusion process are more desirable for the production of long-chain-branched polymers.^{5,15,28–31} Some researchers have prepared long-chain-branched PP by the grafting of PP and a polyfunctional monomer, such as trimethylol propane triacrylate,^{5,6} diethylene glycol diacrylate,⁶ or pentaerythritol triacrylate (PETA).¹⁵ However, during the melt-grafting process, extensive degradation of PP can easily occur. It will result in both the loss of the good mechanical properties of PP and a low degree of monomer grafting.

The key question is whether PP can be prepared not only to have a high degree of grafting of the polyfunctional monomer and long grafted chains but also to retain the backbone structure and good mechanical properties. In our previous work, styrene (St) and maleic anhydride dual monomers (or glycidyl methacrylate, acrylic acid, etc.) melt-grafted to PP (or polyethylene, etc.) have been successfully realized.^{32,33} In the aforementioned system, St preferentially reacts with the PP macroradicals to form more stable styryl macroradicals, which then copolymerize with other monomers to form branches. Therefore, the addition of St as a comonomer could significantly enhance the glycidyl methacrylate or maleic anhydride grafting levels on PP, reduce the extent of β scission of PP, and retain their good mechanical properties.³²

The objective of this study was to examine the effect of using a comonomer for the free-radical grafting of PETA onto PP without the loss of their good mechanical properties. A triacrylate as a grafting monomer and St as a comonomer were used to prepare the grafted PP in this study.

EXPERIMENTAL

Materials

The PP (grade 2401), having a melt flow rate (MFR) of 2.8 g/10 min, was obtained from Yanshan Petrochemical Co. PETA (AR) and St (AR) monomers were products of Tianjin Tianjiao Chemical Co. and Beijing Chemical Co., respectively. The peroxide, dicumyl peroxide (DCP) from Beijing Xizhong Chemical Co., was selected as the initiator. These products were used without further purification.

Melt grafting

The melt-grafting reaction was carried out in an SJ single-screw extruder (diameter of screw (Φ) = 30 mm, length/diameter = 25 : 1). For a typical experimental run, the peroxide was added to the liquid monomer. The resulting mixture was then premixed with PP pellets in a small bottle for about 15 min so the liquid reagents could be absorbed into the PP. The temperature of the cylinder was set at 170–210°C. The screw speed was fixed at 35 rpm. Extrudates were cooled in water and then pelletized.

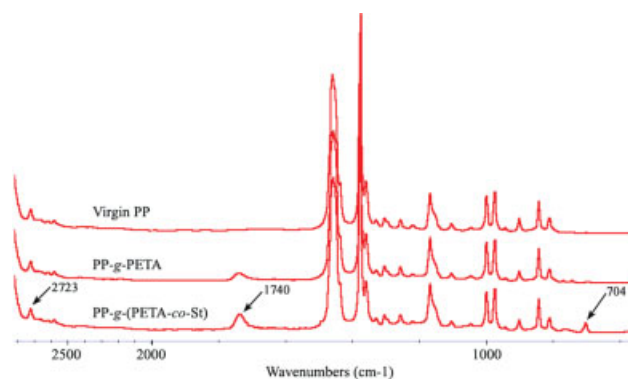


Figure 1 FTIR spectra of PP, PP-g-PETA, and PP-g-(PETA-co-St). The PETA and DCP concentrations were fixed at 3 and 0.03 wt % with respect to PP, respectively. In the case of PP-g-(PETA-co-St), the molar ratio of St to PETA was 3 : 1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Purification and characterization of grafted PP

The grafted PP samples were first dissolved in refluxing xylene at a concentration of 1% (wt/vol), and excess acetone was then added to precipitate them. Acetone could precipitate only the grafted and ungrafted PP. With this procedure, any homopolymer or copolymer of PETA and St and unreacted monomers were separated. The precipitated samples were filtered, washed, and dried *in vacuo* at 80°C for 24 h.

Fourier transform infrared (FTIR) was used to measure the grafting yields of PETA and St. The purified samples were hot-pressed under 200°C into thin films (50–100 μ m) and analyzed with a Nicolet 560 FTIR apparatus. MFR measurements of the PP samples were carried out with XRZ-400 type equipment at 230°C with a load of 2.16 kg according to the ASTM D 1238-86T standard. The molecular weights of the virgin PP and grafted samples were determined by gel permeation chromatography (GPC; PL-GPC-220, Polymer Lab) at 140°C with 1,2,4-trichlorobenzene as a solvent. The melting and crystallization behaviors of the modified PP were investigated with a Shimadzu DSC-60. All the operations were carried out under a nitrogen environment with samples (4–5 mg) sealed into aluminum pans. The temperature and melting enthalpy were calibrated with standard indium and zinc. To eliminate the influence of the thermal history on the crystallization and melting behavior, the sample was first heated to 210°C at a heating rate of 20°C/min and maintained at this temperature for 5 min and then cooled to room temperature at a cooling rate of 10°C/min. A second heating run was carried out again at a rate of 10°C/min for the melting behavior. The specimens for X-ray measurement were injection-molded into sheets. X-ray diffraction results were recorded on a D/max-RB diffractometer (Rigaku, Japan). The data were collected in the 2θ region of 10–30° at a scanning

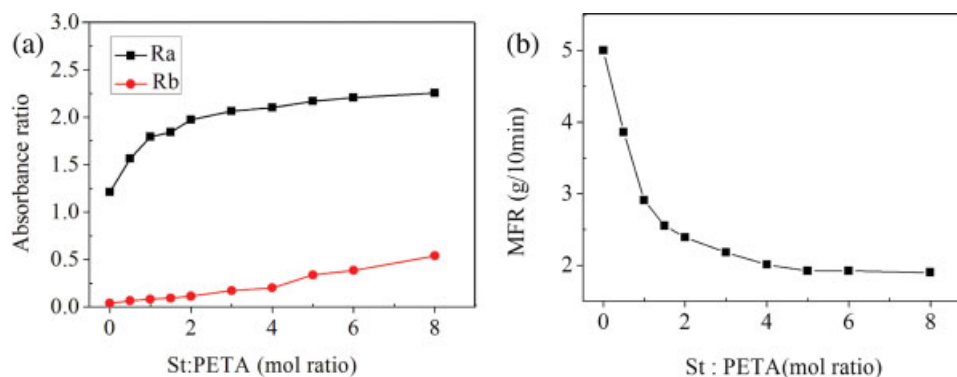


Figure 2 Effect of the St concentration on (A) the graft degree of PETA (R_a) and St (R_b) and (B) the MFR value of the grafted PP (PETA = 3 wt %, DCP = 0.03 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rate of $3^\circ/\text{min}$. The mechanical property measurements of the samples were carried out at room temperature according to ASTM standards. Tensile and flexural tests were carried out with a GOTECH-2000 universal testing machine. The test speeds were set at 50 and 10 mm/min, respectively. The average of at least five measurements for each sample was reported. The Izod notched impact strength of the samples was measured with an XJUD-5.5 impact-testing machine. For each type of sample, seven specimens were tested, and the average value was reported. To determine the gel content, the grafted PP samples were placed in a 120-mesh steel net. Then, the net was put in a Soxhlet extractor and extracted in xylene for 4 h.

RESULTS AND DISCUSSION

FTIR spectroscopy analysis of the grafted PP

The FTIR spectra of the virgin PP, PP-g-PETA, and PP-g-(PETA-co-St) are shown in Figure 1. In the case of PP-g-PETA and PP-g-(PETA-co-St), a new absorption

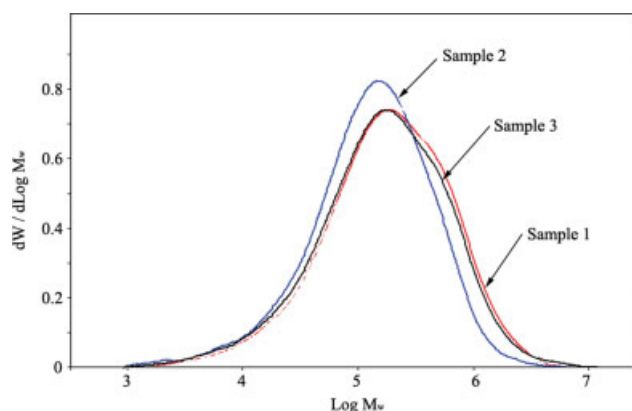


Figure 3 GPC chromatograms of the grafted PP. Samples 1, 2, and 3 were virgin PP, 0 : 1 St/PETA, and 3 : 1 St/PETA, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

band at 1740 cm^{-1} is observed, which can be assigned to the absorption of the carbonyl groups ($-\text{C}=\text{O}$) of PETA. The absorptions at 2723 and 704 cm^{-1} can be assigned to the characteristic absorption of the PP skeleton and the grafted St, respectively. The absorption band at 2723 cm^{-1} is chosen as an internal reference in this case. The relative graft degree of PETA is described as the absorbance ratio of the areas of the bands at 1740 and 2723 cm^{-1} ($R_a = A_{1740}/A_{2723}$). Similarly, the absorbance ratio of 704 and 2723 cm^{-1} ($R_b = A_{704}/A_{2723}$) shows the relative graft degree of St.

The spectra show that the addition of St can effectively increase the graft degree of PETA. The intensity of the carbonyl absorption at 1740 cm^{-1} of PP-g-(PETA-co-St) is much stronger than that of PP-g-PETA. The results of increased grafting yields are discussed in detail later.

Effect of the St concentration on the graft degree and MFR of grafted PP

Figure 2(A) shows the effect of the St concentration on the graft degree of PETA and St of the grafted PP. The PETA and DCP concentrations are fixed at 3 and 0.03 wt % with respect to PP, respectively. As the St concentration increases, the graft degree of St increases. However, the graft degree of PETA first increases with an increasing amount of St and then levels off because of the limiting reagent of PETA. Figure 2(B) shows the effect of the St concentration on the MFR

TABLE I
Effect of St on the Molecular Weight and MWD Values of Grafted PP

	M_n	M_w	M_z	M_w/M_n
Sample 1 (virgin PP)	69,710	353,140	985,000	5.07
Sample 2 (St/PETA = 0 : 1)	51,120	239,590	650,900	4.69
Sample 3 (St/PETA = 3 : 1)	61,330	343,850	1,162,400	5.61

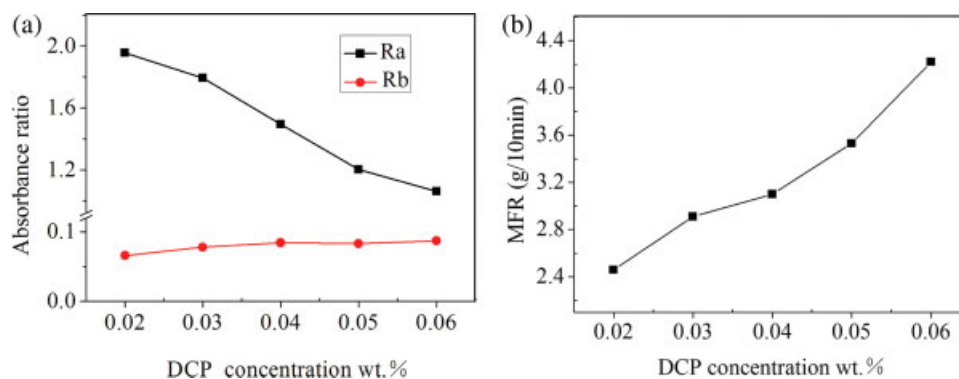


Figure 4 Effect of the DCP concentration on (A) the graft degree of PETA (R_a) and St (R_b) and (B) the MFR value of the grafted PP (St/PETA = 1 : 1 mol/mol, PETA = 3 wt %). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

values of the grafted PP obtained under the same conditions used for Figure 2(A). As expected, the addition of St effectively suppresses the degradation of PP. MFR decreases with an increasing St/PETA ratio and then levels off at 1.9 as the St/PETA ratio approaches 8.

To examine the true changes in the molecular weight of the grafted samples, high-temperature GPC was conducted. Figure 3 shows the GPC results of the virgin PP and the grafted samples (St/PETA = 0 : 1 and St/PETA = 3 : 1). The molecular weights [weight-average molecular weight (M_w), number-average molecular weight (M_n), and z -average molecular weight (M_z)] and molecular weight distribution (MWD) are summarized in Table I. Compared with that of the virgin PP, the molecular weight of the PP-*g*-PETA sample is lower. MWD also becomes narrower. These results are due to the degradation of the PP chain. However, in the presence of St (St: PETA = 3 : 1), M_n

and M_w of the grafted sample are not substantially different from those of the virgin PP, thus indicating a remarkable effect of St on inhibiting the PP chain scission. Moreover, the MWD becomes even higher than that of virgin PP. This result also suggests a slightly broader MWD for PP-*g*-(PETA-*co*-St). The molecular weight data correlate well with the MFR data.

Effect of the DCP concentration on the graft degree and MFR of grafted PP

Figure 4(A) shows the effect of the DCP concentration on the graft degree of PETA and St. The PETA concentration was fixed at 3 g/100 g of PP, and the molar ratio of PETA to St was fixed at 1 : 1. The DCP concentrations were varied from 0.02 to 0.06 g/100 g of PP. As shown in Figure 4(A,B), the PETA graft degree decreases and MFR increases along with increasing

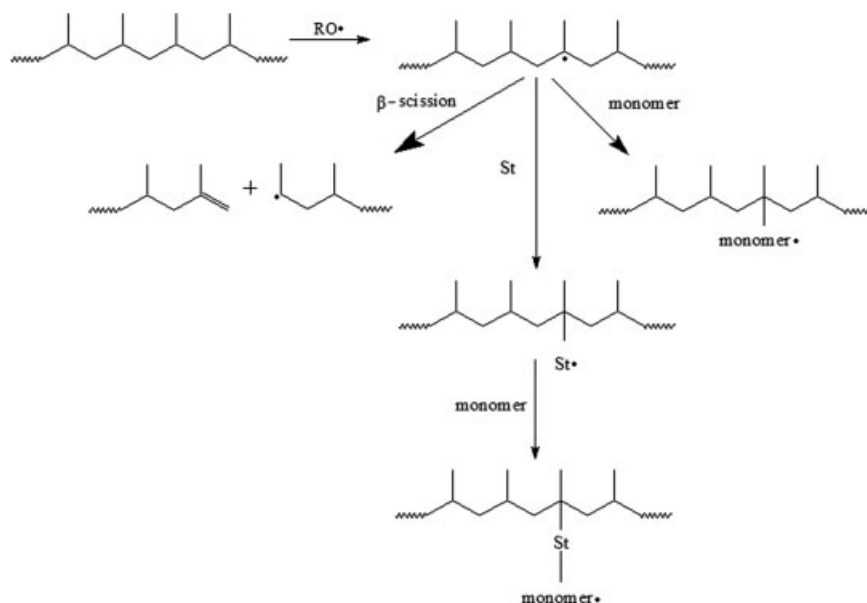


Figure 5 Scheme of the reactions in the melt free-radical grafting system of PP.

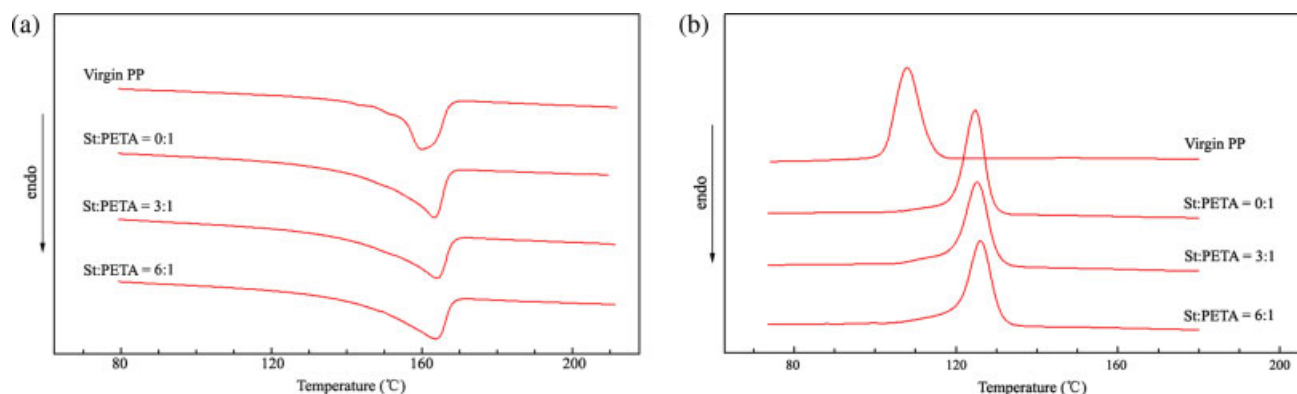


Figure 6 DSC (A) melting and (B) crystallization curves of PP, PP-g-PETA, and PP-g-(PETA-co-St). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

DCP concentration, whereas no substantial change can be observed in the St graft degree. When the concentration of the DCP is high, severe degradation of the PP backbone becomes a dominating reaction [as shown in Fig. 4(B)], thus depressing the grafting process. This result suggests that lower amounts of peroxide are better for the grafting efficiency.

Mechanism of St-assisted free-radical grafting of PETA onto PP

The aforementioned results obtained in this study substantiate the effect of using the comonomer St to promote the free-radical grafting of PETA onto PP and to enhance the graft degree [see Fig. 2(A)]. As a result, the chain scission is depressed [see Fig. 2(B) and Table I]. The melt free-radical grafting process starts with the formation of macroradicals along the PP chain by a hydrogen abstraction reaction. That is, in the presence of a peroxide initiator, the reactivity of PP stems from its hydrogen atoms along the hydrocarbon skeleton that are subjected to free-radical attack. The free radicals generated by peroxide decomposition abstract primarily the labile proton on the tertiary carbon. The resulting macroradicals of PP undergo either degradation leading to chain cleavage by β scission or grafting. However, because of the high instability of tertiary macroradicals, the degrada-

tion process is extremely fast at a high temperature (greater than the melting temperature).⁵ Because the PETA monomer is not sufficiently reactive toward PP macroradicals, its addition would result in severe degradation for PP and a low graft degree for PETA. Thus, stabilizing and consuming macroradicals of PP in favor of grafting is the means to reduce the chain degradation. In the case of adding St as a comonomer to the system, it is recognized that St reacts first with PP tertiary macroradicals to form more stable styryl macroradicals,^{34,35} and the resulting styryl radicals then copolymerize with PETA to form branches. In other words, most of PETA is grafted not directly onto PP macroradicals but via St and more specifically styryl macroradicals. Therefore, the graft degree of PETA can be effectively improved, and the degradation of PP can be suppressed. The suggested free-radical grafting mechanism is shown in Figure 5. Of course, PETA can also react with St grafted to PP. That may explain why PETA has a much higher grafting level than St to PP instead of a 1 : 1 grafting ratio, as shown in Figure 2(A).

Physical properties of grafted PP

Figure 6 shows the DSC curves of the melting and crystallization of the virgin PP, purified PP-g-PETA, and PP-g-(PETA-co-St) samples. In comparison with the virgin PP, the endothermic peak of the grafted samples has become broader. The wider peak is due to the melting and recrystallization or reorganization

TABLE II
Thermal Properties of Virgin PP, PP-g-PETA, and PP-g-(PETA-co-St)

Grafted PP	Virgin PP	St/PETA (molar ratio)		
		0 : 1	3 : 1	6 : 1
T_m (°C)	160.0	163.3	163.9	163.7
T_c (°C)	107.9	124.8	125.3	126.1
ΔH_m (J/g)	61.4	76.4	78.5	80.5
ΔH_c (J/g)	87.4	94.6	98.7	98.9

ΔH_c , crystallization enthalpy; ΔH_m , melting enthalpy; T_c , crystallization temperature; T_m , melting temperature.

TABLE III
Thermal Properties of the PP/PETA Physical Blend

PP/PETA mixture	Virgin PP	1 wt %	3 wt %	6 wt %
T_m (°C)	160.0	161.9	162.4	163.2
T_c (°C)	107.9	119.4	121.5	122.5

T_c , crystallization temperature; T_m , melting temperature.

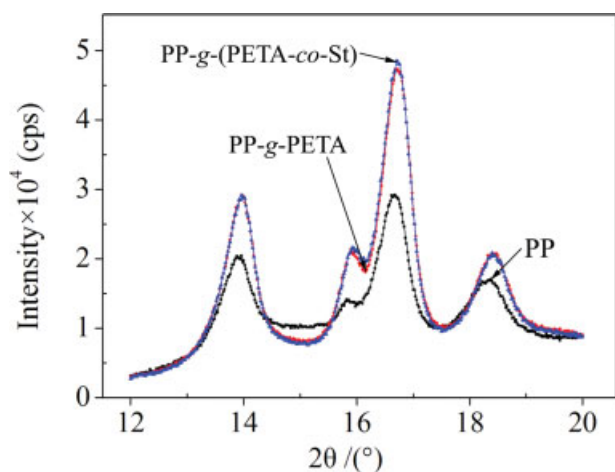


Figure 7 X-ray diffraction patterns of PP, PP-g-PETA, and PP-g-(PETA-co-St). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the defective crystals during heating. Table II shows thermal properties of the virgin PP, PP-g-PETA, and PP-g-(PETA-co-St). The melting temperatures of the grafted samples are slightly higher than that of the virgin PP. Moreover, the values of the melting enthalpy, which correspond to the crystallinity of the grafted PP, are all higher than that of the virgin PP. The crystallization temperatures and crystallization enthalpies of the grafted PP are considerably higher than those of the virgin PP. The crystallization temperature rises substantially to 126.1°C from 107.9°C. The increase in the crystallization temperature and crystallization enthalpy for the grafted samples is probably due to the presence of the grafted PETA-co-St chains, which act as a good nucleating effect. Therefore, PP can crystallize at a higher temperature. To investigate whether PETA has a nucleating effect, physical blends of PP and PETA were prepared and studied. The PETA contents in the PP/PETA physical blends were 1, 3, and 6 wt %. Table III shows additional DSC data of the PP/PETA mixtures. Indeed, the presence of PETA increases both the melting and crystallization temperatures, but the values are slightly lower than those of PETA-grafted PP samples.

Wide-angle X-ray diffraction results of the virgin PP and grafted samples are shown in Figure 7. The

diffraction peaks are located at the 2θ diffraction angles of 14.00, 16.79, and 18.48°, which correspond to (110), (040), and (130) planes, respectively, and are characteristic of the typical α -form monoclinic structure of PP. The grafted samples show a sizable increase in the intensity of the α -crystal form, which suggests that the α -crystal content is greatly enhanced by grafted St-co-PETA chains as a nucleating effect. In addition, compared with the diffraction peaks of homo-PP, the peak intensity at 15.9° has clearly increased. The peak at 15.9° can be assigned to the typical β -form structure of PP.^{36,37} This result indicates that the presence of grafted PETA chains could induce the formation of PP β -form crystals.

Table IV gives the mechanical properties of the virgin and grafted PP. The grafted PP samples increase in tensile and flexural strength, and the elongation at break decreases considerably compared to that of the virgin PP. With increasing St concentration, the tensile, flexural, and impact strength of the grafted samples also increases, but the impact strength remains below that of the virgin PP. The good mechanical properties of the grafted samples may be due to increased interactions of PP molecules caused by the grafted PETA groups. The results of sample solution extraction showed that the grafted PP was gel-free.

CONCLUSIONS

In this study, the melt free-radical grafting of PETA onto PP has been investigated. It has been shown that the use of St as a comonomer can effectively increase the PETA graft degree and decrease degradation of PP. Increasing the peroxide level decreases the PETA graft degree and increases degradation of PP. The PP with grafted PETA-co-St branched chains exhibited enhanced mechanical properties.

The effect of the addition of St as a comonomer to the melt-grafting system of PETA onto PP can be explained as follows. In the presence of St, St reacts first with PP tertiary macroradicals, and the resulting styryl macroradicals then copolymerize with PETA, leading to grafted PETA. This allows a pathway for a reaction between PETA and macroradical PP and increases the efficiency of the grafting.

TABLE IV
Mechanical Properties of the Modified PP

	Tensile strength (MPa)	Elongation (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (kJ/m ²)
PP	32.49	535.28	45.69	1262.77	5.68
0 : 1 St/PETA	34.11	15.9	56.70	1656.28	4.08
1 : 1 St/PETA	36.90	9.73	56.77	1732.08	4.94
3 : 1 St/PETA	36.91	14.43	57.96	1726.53	5.12
6 : 1 St/PETA	37.55	20.10	58.19	1739.95	6.25

An increase in the crystallization and melting temperatures of PP has been observed in the presence of PETA. The increase is slightly more significant for the grafted samples than physically compounded mixtures of PETA and PP. X-ray diffraction results further demonstrate that the grafted chains not only have a good nucleating effect for PP crystallization, but may also induce the formation of β -form crystals. Meanwhile, the grafted PP displays higher tensile and flexural strength but lower elongation than virgin PP.

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