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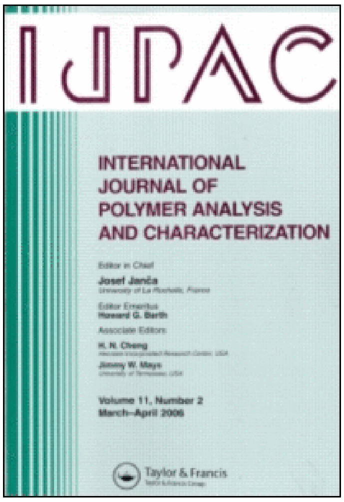

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Characterization of a Poly(propylene-*g*-styrene) Graft Copolymer by Temperature Rising Elution Fractionation

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Abstract: A polystyrene-grafted polypropylene sample was prepared by solid-state grafting polymerization in the presence of 2,2,6,6-tetramethyl-piperidinyloxy. Temperature rising elution fractionation of the grafted PP was performed and the fractions were characterized by ^{1}H- and ^{13}C-NMR, FT-IR, GPC, DSC, and WAXD. Results show that the grafted PP fraction eluted at 114°C accounts for 42% of the graft copolymer and has the highest grafting degree, high melting temperature and crystallinity, and high molecular weight. All the phenomena suggest that the grafted polymer contains a major component that has low branch density and long branch chain and a minor component with high branch density and short branches.

Keywords: 2,2,6,6-Tetramethyl-piperidinyloxy; Isotactic polypropylene; Solid-state graft polymerization; Styrene; Temperature rising elution fractionation

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INTRODUCTION

Modification of polypropylene (PP) in the solid state is the basis of an industrial process developed by Montell in the early 1990s[1] that resulted in the commercialization of the Hivalloy products. Among the many modification methods, graft copolymerization of PP with styrene, maleic anhydride, or other monomers plays an important role in the development of PP-based polymer alloys and composites.[1–4] Introduction of polar groups on the nonpolar PP backbone can overcome the disadvantage of low surface energy of PP and improve the printing, coating, compatibility, and antistatic properties of the PP surface.

Modification of polypropylene through grafting copolymerization is always accompanied by side reactions like chain scission, branching, and cross-linking that complicate the chain structure of modified PP. Characterizations of modified PP have been reported in many articles, but most focused on the average chain structure of graft copolymer.[2,5–7] To gain deep insight into the chain structure of graft polymerization products, it is necessary to determine the various structures formed and their distribution. On this basis the structure-properties relationship of the graft copolymer can be established. Knowledge of chain structure distribution of the graft copolymer can also greatly help the understanding of the mechanism of grafting polymerization. The aim of this work is to obtain a complete description of the molecular structure of the graft copolymer with the use of preparative temperature rising elution fractionation (TREF).

TREF has been regarded as a powerful technique for the study of semicrystalline polymers. It can isolate the polymer fractions according to their ability of crystallization, which will reflect the chemical structure of the analyzed polymer, including monomer sequence distribution, branching degree, tacticity, and so on.[8–11] However, no studies on the chain structure of PP graft copolymers with preparative TREF have been reported in the literature before.

In the present study, we used preparative TREF to separate PP-*g*-PS obtained in solid-state grafting polymerization into different fractions. These fractions were then characterized for their molecular structure and physical properties by means of ^{13}C nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and Fourier transform-infrared spectrometry (FT-IR). A sample of virgin PP used for the grafting polymerization was also fractionated and characterized in the same way. Based on the comparison between the virgin PP and the grafted PP, information on the mechanism of the grafting reaction of styrene (St) onto PP during solid-state modification is obtained.

EXPERIMENTAL SECTION

Materials

Nascent spherical PP granules with porosity of 23% and diameter of 1.43–2.0 mm (kindly provided by Sinopec Corp., China) were used as the matrix for grafting polymerization. Styrene (>98%) was purified by washing with 10% NaOH and then distilling under reduced pressure. 2,2,6,6-Tetramethyl-piperidinyloxy (TEMPO) was purchased from Wenzhou Plastic Additives Factory and purified by sublimation. *Tert*-butyl perbenzoate (TBPB, Acros) was used as initiator without further purification. Xylene was purified by evaporating in a rotary evaporator.

Preparation of Grafting Samples

The grafting reaction was carried out in a Schlenk flask equipped with mechanical stirrer. According to the designed ratio, 10.0 g PP granules were charged into the reactor. After three vacuum-thaw treatments, a solution of TEMPO, TBPB, and styrene (TBPB/PP = 0.5 wt.%, TEMPO/TBPB = 0.05 mol/mol, St/PP = 90.9 wt.%) was injected into the reactor by syringe and pressurized with nitrogen. Then the content was stirred for 60 min at 60°C to ensure complete sorption of the liquid phase into the granules. The reactor was then quickly heated to 130°C and maintained for 2 h to initiate the grafting reaction. The product, still in spherical morphology, was then washed with a mixture of ethanol/*n*-pentane to remove the residual styrene in the granules. The TEMPO was added in the system to reduce the degradation and cross-linking of PP chains, as reported in our previous work.[12] The product was then dried in vacuum for 24 h at 50°C.

Primary fractionation of the product was conducted in a three-necked flask. A 1 g amount of sample was wrapped in a stainless steel mesh, immersed in 250 mL xylene, and refluxed under the protection of nitrogen for about 36 h. Both the graft copolymer PP-*g*-PS and the possibly remaining PP homopolymer were dissolved in xylene. Then the solution was concentrated and poured into excess of ethyl acetate to settle down the PP-*g*-PS. (The ungrafted polystyrene is soluble in ethyl acetate.) The precipitate was recovered as PP-*g*-PS and dried in vacuum for 24 h at 50°C, which was then used for TREF. The residue left in the mesh was defined as gel. No gel was found in the sample used in this work.

Fractionation by TREF

In this work, a home-made preparative TREF apparatus was used. It consists of a glass column packed with an inert support (quartz sand, particle diameter 0.3–0.6 mm, pretreated at 500°C for 5 h). The temperature of the column is controlled by a Polystat constant temperature circulator. A sample of virgin PP used for the grafting polymerization and the product of the above-mentioned styrene grafting polymerization was used for TREF.

The polymer samples were first dissolved in xylene under the protection of N_2 at 130°C for 30 min and immediately introduced into the column of the TREF apparatus, the temperature of the column being initially fixed at 130°C for 30 min. Both the ungrafted PP and the grafted copolymer were completely dissolved in boiling xylene. As the first step of the fractionation, the solution was gradually cooled to room temperature at a rate of 1.5°C/h to let the PP segments crystallize. The following fractionation was done with the same solvent by raising and maintaining the temperature in 16 steps (25 – 70 – 90 – 100 – 102 – 104 – 106 – 108 – 110 – 112 – 114 – 116 – 118 – 120 – 125 – 130°C). Polymer fractions were eluted from the column using xylene as solvent at each step after the temperature was stabilized for 30 min. The polymer fractions were recovered by evaporating the xylene and drying in a vacuum oven at 50°C for 24 h and finally were stored at room temperature under nitrogen.

Measurements

FT-IR spectra were recorded by a Bruker Vector 22 infrared spectrometer, and the grafting degree of the grafted PP was determined as reported in the literature.[4,6,13] The grafting degree of the sample was found to be 17.9%.

The isotacticity of PP main chain was also calculated from the FT-IR spectrum. The absorbances at 998 cm^{-1} (A_{998}) and 974 cm^{-1} (A_{974}) correspond to helical and non-helical conformations that result from crystalline and noncrystalline polypropylene segments, respectively. The ratio A_{998}/A_{974} linearly correlates to the amount of [mmmm] pentads and the degree of crystallinity.[14] The FT-IR measurements of [mmmm] pentads have been found to agree reasonably well with the ^{13}C NMR calculations as reported by Robert et al.[15]

Molecular weight and its distribution were measured by gel permeation chromatography (GPC) using a PL-220 GPC instrument (1,2,4-trichlorobenzene eluent, 150°C, PL mixed-B columns) employing universal calibration based on polystyrene (PS) standards.

^{13}C-NMR spectra of the fractions were measured on a Varian Mercury Plus 300 NMR spectrometer. 1,1,2,2-Tetrachloroethane-d_2

was used as a solvent to prepare the solution of the fractions of about 20% (wt/v). The spectra were recorded at 120°C, with hexamethyldisiloxane as internal reference.

Thermal behavior of the fractions of PP and those of the grafted product were examined by differential scanning calorimetry (DSC) on a Perkin Elmer Pyris1 DSC instrument under nitrogen atmosphere. About 3.6 mg of sample was sealed in an aluminum sample crucible under nitrogen protection. Then the DSC scan was recorded at a heating rate of 10°C/min from 50° to 190°C, held for 5 min at 190°C, followed by cooling from 190° to 50°C, then again heated from 50° to 190°C at 10°C/min.

Wide-angle X-ray diffraction (WAXD) measurements were performed on a Rigaku D/max 2550PC rotating anode X-ray diffractometer. The incident beam wavelength was 1.54 Å, corresponding to 40 kV CuKα radiation. Samples for WAXD were compression-molded into films at 230°C and cooled to room temperature in air.

RESULTS AND DISCUSSION

Results of TREF

A PP sample and a graft polymer were fractioned into 16 fractions. The graft copolymer was prepared by solid-state grafting polymerization of St in PP granules as described in the experimental part. PS homopolymer was not removed from this sample before the TREF process.

The fraction eluted at 25°C was 36 wt.% for the graft polymer and 7.4 wt.% for PP, respectively. Because both the PS homopolymer and atactic PP are soluble at room temperature in xylene, the 25°C fraction of the graft polymer should include both the ungrafted PS and atactic PP. As the content of homopolystyrene in the graft polymer was 27.6 wt.%, calculated according to the IR result and St conversion, the weight of atactic PP eluted at 25°C was found to be 8.4 wt.%, 1.0 wt.% larger than the content of atactic PP in the virgin PP.

Figures 1 and 2 are the TREF profiles of the graft polymer and the PP in the elution temperature range 70°–130°C, respectively. In these figures the weight percentages of the 25°C fractions are not shown.

Comparing Figure 1 with Figure 2, one can see that the differences of TREF curves between the two samples are not so large. The major fractions of both the PP and the grafted PP were eluted around 114°C. There is an increase in the fractions of 100° to 110°C and decrease in the fractions of 116° to 130°C of the graft polymer over the pure PP.

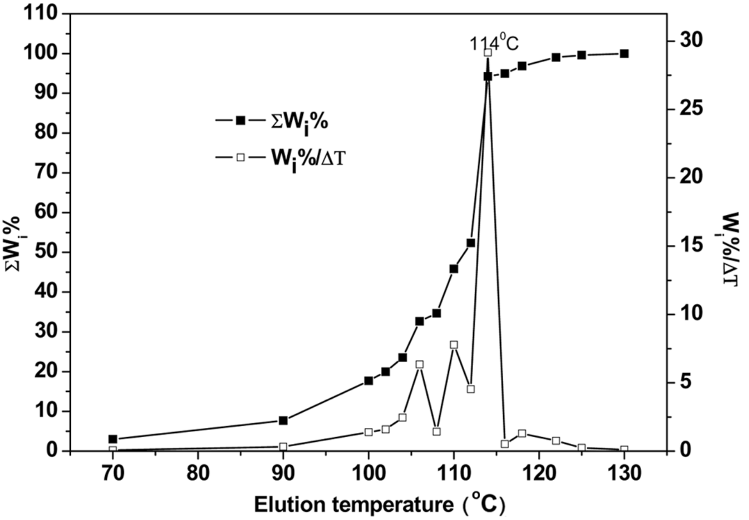


Figure 1. TREF profile of the grafted PP in the range of 70° to 130°C.

Grafting Degree of Fractions

Figure 3 shows FT-IR spectra of the fractions eluted at 114°C from PP and the grafted PP. The presence of styrene units in the grafted chains

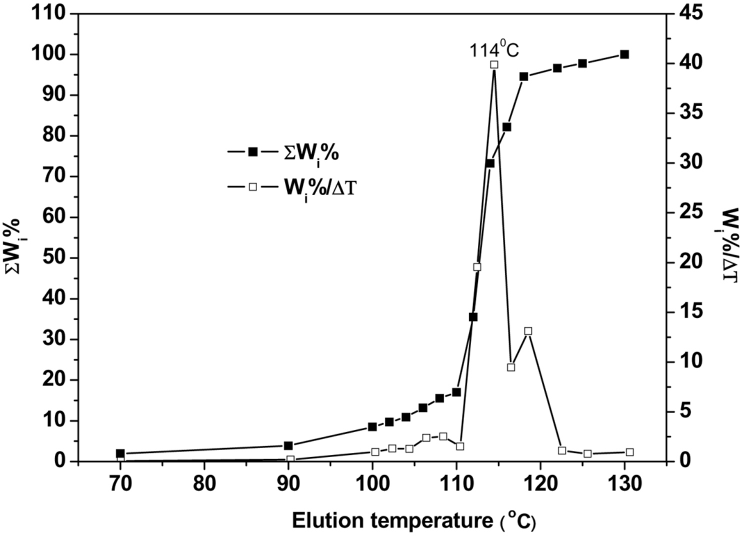


Figure 2. TREF profile of PP in the range of 70° to 130°C.

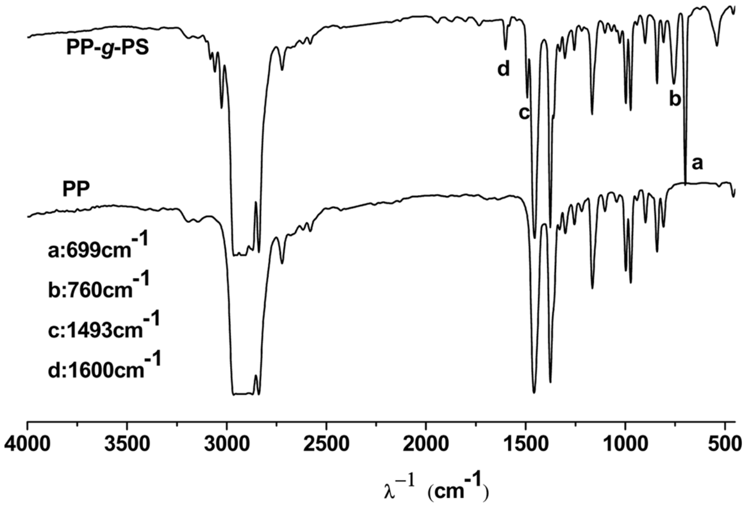


Figure 3. FT-IR of the fractions eluted at 114°C from PP and grafted PP.

is confirmed by two absorption bands at 1601 cm^{-1} and 1493 cm^{-1}, which are attributed to stretching of benzene ring. The two strong bands observed at 760 cm^{-1} and 699 cm^{-1} are due to C–H out of plane deformation of the PS units.

The ^{1}H-NMR spectrum of the grafted PP eluted at 114°C is shown in Figure 4. In addition to the peaks at 2.24, 2.61, and 2.92 ppm, corresponding to CH_3, CH_2, and CH, respectively, in the main chain, there are two minor peaks at 7.96 and 8.42 ppm that are from aromatic protons

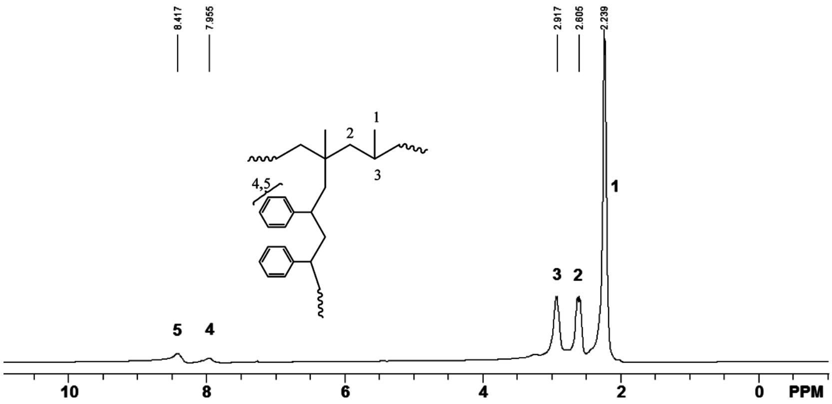


Figure 4. ^{1}H-NMR spectra of the grafted PP eluted at 114°C.

on PS units, also indicating the presence of PS graft chains in this fraction.

The ^{13}C-NMR spectra of the fractions extracted at 114°C from PP and the grafted PP are shown in Figure 5. Compared with PP material, two additional peaks at 128.6 and 126.1 ppm can be observed in the fraction of the grafted PP, corresponding to the –CH groups in phenyl. The tiny peak at 41.4 ppm may be attributed to the –CH– (methine) carbon on polystyrene main chain. No signals from the grafting point on PP main chain can be obtained in the ^{13}C-NMR spectrum, indicating very few grafting points produced on PP main chain.

Figure 6 shows the grafting degree of the fractions eluted from the graft polymer. As we know, solid-state grafting reactions occur only in amorphous phase. Because the fractions eluted at lower temperature have lower crystallinity and thus contain more amorphous phase, they are expected to be grafted more efficiently than the chains eluted at higher temperatures. But in Figure 6, an unexpected tendency is seen, that is, the fractions eluted from 110° to 114°C have higher grafting degree than those eluted at lower temperature. Only in the range of 114° to 118°C is there a decrease of grafting degree with the increase of elution temperature. The reasons for such a strange distribution of grafting degree will be discussed in the following section. It should be noted that all the fractions contain some styrene, implying that in the solid-state reaction system almost all the PP chains are accessible to the radicals and styrene monomer to induce the grafting polymerization.

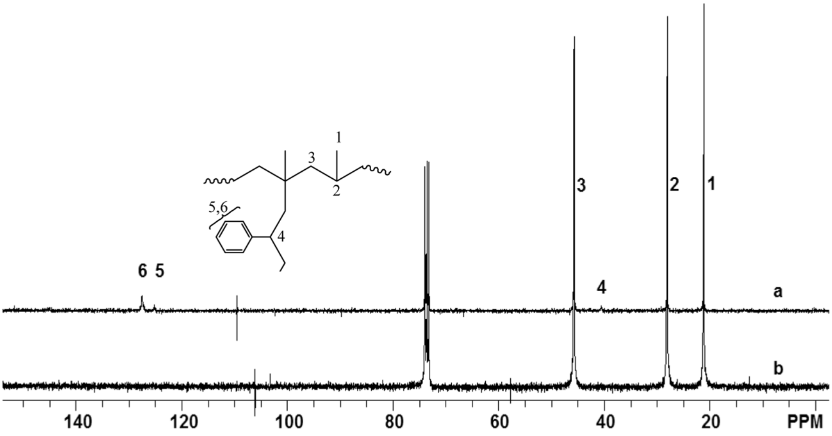


Figure 5. ^{13}C-NMR spectra of two fractions eluted at 114°C from (a) PP and (b) the grafted PP.

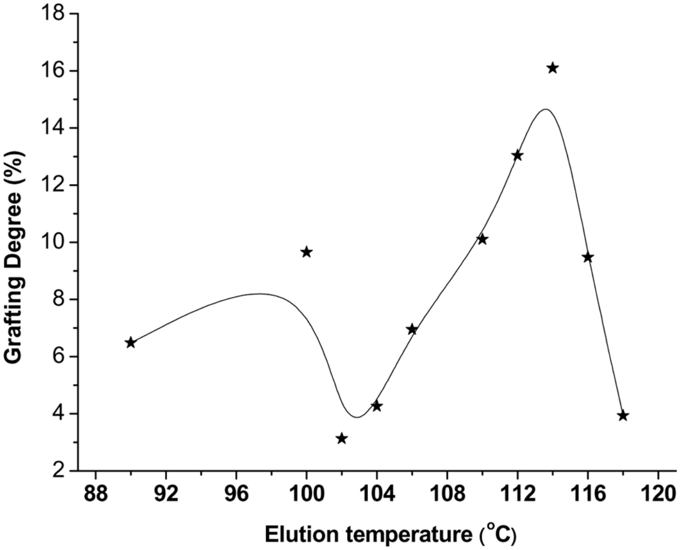


Figure 6. Grafting degree and mass ratio of St in the fractions from the graft polymer.

Molecular Weight and Its Distribution in the Fractions

GPC curves of the fractions eluted from the grafted PP and pure PP are shown in Figures 7 and 8, respectively. The GPC curves of the

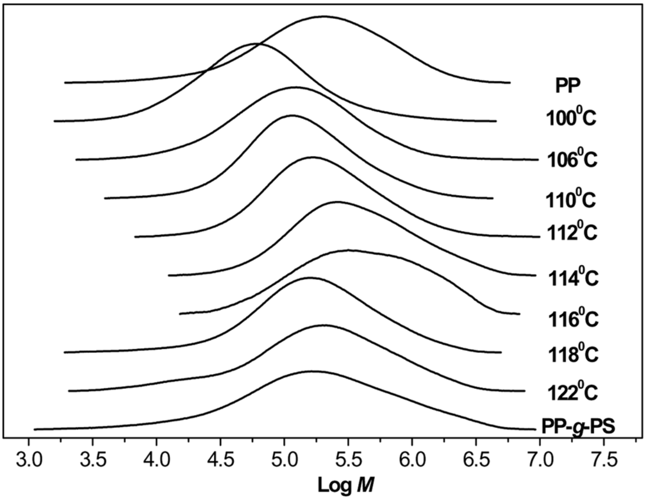


Figure 7. GPC curves of the fractions eluted from grafted PP.

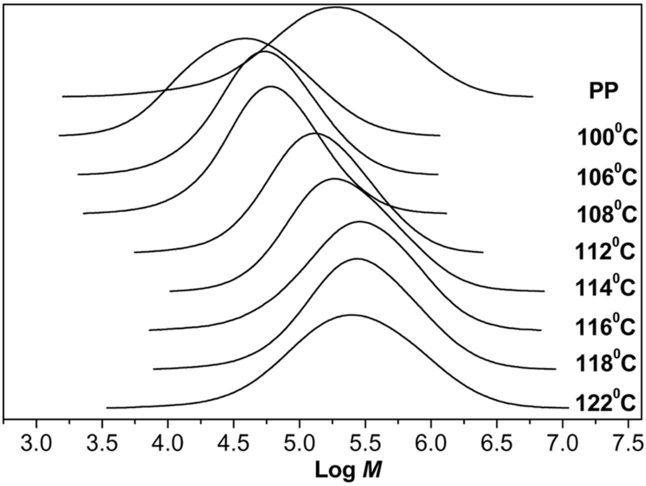


Figure 8. GPC curves of PP fractions.

unfractionated PP and grafted PP samples are also displayed in the same figures for comparison. In both cases, the molecular weight of the fractions increases with the increase of eluting temperature. The molecular weights of grafted PP fractions are larger than those of PP fractions eluted at the same temperature (see Table I), and the former have broader molecular weight distributions.

Table I. Molecular weight and polydispersity of the fractions from grafted PP and PP

	PP			Grafted PP		
Elution temperature (°C)	M_w ($\times 10^{-4}$)	M_w/M_n	Weight percent of fractions (%)	M_w ($\times 10^{-4}$)	M_w/M_n	Weight percent of fractions (%)
100	6.6	2.8	4.9	12.0	3.3	7.0
106	8.2	2.2	2.4	22.4	3.5	6.3
108	9.1	2.2	2.5	—	—	—
110	—	—	—	22.9	2.7	7.7
112	20.8	2.2	19.6	34.4	2.8	4.5
114	34.7	2.4	39.9	60.7	2.9	29.0
116	44.3	2.7	9.5	67.6	3.1	0.5
118	47.2	2.6	13.1	30.5	3.6	1.3
122	47.0	3.5	2.2	37.8	5.1	1.5
PP/ grafted PP	30.0	4.5		43.9	7.0	

In the literature, it has also been reported that the molecular weight of PP fractions increases with the rise of elution temperature.[16,17] Molecular weight of the grafted PP fractions increases with the increase of elution temperature from 100° to 116°C, indicating that the isotactic PP segments have not changed much after the grafting polymerization. This means that the main factor determining the fractionation, the crystallization ability of polymer chains, remains unchanged after grafting. However, molecular weights of the grafted PP fractions eluted at 118°C and 122°C are lower than that of the 116°C fraction. Meanwhile, their grafting degree is also lower (see Figure 6). As can be seen in Figure 8, the PP fractions eluted at 118°C and 122°C have molecular weights no higher than that of the 116°C fraction. This means that there are some PP chains that have very high isotacticity but not so high molecular weight. These PP chains should have very high crystallinity in the solid state and thus have low grafting degree when they are subjected to grafting, owing to their very low percentage of amorphous phase. As the molecular weights of the 118°C and 122°C fractions of graft polymer are lower than those of pure PP, a certain degree of chain degradation may have happened in these chains. However, the molecular weights of the remaining fractions of graft polymer are all higher than those of the corresponding PP fractions. This difference may be explained by the presence of PS side chains. In summary, it is reasonable to say that TREF fractionation of the graft polymer is still determined by the isotacticity of the PP main chain. The PS side chain may have a relatively minor influence.

Thermal Properties of Fractions

The DSC melting thermograms of the fractions eluted from the graft polymer and from pure PP are shown in Figures 9 and 10, respectively. Compared with the PP fractions (Figure 10), the obvious double melting peaks in the 100° and 106°C fractions of PP disappeared after grafting. According to previous reports,[18,19] the lower of the double peaks corresponds to PP segments with lower isotacticity (confirmed by Figure 5 and Table II). These segments form more amorphous phase and can be grafted with styrene to form many short branches. It is possible that crystallization of these segments was depressed by the densely grafted PS branches, leading to disappearance of the peak with lower melting temperature.

The melting temperatures (T_{m1} and T_{m2}) of the grafted PP fractions (see Table II) eluted below 106°C are lower than those of PP fractions eluted at the same temperatures but begin to increase after the elution temperature reached 110°C. These data suggest that PP chains of the fractions eluted at lower temperature are easily attacked by the radicals

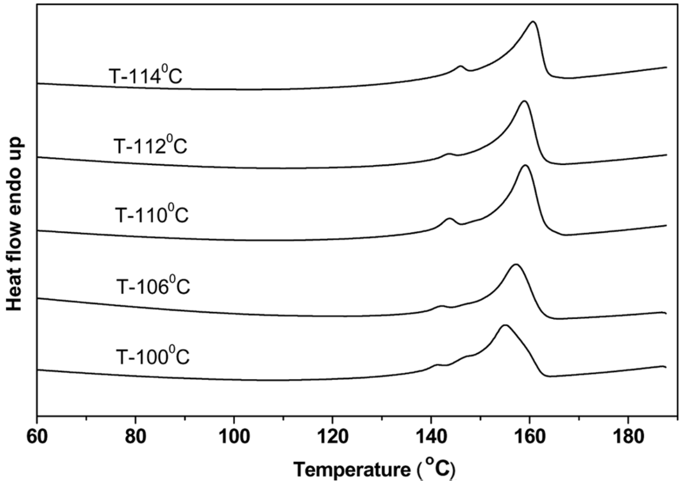


Figure 9. DSC melting thermograms of the grafted PP fractions.

and thus form shorter branches. This will reduce the length of isotactic PP segments and lead to low crystallinity and low melting temperatures.

The degree of crystallization (X_c) of the graft polymer was calculated based on 100% defect-free polypropylene crystalline with a 209 J/g fusion heat,[20] and the weight of PS in the sample has been deducted in the calculation. Obviously, the grafting reaction reduced the crystallinity value of PP, especially those fractions eluted at temperatures lower than 110°C.

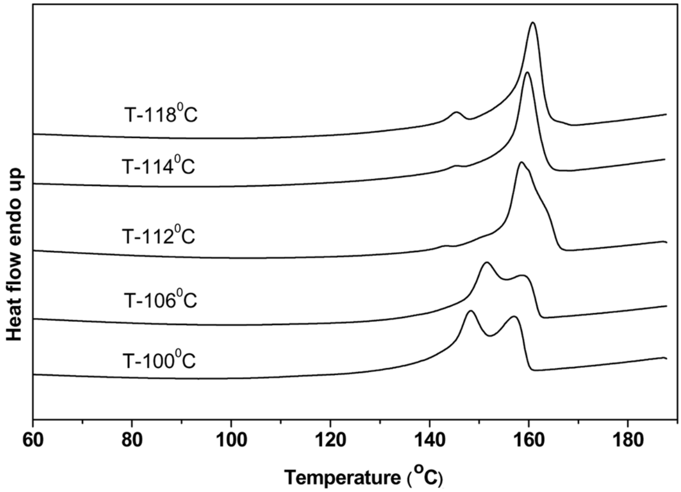


Figure 10. DSC melting thermograms of the PP fractions.

Table II. Results of DSC analysis on the TREF fractions

		Melting (Heating scan)			Crystallization (Cooling scan)		
Sample	Elution temperature (°C)	T_{m1}[a] (°C)	T_{m2}[a] (°C)	X_c[b] (%)	ΔH_m[c] ($J\,g^{-1}$)	T_c[d] (°C)	Isotacticity (%)
PP-*g*-PS	100	—	155.1	25.9	48.9	113.3	66.4
	106	—	157.2	23.5	45.7	112.5	78.6
	110	143.6	159.0	32.9	61.8	114.6	79.5
	112	143.4	158.9	28.1	51.1	114.5	74.3
	114	146.0	160.5	32.6	57.1	117.5	73.7
	118	—	—	—	—	—	73.7
PP	100	148.1	157.4	38.9	81.4	109.1	71.4
	106	151.6	159.8	30.6	64.0	109.9	—
	110	—	—	—	—	—	77.2
	112	142.9	158.6	32.3	70.1	114.4	71.8
	114	145.1	159.7	30.9	67.6	114.0	78.1
	118	145.4	160.8	25.9	64.6	114.4	78.5

[a] Melting temperature.
[b] Degree of crystallization.
[c] Enthalpy of melting.
[d] Crystallization peak temperature.

This means that the grafted PS chains can restrict the orderly arraying of a part of the PP segments, and the fractions eluted at lower temperatures may have higher branch density. It is interesting to see that the crystallinity of the PP fractions decreases with increasing elution temperature. As the molecular weight of the fractions increases with the elution temperature, this phenomenon may be explained by retarding of crystallization by chain entanglement. On the other hand, the crystallization peak temperature (T_c) of the grafted PP fractions was 2°–3°C higher than that of the PP fractions. Similar phenomena have been reported by Guan et al.[21] and can be explained by the heterogeneous nucleation effect of the graft chains on the crystallization of PP.

It is reported[22] that high T_c is beneficial to foaming of PP. In the course of foaming, when the mixture of PP and blowing gas is extruded out of the die, the pressure sharply decreases. Consequently PP and the gas will expand instantaneously, the gas in particular. At this time if the crystallization temperature of PP is higher, the crystallization of PP will proceed rapidly, thus benefiting the stability of foaming. The results also imply that the grafted PP could induce rapid case-hardening of the foams, which will be confirmed in our further work.

In the DSC curves of the 100°–118°C fractions from the grafted PP and 114°–118°C fractions from the ungrafted PP, a small peak at around 145°C can be seen. This peak might be due to transition of a metastable crystal form (β, γ, or smectic form) into the stable monoclinic form (α-form).[23–25] To confirm this, wide angle X-ray diffraction patterns of the 114°C fraction of the grafted and ungrafted PP were recorded (see Figure 11). It can be seen that besides the peaks of α-form at $2\theta = 14.1°$, 16.8°, and 18.4°, a strong peak at $2\theta = 16.0$–$16.1°$ is also present, which can be ascribed to β-form crystal. The peak of β-form in the grafted PP fraction was stronger than that of the PP fraction, due to the influence of PS side chains on the crystallization of PP main chains.

It is worth noting that the grafted PP fraction obtained at 114°C, accounting for 42% of the whole graft polymer, has the highest grafting degree combined with an unexpectedly high melting temperature. It implies that these chains have a low branch density but their PS branches must be rather long. Formation of such structure may be understood when we consider the confinement effect of crystalline phase on grafting polymerization. As shown in Scheme 1, PP chains with high isotacticity can form thick and large crystalline lamella, and the amorphous regions sandwiched between them are thin and flat. In this situation, the PS• radicals grafted from the PP chains in the amorphous region are seriously confined in a thin and flat space between the lamellas. The PS• radicals formed by St homopolymerization in the voids of a PP particle will meet a great diffusion barrier when they enter the flat amorphous region, resulting in low probability of termination between the ungrafted PS• and grafted PS•. On the other hand, because there are few PP chains in the amorphous region, the probability of termination between the grafted

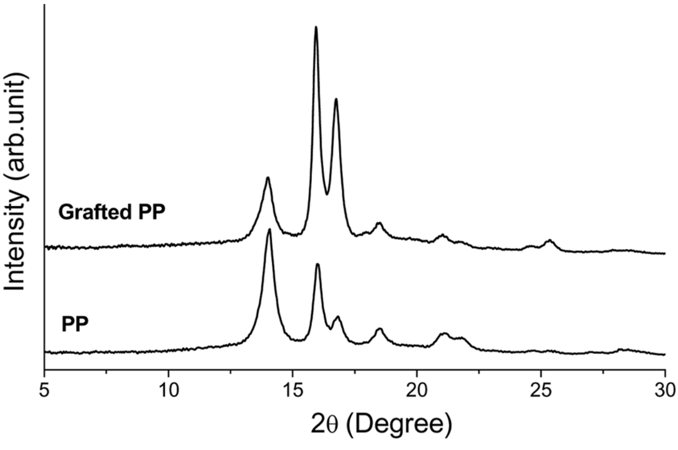
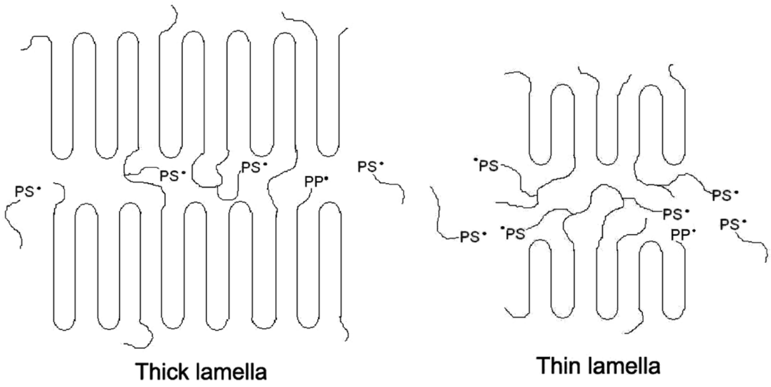


Figure 11. WAXD patterns of the grafted PP and PP fractions eluted at 114°C.



Scheme 1. Confinement effect of the PP lamella on the grafting polymerization.

PS• is also low. This can lead to the formation of PP-*g*-PS chains with low branch density and high grafting degree. In contrast, when the PP chains have low isotacticity and thus form thin lamellas, the amorphous regions between these lamellas will be less confined. In this case, the ungrafted PS• can diffuse more easily into the amorphous regions, and the grafted PS• can also stretch out into the voids, thus greatly increasing the probability of radical-radical termination. Thus, shorter PS side chains will be formed on the PP chains of lower isotacticity.

Summarizing the above results, it can be seen that there are basically two kinds of polymer chains in the grafted polymer. One kind of chain has low branch density and long PS branches and constitutes the major component of the graft copolymer. The other kind of chain, having high branch density and short branches, constitutes the minor component. This kind of chain structure distribution should be closely related to the spatial confinement effects unique to solid-state grafting polymerization.

CONCLUSIONS

TREF profiles of the grafted PP and virgin PP samples were similar. Grafting degree of the fractions increases with the rise of elution temperature from 104° to 114°C. Molecular weights of the fractions of both the grafted PP and virgin PP increase with the elution temperature. Melting temperatures of the fractions of grafted PP are very close to those of the PP fractions, and crystallinity of the former is even slightly higher than that of the latter when the elution temperature is higher than 110°C. The grafted PP fraction eluted at 114°C, which accounts for 42% of the whole graft polymer, has the highest grafting degree among all the fractions and rather high melting temperature and crystallinity. Based on these results, it becomes clear that the grafted polymer is composed of a major component that has both low branch density and high grafting degree and some minor components that have high branch density and medium-to-low grafting degree. There are also small amounts of chains with both low branch density and low grafting degree.

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