Solid-State Graft Polymerization of Styrene in Spherical Polypropylene Granules in the Presence of TEMPO

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ABSTRACT: A series of polypropylene-*graft*-polystyrene (PP-*g*-PS) were prepared by solid-state graft polymerization of styrene (St) in the presence of *tert*-butyl perbenzoate (TBPB) and 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO) using nascent spherical isotactic polypropylene (PP) granules as matrix. Reaction conditions such as ratio of TEMPO to TBPB, amount of TBPB and St, reaction time and temperature were investigated. The grafting degree (GD) decreased slightly with the addition of TEMPO, but the introduction of TEMPO reduced gel formation and degradation of PP chain. Introduction of camphor sulfonic acid in the TEMPO-mediated grafting polymerization system lead to evident increase in molecular weight of PP-*g*-PS and decrease of gel formation with slight changes of GD. GPC curves of the product synthesized with TEMPO addition showed obvious tailing at high molecular weight end. Complex viscosity in dependence on angular frequency of the melt of product showed obvious shear-thinning behaviors. All the experimental results indicated existence of long-chain branches in the product of graft polymerization. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 275–282, 2009

Key words: solid-state graft polymerization; styrene; polypropylene; 2,2,6,6-tetramethyl-piperidinyloxy

INTRODUCTION

Modification of polypropylene (PP) through its grafting with vinyl monomer has received increasing attentions. Applications of PP graft copolymers include either high-performance structural materials or compatibilizer for blends of PP. In principle, the grafting polymerization can be carried out in melt, solution, or in solid state. Compared with other techniques, solid-state graft polymerization has many advantages, such as low solvent amount, low reaction temperature, and high grafting degree (GD).[1]

However, even the solid-state graft copolymerization is also accompanied by some side reactions, mainly degradation and crosslinking of the polymer chains, which affects not only the mechanical properties of PP but also its processing performances. Reports showed that in a heated mixture of PP with free radical initiator *tert*-butyl perbenzoate (TBPB), degradation of PP prevailed at TBPB concentration of ≤37.0 mmol/kg PP, and buildup reactions predominated at TBPB concentration ≥74.4 mmol/kg PP.[2] To find ways to control PP chain degradation, many studies have focused on the grafting mechanism.[3–5] Recently, new efforts have been made to reduce PP chain degradation during the grafting reactions. Examples include application of nanoreactors where a free radical initiator of the type ROOR was first confined in (or encapsulated by) the galleries of an organically modified montmorillonite[4] or application of supercritical carbon dioxide.[6] In this work, 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO) was used to control the degradation and crosslinking of PP during solid-state grafting polymerization of styrene (St) in PP granules. TEMPO is a kind of stable radical, which can mediate the reactivity of growing polymer chains by forming thermally unstable alkoxy amine chain ends. Thus, an equilibrium is formed between the dormant alkoxy amine chain end and active chain radical upon homolysis of the carbon–oxygen bond of the alkoxy amine.[7] It has been reported that application of TEMPO in controlling the concentration of radicals may depress crosslinking and degradation reactions in a reactive extrusion grafting system.[8] It is expected that concentration of radicals in a solid-state grafting system can be controlled with TEMPO, and the side reactions accompanying the graft polymerization can be greatly depressed.

EXPERIMENTAL

Materials

Nascent PP granules were used as matrix for the grafting polymerization, which are product of an industrial reactor. The granules have spherical shape with diameter of 1.43–2.0 mm and a porosity of about 23%.

St (>98%) was purified by washing with 10% NaOH and then distilling under reduced pressure. TEMPO was purchased from Wenzhou Plastic Additives Factory, Wenzhou, China, and purified by sublimation. TBPB (Acros, Beijing, China) was used as an initiator without further purification. Camphor sulfonic acid (CSA) was purchased from Shanghai Chemical Reagent Corporation (Shanghai, China) and was used without further purification.

Grafting reaction

The grafting reaction was carried out in a three-necked Schlenk flask equipped with mechanical stirrer. First, 10.0 g PP granules were charged into the reactor. After three vacuum-thaw treatments, a solution of TBPB and TEMPO in St was injected into the reactor under vacuum by syringe and then pressurized with pure nitrogen (99.999%), and the PP granules were stirred at 60°C for 1 h to ensure complete sorption of the liquid phase into the granules. The closed reactor was then quickly moved into an oil bath set at 130°C and stirred for 2 h to complete the grafting reaction. The product granules, which were still in spherical morphology, were washed with a mixture of ethanol/n-heptane to remove the residual St and then dried in vacuum for 24 h at 50°C. Conversion of St was calculated as follows:

$$C_v(\text{wt \%}) = \frac{\mu_w - \mu_0}{\mu} \times 100$$

where C_v is conversion of St, μ_w is the weight of recovered product, μ_0 is the weight of PP before grafting polymerization, and μ is the amount of St initially added.

Fractionation of the product was conducted in a three-necked flask. About 1 g of sample was wrapped in a stainless steel net and immersed into 250 mL xylene, which was then heated to boiling under nitrogen protection for 36 h. The solution was concentrated and poured into excess of ethyl acetate to precipitate the graft polymer (PP-g-PS), which was recovered by filtration. The St homopolymer remained in the solution. The residue left in the net was defined as gel. Gel content of the product was calculated using the following equation:

$$\text{Gel(wt \%)} = \frac{\theta}{\theta_0} \times 100$$

where θ is weight of the gel, and θ_0 is weight of the sample used in the fractionation.

Measurements

GD of the polymerization product was measured by FTIR using a Bruker Vector 22 infrared spectrometer. This method was found to give more precise results when compared with measurement of the weight increment of product after the reaction. Thin films of the samples were prepared by hot-compression molding at 175°C for about 10 s at 20 MPa. The GD was determined from its FTIR spectrum according to the following calibration equation:[9]

$$y = -1.60 + 77.05x$$

where y is the ratio of peak area of the 700 cm^{-1} band (assigned to out-of-plane bending of the aromatic C—H) to that of the 808 cm^{-1} band (assigned to the CH$_2$ and CH rocking of PP), x is the ratio of the weight of PS to that of PP.

The GD was defined as follows:

$$\text{GD(\%)} = \frac{W_g}{W_g + W_{\text{PP}}} \times 100$$

where W_g is the weight of polystyrene grafted onto PP, W_{PP} is the weight of PP.

The grafting efficiency (GE) was defined as follows:

$$\text{GE(\%)} = \frac{W_g}{W_g + W_h} \times 100$$

where W_g is the weight of polystyrene grafted onto PP, W_h is the weight of St homopolymer.

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 PS standards.

An ARES rotational rheometer (TA Instrument) was used to measure the complex modulus and complex viscosities of PP and PP-g-PS copolymers. The frequency range was 0.01–100 s^{-1}, and the temperature was 190°C. Measurements of the dynamic viscosity were performed with a parallel-plate fixture (diameter = 25 mm), with a gap distance of 2.5 mm, and the strain was kept at 10% to ensure linear viscoelasticity. The measurements were conducted under nitrogen atmosphere to prevent degradation.
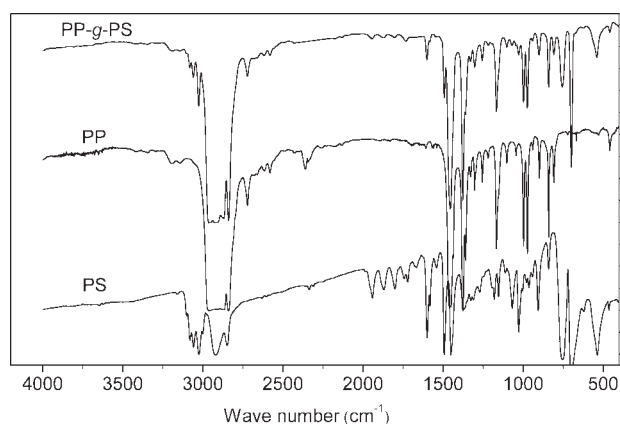
Figure 1 FTIR of pure PP, PS, and the graft polymerization product (soluble in xylene, and insoluble in ethyl acetate).

RESULTS AND DISCUSSION

Effect of TEMPO on graft polymerization

It has been reported that TBPB is a better initiator than benzoyl peroxide (BPO) in improving GD of St graft polymerization.[10] In this work, a series of solid-state graft polymerization of St in PP were conducted using TBPB as initiator. Figure 1 shows a typical FTIR spectrum of PP grafted by St. The peaks at 700 and 756 cm^{-1} are assigned to out-of-plane bending mode of the aromatic C—H, and the peaks at 1493 and 1600 cm^{-1} are the vibration of aromatic ring. It is clear that PS side chains have been grafted onto the PP chains. The degree of grafting of this sample was found to be 11.1%. On the other hand, there are no bands of carbonyl groups in 1650–1800 cm^{-1}, which means that the oxidation of the PP chains is negligible.

To depress the PP chain degradation and cross-linking in the graft polymerization, reactions with
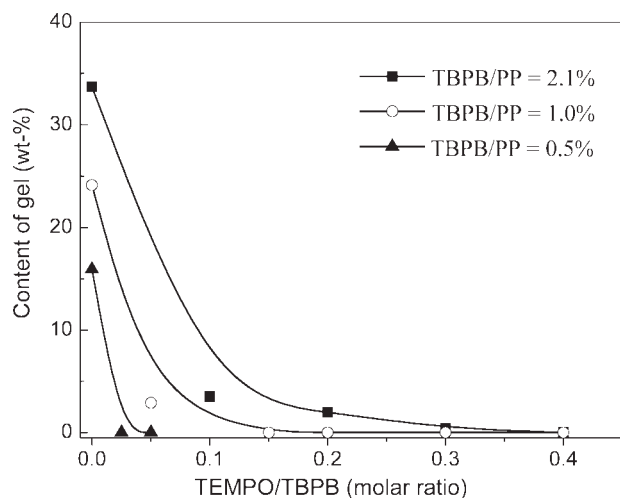
addition of TEMPO were conducted. Because a St homopolymerization can reach conversion higher than 98% in 2 h at 130°C, the reaction time of the graft polymerization was also fixed at 2 h. Figure 2 shows the influence of TEMPO on the formation of gel with different TBPB concentration and the same St feed (54.5 wt % based on PP). Without the addition of TEMPO, 15.9–33.7 wt % of gel was present in the product. In contrast, adding small amount of TEMPO in the system greatly reduced the gel content. In this system, we believe that TEMPO played the role of trapping a part of radical, thus maintaining radical concentration at a lower level. Accordingly, the probability of crosslinking reaction leading to gel formation was reduced. However, the GD and GE also decreased with increase of TEMPO amount, though the extent of decrease was moderate (see Fig. 3). This can be explained by termination of a part of the PP chain radicals by TEMPO.

It has been reported in literatures that adding CSA in TEMPO-mediate radical polymerization system can accelerate the polymerization.[11] In this work, a small amount of CSA was also used to improve the GD, and the results are shown in Figure 4. It can be seen that addition of CSA has less effects on the GD, because the amount of TEMPO used in this system was small. However, as shown in Figure 4, the amount of gel was further reduced to very low level at TEMPO/TBPB = 0.1 with the addition of CSA (CSA/TEMPO = 0.6). This reduction of gel content might be due to accelerated PP-TEMPO/ TEMPO transformation by CSA, which reduces the possibility of coupling reaction between PS· radicals of the graft polymer chains.

Influences of polymerization conditions

To better understand the solid-state graft polymerization in the presence of TEMPO, influences of
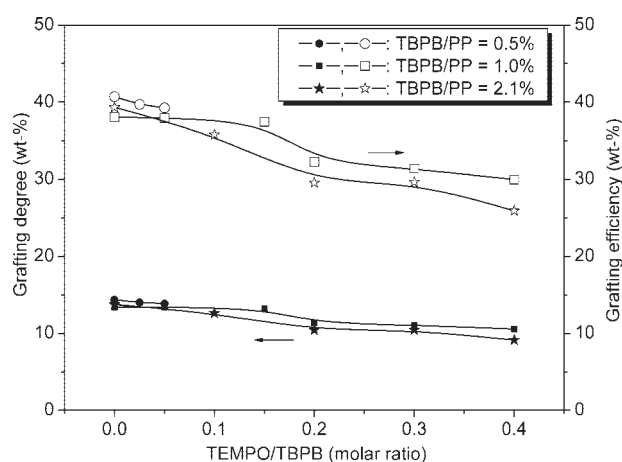

Figure 2 Influence of TEMPO on the formation of gel. Reaction temperature = 130°C, reaction time = 2 h.

Figure 3 Influence of TEMPO on grafting degree (GD) and grafting efficiency (GE).
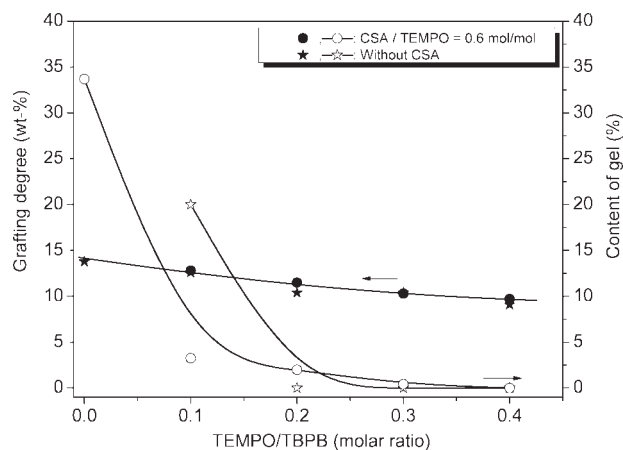
Figure 4 Effects of CSA on grafting degree and content of gel. St/PP = 54.5 wt %; TBPB/PP = 2.1 wt %; reaction temperature = 130°C; reaction time = 2 h.

various conditions on the reaction have been studied. Figure 5 shows the influence of St amount on the GD and the content of gel. It can be seen that GD increased with St amount when it is lower than about 50% (weight ratio of St to PP), but leveled off at higher St feed. This means that absorption and swelling of St in the PP matrix has a limit. St that is not well absorbed in the PP phase can only form PS homopolymer.

As shown in Figure 5, no gel was formed when no St was added to the PP granules, but the gel began to form at high St load when the initiator concentration was relatively high. This fact further proved that St monomer participated in the formation of gel.[12–14]

It is reported that the initial concentration of TBPB had great influences on the grafting polymerization.[2] Therefore, the effects of TBPB on GD and content of gel were studied at St feed of 54.5 wt % and

TEMPO/TBPB molar ratio 0.4. Results in Figure 6 showed that as the amount of TBPB increased, the GD decreased, while the amount of gel increased. The decrease in GD might reflect the limitation of TBPB concentration in the solid phase of PP granules. It is highly probable that in the PP granule there are many St-rich domains, resulted by the porous structure of PP granule.[5] As TBPB has a larger molecule volume than St, it might have a lower concentration limit in PP solid phase than St. As a result, when TBPB concentration is too high, it will be enriched in the St-rich domains. This part of TBPB will initiate more St homopolymerization than graft reaction. On the other hand, high TBPB concentration can still lead to more branches on PP chains, which leads to higher probability of gel formation. Therefore, the initial concentration of TBPB in grafting polymerization system should be limited to a proper level.

Reaction temperature is also an important factor in the grafting polymerization. It has been found that the PP granules were softened when the temperature was too high, leading to difficultly in stirring of the reactants, whereas at low temperatures, the reaction was incomplete in short time. A series of grafting polymerization were conducted at different temperatures with TBPB concentration 1.0 wt %, St feed 54.5 wt %, and TEMPO/TBPB molar ratio 0.4. Results in Figure 7 showed that as the reaction temperature was raised from 120 to 140°C, the GD increased, and then decreased when the temperature was further raised to 145°C. As reported in the literature, the GD of such a solid-state polymerization is influenced by several factors, including the amount of PP macroradicals initiated by TBPB, the efficiency of PP macroradicals participating in grafting reaction, and the rate of St homopolymerization.[1] It was reported by Laszlo-Hedvig et al.[15] that in the solid-
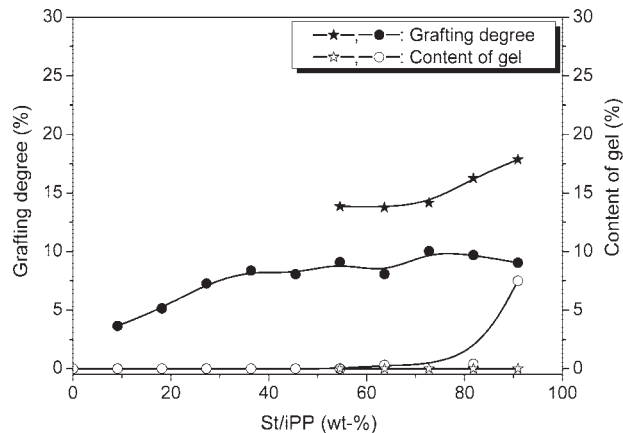

Figure 5 Effects of St on grafting degree and content of gel. Reaction temperature = 130°C; reaction time = 2 h; (☆, ★) TBPB/PP = 0.5 wt %; TEMPO/TBPB = 0.05 mol; (●, ○) TBPB/PP = 2.1 wt %; TEMPO/TBPB = 0.4 mol.
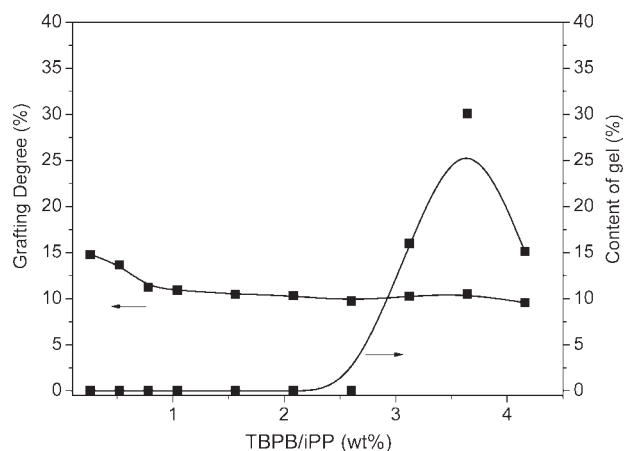

Figure 6 Effects of TBPB on grafting degree and content of gel. Reaction temperature = 130°C; reaction time = 2 h.
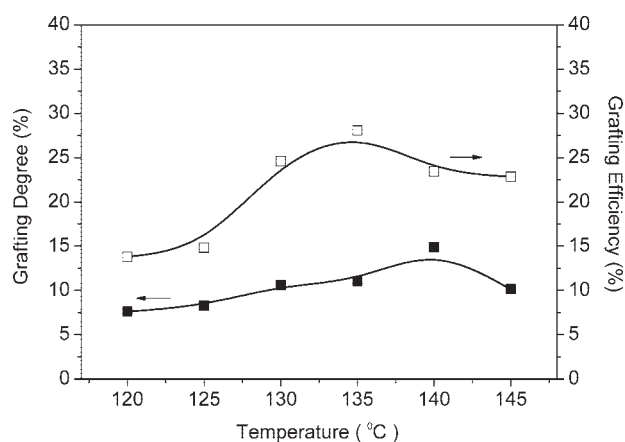
Figure 7 Effects of temperature on the grafting degree and grafting efficiency. Reaction time = 2 h; TBPB/PP = 1.0 wt %; St/PP = 54.5 wt %; TEMPO/TBPB = 0.4 mol/mol.

state modification of PP with TBPB as initiator, the highest intensities of PP macroradicals in ESR spectra were attained at 145°C. As the temperature increased, the initiation efficiency of TBPB increased, and accordingly more PP macroradicals would be produced; however, the rate of St homopolymerization will also increase. The changes of GD and GE will be influenced by these competing reactions.

Although studies on TEMPO-mediated polymerization revealed that conversion of St could be improved by prolonged reaction time,[16] in this system, GD and GE were not improved by long reaction time (see Fig. 8). This might be resulted by the lower amount of TEMPO used, as the St polymerization can only be markedly retarded when high amount of TEMPO is added. In this system, high conversion of St (>96%) at reaction time as short as 1 h was reached.
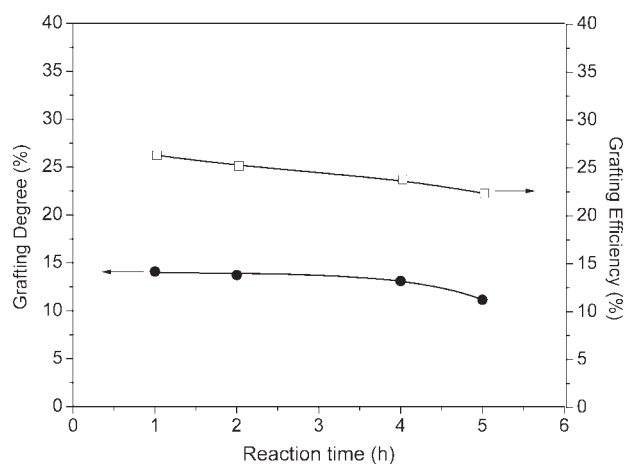

Figure 8 Influence of reaction time on grafting degree and grafting efficiency. Reaction temperature = 130°C; TBPB/PP = 1.0 wt %; St/PP = 54.5 wt %; TEMPO/TBPB = 0.1 mol/mol.
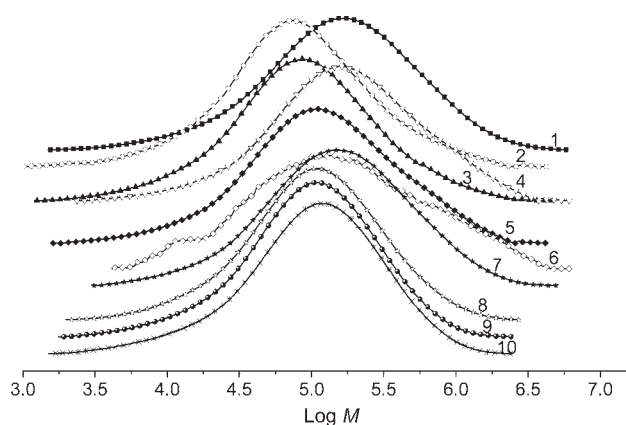

Figure 9 Influence of TEMPO/TBPB on the molecular weight distribution of PP-g-PS. TBPB/PP = 2.1 wt %; St/PP = 54.5 wt %; reaction temperature = 130°C; reaction time = 2 h. The mole ratio of TEMPO to TBPB; 1: pure PP; 2: without addition of TEMPO; 3: TEMPO/TBPB = 0.1; 4: TEMPO/TBPB = 0.2; 5: TEMPO/TBPB = 0.3; 6: TEMPO/TBPB = 0.4; 7: TEMPO/TBPB = 0.6; 8: TEMPO/TBPB = 0.8; 9: TEMPO/TBPB = 1.0; 10: TEMPO/TBPB = 1.1.

Molecular weight and molecular weight distribution of PP-g-PS

As shown in Figure 9 and Table I, molecular weight of PP-g-PS prepared with the addition of suitable amount of TEMPO was higher than that prepared without TEMPO. When no TEMPO was added, weight-average molecular weight of the graft product was about half of the PP matrix. When TEMPO/TBPB molar ratio was increased to 0.4, molecular weight gradually increased with increasing TEMPO amount. At TEMPO/TBPB = 0.4, molecular weight of the graft product even exceeded that of the PP matrix. This implies that the degradation of PP has been depressed by the added TEMPO. It is believed that degradation of PP is mainly ascribed to β-scission of the tertiary radicals.[1] The degradation

TABLE I
Influence of TEMPO Amount on the Molecular Weight and Polydispersity of PP-g-PS[a]

TEMPO/TBPB (mol/mol)	M_n ($\times 10^{-4}$)[b]	M_w ($\times 10^{-4}$)[b]	M_w/M_n[b]
PP	6.6	30	4.5
0	3.8	16	4.2
0.1	4.0	17	4.3
0.2	5.5	28	5.1
0.3	5.4	23	4.2
0.4	6.7	36	5.4
0.6	7.3	27	3.7
0.8	5.5	18	3.2
1.0	5.0	16	3.2
1.1	4.9	17	3.5

[a] Polymerization conditions: TBPB/PP: 2.1%; St/PP: 54.5%; temperature: 130°C; time: 2 h.
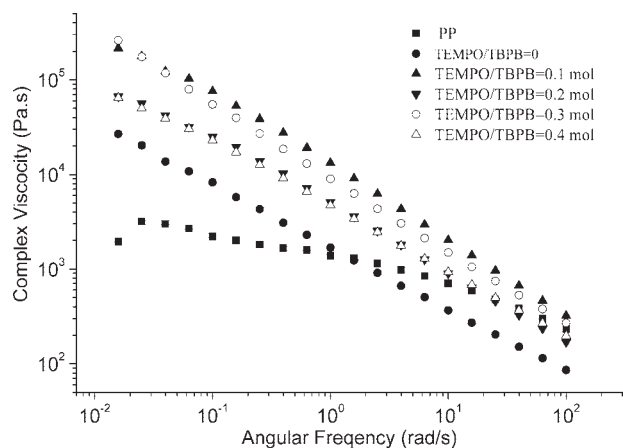[b] Determined by GPC.

Figure 10 Complex viscosities in dependence on angular frequency for graft polymers prepared in the presence of TEMPO. Conditions of graft polymerization: TBPB/PP = 2.1 wt %; St/PP = 54.5 wt %; reaction time = 2 h; reaction temperature = 130°C.

reaction prevailed over the buildup reactions at the beginning of peroxide decomposition. However at higher concentrations of peroxide, buildup reactions leading to increase in molecular mass or crosslinking can prevail as well.[2] Addition of the tertiary radicals to some monomers like St can stabilize the PP macroradicals and reduce the degradation reaction.[1] These results imply that TEMPO as a radical trapper can do better than St in stabilizing PP macroradicals. Because of the reversible nature of its reaction with the PP macroradicals, the radicals released from PP-TEMPO may predominantly react with St, rather than undergo β-scission reactions. The increase in high-molecular weight fractions as compared with the PP matrix (see Fig. 9) may be resulted by the formation of long-chain branching structure through recombination of the PP-g-PS· with the PP· segments formed in β-scission. Based on these considerations, we believe that TEMPO can play multiple roles in the solid-state graft polymerization system. It can stabilize the PP macroradicals formed at the early stage of peroxide decomposition, suppressing the degradation of PP chain. Then, it can control the number of active radicals in the middle and later stages of the reaction, reducing the formation of gel. However, adding too much TEMPO in the system leads to decrease in the molecular weight (see Table I). This may be related to the formation of too many PP-TEMPO instead of PP-g-PS·.

Furthermore, from the rheological behaviors of the melt of graft polymer samples (see Fig. 10), evident shear-thinning behavior at high frequencies can be found. Such properties are closely connected with long-chain branching structure of the polymer. These long-chain branches are believed to be formed mainly through coupling of PP-g-PS• and PP• radicals.[13]

TABLE II
Influence of TEMPO Amount on Molecular Weight of PP-*g*-PS in the Presence of CSA[a]

TEMPO/TBPB (mol/mol)	M_n $(\times 10^{-4})$[b]	M_w $(\times 10^{-4})$[b]	M_w/M_n[b]
PP	6.6	30	4.5
0.1	6.0	24	4.0
0.2	7.6	39	5.1
0.3	8.5	44	5.2
0.4	6.8	38	5.7

[a] Polymerization conditions: TBPB/PP: 2.1 wt %; St/PP: 54.5 wt %; CSA/TEMPO: 0.6 mol/mol; temperature: 130°C; time: 2 h.
[b] Determined by GPC.

Effects of CSA on graft polymerization

In literatures studying TEMPO-mediated polymerizations, CSA was used to accelerate the reactions.[11] In this work, it has also been found that adding proper amount of CSA together with TEMPO in the polymerization system resulted in better control over the side reactions than using TEMPO alone. As shown in Table II, in the presence of CSA/TEMPO (CSA/TEMPO = 0.6 mol/mol, TEMPO/TBPB ≥0.2 mol/mol), the weight-average molecular weight of PP-g-PS was higher than 3.9×10^5, which was much higher than that of the samples prepared in the absence of CSA, and even higher than the PP feedstock. The GPC curves (Fig. 11) show that in the samples prepared with CSA addition, there are much more fractions in the molecular weight range of $\geq 10^6$ than the PP feedstock. Strong shear-thinning effects at high frequencies have also been observed in the graft polymers (Fig. 12). All these facts imply that PP-g-PS graft copolymer with less PP chain degradation has been synthesized using a TEMPO/CSA/TBPB initiation system. It has been reported
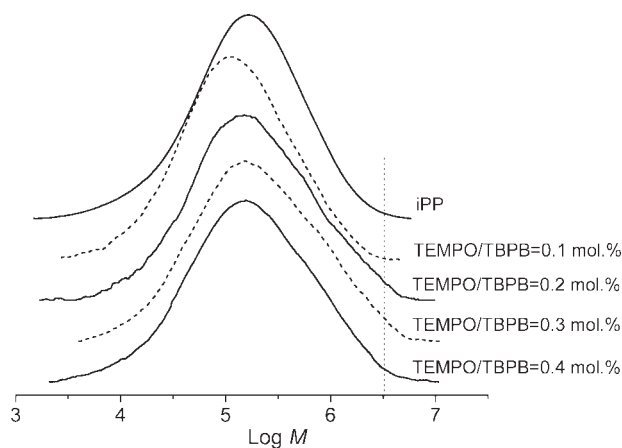

Figure 11 Effect of CSA on the molecular weight distribution of PP-*g*-PS. TBPB/PP = 2.1 wt %, St/PP = 54.5 wt %, CSA/TEMPO = 0.6 mol/mol, reaction temperature = 130°C, reaction time = 2 h.

that PP-TEMPO bond can be weakened by CSA. Therefore, the main role of CSA may be the acceleration of the reactions between PP-TEMPO and St, producing more branch chains on PP.

To discover the effect of St on the molecular weight of PP-*g*-PS, graft polymers synthesized at different St feed ratio (weight percentage of St to PP) were analyzed by GPC, and the results are shown in Table III. It is clear that the molecular weight of PP-*g*-PS increased with increasing feed of St, indicating the growth of PS side chain on PP. The role of St in stabilizing PP macroradicals should also be considered, as this effect can depress PP degradation. However, because the PS side chains give differential refraction index signal in the opposite polarity to that of the PP main chain in GPC analysis, GPC curves of the graft polymer may not reflect their true molecular weight distribution when the samples have high St content, because St content of the different GPC fractions may be much different from each other.

In summary, adding small amount of TEMPO in the graft polymerization of St in PP granules exerted slight influences on the reaction rate and GD of the product, but the polymer chain structure was evidently changed. These changes are mostly related with the depression of degradation and β-scission of the PP chains. Adding CSA further strengthened the effects of TEMPO with small influences on the GD. These effects should be connected with the reversible termination of the PP-*g*-PS· and PP· radicals by TEMPO. Reduction in concentration of the former may depress the crosslinking reactions, and reduction in the latter may lower probability of β-scission. However, it is hard to understand why only a
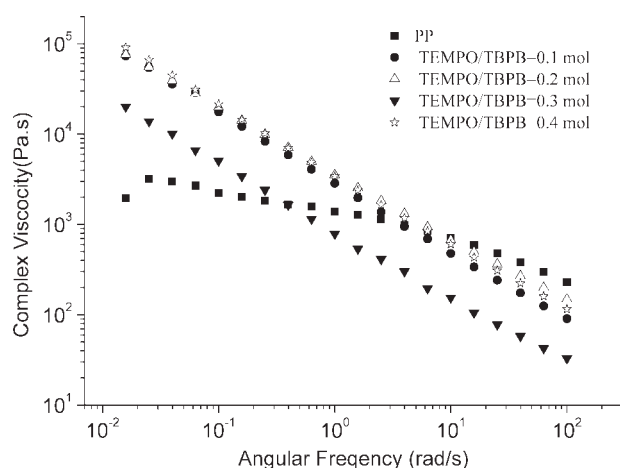

Figure 12 Complex viscosities in dependence on angular frequency for graft polymers prepared in the presence of CSA and TEMPO. Conditions of graft polymerization: CSA/TEMPO = 0.6 mol/mol; TBPB/PP = 2.1 wt %; St/PP = 54.5 wt %; reaction time = 2 h; reaction temperature = 130°C.

TABLE III
Influence of the Amount of Styrene on the Molecular Weight and Polydispersity of PP-*g*-PS[a]

St/PP (wt %)	M_n[b] ($\times 10^{-4}$)	M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]
PP[c]	6.6	30	4.5
0.0[d]	5.5	17	3.2
9.1	5.9	26	4.4
13.6	5.4	25	4.6
54.5	6.7	36	5.4
63.6	7.5	35	4.7
72.7	7.4	33	4.5
81.8	4.2	40	9.5
90.9	4.7	33	7.1

[a] Polymerization conditions: TBPB/PP: 2.1 wt %; TEMPO/TBPB: 0.4 mol/mol; CSA/TEMPO: 0.6 mol/mol; temperature: 130°C; time: 2 h.
[b] Determined by GPC.
[c] PP before the graft polymerization.
[d] PP treated with TBPB without St addition.

TEMPO/TBPB molar ratio as low as 0.1 was still effective. More detailed studies are needed to disclose the mechanism of the system.

CONCLUSIONS

The results presented in this article demonstrated that addition of TEMPO in the solid-state graft polymerization of St onto PP can effectively depress the formation of gel and the degradation of PP chains. However, the GD decreased moderately by the addition of TEMPO. Introduction of CSA in the TEMPO-mediated grafting polymerization system led to evident increase in the molecular weight of PP-*g*-PS and decrease of the gel formation with slight changes in GD. In the TEMPO-mediated graft polymerization system, suitably high reaction temperature and St feed and low molar ratio of TEMPO to TBPB were favorable to the formation of graft polymer. The initiator concentration and reaction time showed less influences on GD. GPC curves of the product synthesized with the addition of TEMPO showed obvious tailing at high molecular weight end. Complex viscosity depending on angular frequency of the melt of reaction product showed obvious shear-thinning behaviors, indicating existence of long-chain branches in the product of graft polymerization.

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