Gel Formed During the Solid-State Graft Copolymerization of Styrene and Spherical Polypropylene Granules. I. Influence of Reaction Conditions on the Gelation and Its Mechanism

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ABSTRACT: Graft copolymers of polystyrene (PSt) with spherical polypropylene (PP) granules were synthesized by solid-state reaction. In the copolymerization as a by-product some gel was formed. The effects of the amount of free radical initiator, feed ratio of St monomer, species of free radical initiator, and composition of the spherical polyolefin granules on the grafting degree of PSt and the gelation were studied. It is found that larger amount of initiator used, and higher feed ratio of St monomer lead to a higher grafting degree and higher content of gel. During the cross-link reaction process, both styrene and free-radical participate in the reaction that discloses the reason of the increment of gel with the increment of styrene consumption or initiator consumption. Using PPR, which is a random copolymer of 95.1 mol % propylene units and 4.9 mol % ethylene units, as grafting matrix, higher grafting degree and higher content of gel can be reached than that using isotactic PP as grafting matrix. Using tert-butyl peroxy benzoate (TBPB) as initiator, under the same conditions there were more PSt grafted to the spherical PP granules and more gel formed than that using benzoyl peroxide (BPO) as initiator. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3682–3687, 2007

Key words: solid-state polymerization; graft copolymers; gels; polystyrene; polypropylene

INTRODUCTION

In the past decade, functionalization of polyolefin has been a challenge scientifically and industrially an important area.[1,2] To improve the properties of polyolefin, copolymer units are usually grafted to them. Such graft copolymerizations are usually conducted by a solution process,[3,4] a melt process,[5,6] or a solid-state graft copolymerization process.[7–10] In contrast, the solid-state graft copolymerization process can be carried out at comparatively low temperatures and atmospheric pressure without solvent which is friendly to the environment and needs relatively low power consumption. Many literatures address the synthesis of polypropylene-*graft*-polystyrene (PP-*g*-PS) copolymers whose prospected application is to be used as an additive improving the compatibility between polypropylene (PP) and polystyrene (PSt). Usually, there are mainly three methods applied to

synthesize PP-*g*-PS copolymers. The first one is that propylene polymerized with styrene directly, catalyzed by Ziegler-Natta or metallocene catalysts.[11–13] The second approach to synthesize propylene-styrene copolymer was the consecutive polymerization: propylene was polymerized first; then styrene was added to the reaction system, and a copolymer was got.[14] The third approach to synthesize propylene–styrene copolymer was the living radical polymerization, such as the work of Shimada and coworkers[15] and that of Chung and Dong.[16] Currently, polypropylene can be produced by a spherical catalyst technique. PP based on this technique is usually of big spherical granules with narrow size distribution and show excellent morphology. Most of the granules were in the range of 1–5 mm. Another very important characteristic of spherical PP granules is their high porosity (from 10 to more than 40 vol % of the spherical PP granules). Such characteristics make spherical PP granules especially suitable for graft copolymerization with styrene through a solid-state reaction because the specific surface area of spherical PP granules is sufficient for contact with styrene and no interfacial agent is needed. During the period of copolymerization, PSt is mainly filled into the tiny pore of the spherical PP granules. Hence, the copolymerization process benefits from the spherical shape

of the polymer granules, as risks of scaling and fouling in the reactor can be lowered. In our previous work,[17] solid-state graft copolymerization of styrene with two kinds of spherical polyolefin granules was studied in detail. The polyolefins were isotactic PP homopolymer (PP) and poly(propylene-co-ethylene) (PPR, content of ethylene unit was less than 5 mol %) each synthesized by using spherical high-yield catalyst. Influence of various reaction conditions on graft copolymerization was investigated. And we found that in the copolymerization process as a by-product some gel was formed, which influenced the crystalline morphology and properties of polypropylene-g-polystyrene copolymer. Up to date, there is no literature on the gel formed in the solid-state graft copolymerization of styrene and spherical PP granules, and the influence of reaction conditions on the gelation and its mechanism have never been reported either. The objective of this work was to reveal the mechanism of the gelation in the copolymerization and point out the approach to avoid gelation. The reaction conditions of the solid-state graft copolymerization, including the amount of the free-radical initiator, the species of the free-radical initiator, feed ratio of the styrene monomer, and the composition of the polyolefin, were studied.

EXPERIMENTAL

Graft copolymerization of styrene and spherical polypropylene granules

Spherical polypropylene (PP) granules (kindly donated by SINOPEC Qilu Petrochemical Co., Zibo, China) and spherical poly(propylene-co-ethylene) (PPR) granules (kindly donated by SINOPEC Shanghai Petrochemical Co., Shanghai, China) were sieved and those granules tether to 1.43–2.0 mm were used to be grafted by styrene. Styrene was distilled after being washed with a sodium hydroxide solution and stored in refrigerator. Benzoyl peroxide (BPO) was purified by recrystallization. Tert-butyl peroxy benzoate (TBPB, 98%) was used directly as a free-radical initiator.

About 5 g of spherical PP or PPR granules was introduced into a 50 mL Shlenk flask. The air in the flask and the tiny pore of the spherical PP or PPR granules was removed by the evacuation of the flask to 5 mmHg for 5 s, and argon was added to the flask to normal atmosphere. TBPB was dissolved in styrene and added to the flask. Vigorous shaking was done to mix the reactant thoroughly. Firstly, the solid-state graft copolymerization was conducted at 60°C for 60 min to make TBPB-styrene solution absorbed adequately into the tiny pores of the spherical PP or PPR granules. Then the reaction system was heated to the designated temperature. The shaking of the flask continued until the copolymerization was finished.

The reaction product was washed with the mixture of ethanol and n-pentane to remove unreacted styrene and dried in a vacuum oven for 4 h. And then the washed polymer was extracted with ethyl acetate for more than 30 h to remove homopolystyrene. Finally, the extracted polymer, namely graft copolymer, was dried in vacuo.

Extraction of the gel from the graft copolymer

About 2 g of the graft copolymer was packaged by iron wire and put into Soxhlet extractor to extract the gel from the graft copolymer. Xylene was used as the solvent to extract the sample for more than 40 h. The part dissolved by xylene purified by concentration, precipitation, washing and drying in vacuo was called as graft copolymer degelatinized. And the remaining polymer, namely gel, was directly dried in vacuo. The content of gel in graft copolymer can be calculated by the equation below:

$$W_g = \frac{(W_1 - W_0)}{W_s} \times 100\%$$

where W_0 refers to the weight of iron wire, W_1 refers to the total weight of gel and iron wire, W_s refers to the weight of the graft copolymer.

Measurements

FTIR spectra of the graft copolymer were recorded on a Bruker Vector-22 spectrometer. Thin films of polymer prepared by hot pressing were used as samples.

The external morphology and cross sectional morphology of the spherical PP or PPR granules was observed by JSM-5510LV scan electronic microscope.

^{13}C NMR spectra of the fractions were measured on a Bruker AMX400 NMR spectrometer at 100 MHz. o-Dichlorobenzene-d_4 was used as solvent to prepare the polymer solution of 20 wt %. The spectra were recorded at 120°C, with hexamethyldisiloxane as internal reference. Broadband decoupling and a pulse delay of 5 s were employed. Typically 1000 transients were collected.

Samples for polarized light microscope observation were prepared by fusing small piece of the polymer placed between two cover glasses. After melting at 230°C for 2 min, they were held at 130°C for 48 h. Photographs were taken using an Olympus BX51 polarized microscope.

RESULTS AND DISCUSSION

### Chain structure of spherical PP and PPR granules

To explore the difference of chain structure between PP and PPR, ^{13}C NMR spectra of spherical PP and

PPR granules were recorded and are shown in Figure 1. The spectrum of the spherical PP granules shows that it is a typical spectrum of isotactic PP. In the spectrum of the spherical PPR granules, there are several strong peaks corresponding to the PPP sequence, like $P_{\beta\beta}$ at 20.0 ppm, $T_{\beta\beta}$ at 26.8 ppm, and $S_{\alpha\alpha}$ at 44.6 ppm, meaning that there are long PP segments in the polymer chain. Meanwhile, there is a weak peak at 28.1 ppm that is the methylene signal of short polyethylene sequences. The sketch map of the chain structure of PPR is shown in Scheme 1. This shows that the PPR is a random copolymer of 95.1 mol % propylene units and 4.9 mol % ethylene units. And the ethylene unit distributes among the propylene units alone.

Effect of the feed ratio of styrene

The reaction product was washed and then extracted with ethyl acetate to remove homopolystyrene. Then the extracted polymer, namely graft copolymer, was analyzed by ^{13}C NMR. A typical ^{13}C NMR spectrum of a sample is shown in Figure 2. The ^{13}C NMR analysis shows the presence of characteristic polystyrene (PSt) peaks alongside the PP peaks. FTIR spectra of graft copolymer, gel and graft copolymer degelatinized were shown in Figure 3. The bands at 1600, 1492, 757, and 699 cm^{-1} show that there are styrene units in the gel and styrene monomers participate in the crosslink reaction.

The effect of the styrene feed ratio (weight percentage of styrene to the spherical PP or PPR granules) on the grafting degree (expressed as the weight percentage of grafted polystyrene in the PP-g-PSt or PPR-g-PSt) and content of gel (expressed as the weight percentage of gel in the PP-g-PSt or PPR-g-PSt) is shown in Figures 3 and 4. As shown in Figures 3 and 4, the grafting degree and content of gel increased with the increment of the feed ratio of
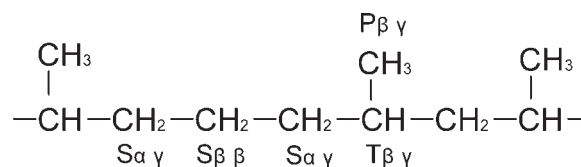
Scheme 1 The hypothetic structure of JSPP(PPR).

styrene. It is farther proved that styrene monomer participates in the crosslink reaction.

Effect of the initiator amount

The influence of the initiator concentration on the grafting degree and content of gel is shown in Figures 5 and 6. As shown in Figures 5 and 6, the grafting degree increased with the increment of the amount of initiator. And when the amount of initiator was less than 1 wt % (weight percentage of initiator to the spherical PP or PPR granules), there was no gel formed. However, when the amount of initiator was more than 2 wt %, the content of gel increased as the amount of initiator increased. Obviously, an adequate increment of the amount of initiator is beneficial for initiating more radical coupling with each other to carry out crosslink reaction and form gel.

Effect of the composition of the polyolefin

As shown in Figures 3–6, under the same conditions the content of gel formed in the graft copolymerization of styrene and PPR was more than that formed in the graft copolymerization of styrene and PP. That is may be due to the difference of chain structure between PPR and PP as shown in Scheme 1. PPR is a random copolymer of propylene units and few ethylene units with the ethylene unit distributes among the propylene units alone. This character of
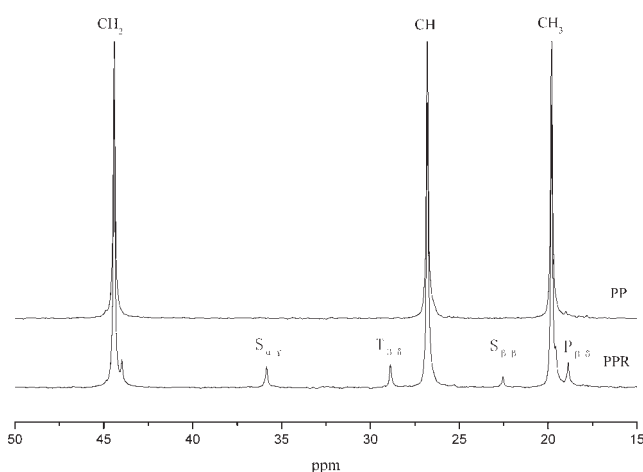
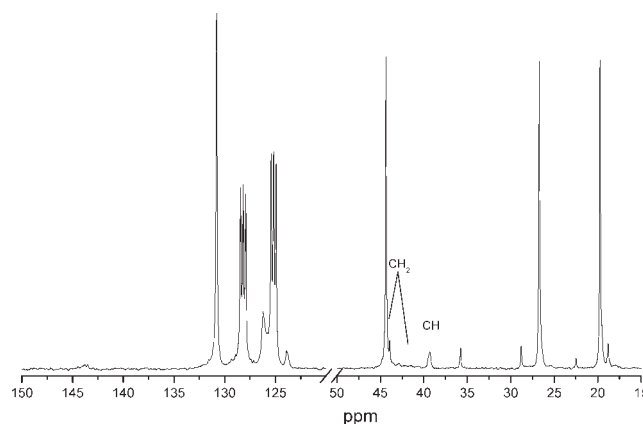**Figure 1** ^{13}C NMR of PPR and PP materials.

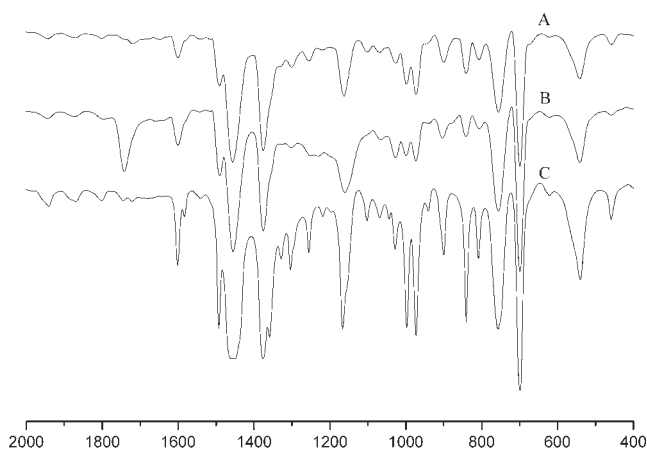**Figure 2** ^{13}C NMR spectrum of PPR-g-PS (ethyl acetate insoluble part).

Figure 3 FTIR of (A) the graft copolymer (ethyl acetate insoluble part); (B) gel; and (C) the graft copolymer degelatinized.

Figure 5 Effect of the feed ratio of styrene on the grafting degree and the content of gel [graft copolymerization of styrene and PPR for 2 h at 120°C with 4 wt % TBPB (weight percentage of TBPB to PPR)].

chain structure endows the macromolecule chain of PPR with better mobility than that of PP. As a result, the macromolecule radical formed in the graft copolymerization of styrene and PPR is easier to couple with radical, such as macromolecule radical, monomer radical and so on, than that formed in the graft copolymerization of styrene and PP.

Effect of the species of the free-radical initiator

To disclose the effect of the species of initiator on the content of gel formed in the graft copolymerization, we used benzoyl peroxide (BPO) to initiate styrene grafting on the chain of PPR. The result was listed in Table I. As Table I shown, although the feed ratio of styrene was as high as 60 wt %, there was no gel formed in the graft copolymer. But using TBPB as initiator, under the same conditions, as the
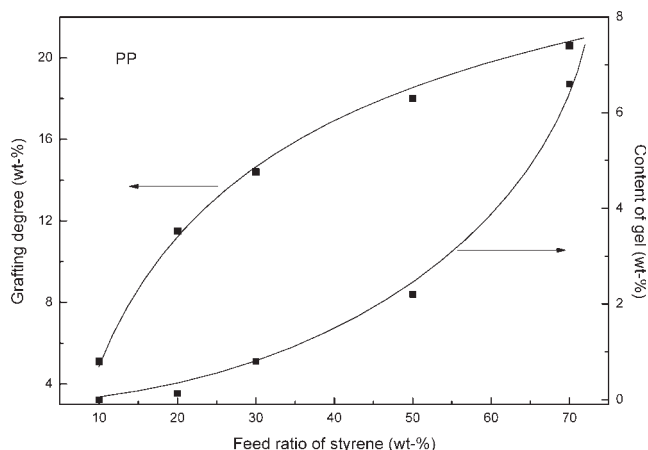
feed ratio of styrene was 10 wt % there were 0.5 wt % gel formed in the graft copolymer (as shown in Fig. 3). The decomposition temperature of BPO and TBPB, $t_{1/2} = 10$ h, is 73°C and 105°C, respectively. Hence at 120°C the decomposition speed of BPO is much higher than that of TBPB. In the initial stage of graft copolymerization, there are much more macromolecule free radical initiated by BPO· (represents a primary free radical formed from BPO) than that initiated by TBPB· (represents a primary free radical formed from TBPB). But the diffusion speed of macromolecule free radical is relatively low. Therefore, before they meet with styrene monomer, most of the macromolecule free radicals meet with each other and couple termination or disproportionate termination happens. The degradation of PP and low graft degree are indirect evidences of couple

Figure 4 Effect of the feed ratio of styrene on the grafting degree and the content of gel [graft copolymerization of styrene and PP for 2 h at 120°C with 4 wt % TBPB (weight percentage of TBPB to PP)].
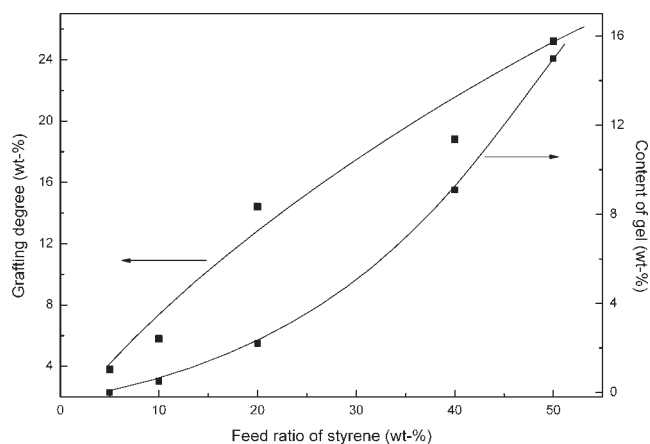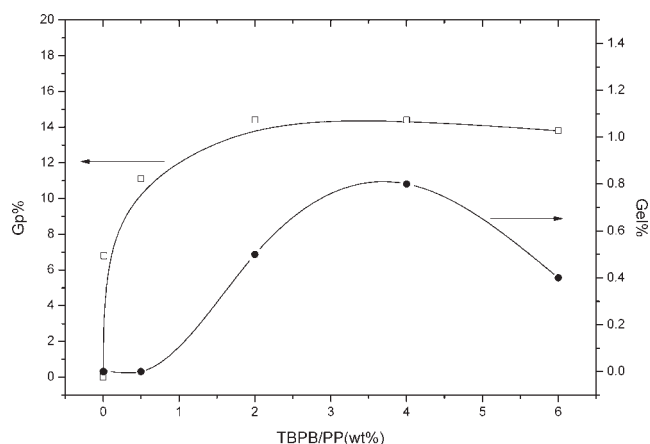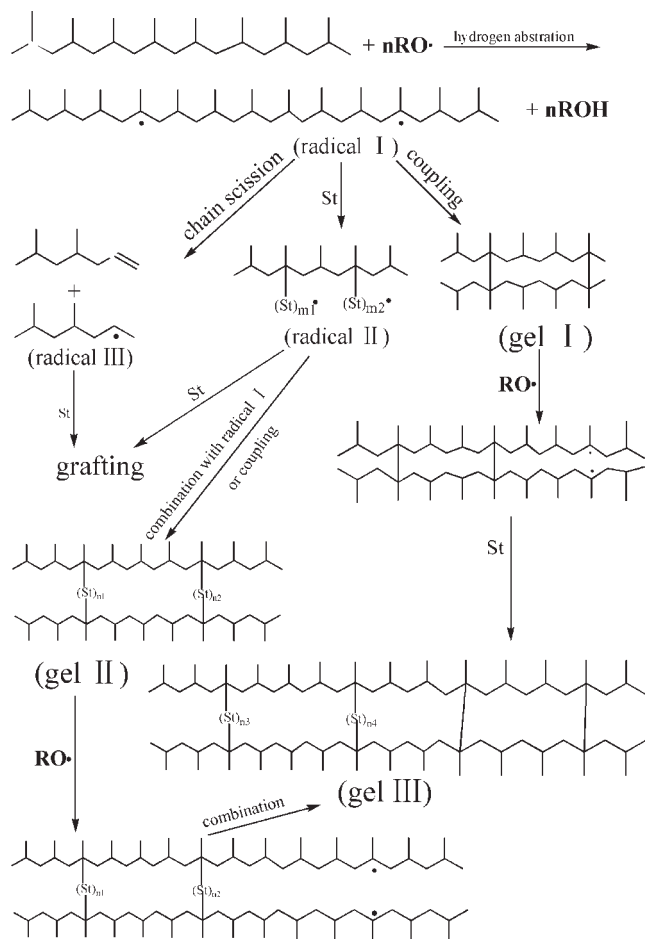

Figure 6 Effect of the initiator concentration on the grafting degree and the content of gel (graft copolymerization of styrene and PP for 2 h at 120°C).

Cat.	Run	St/PP	G_p (%)	Gel (%)
BPO	2122002	0.6	12.5	0
BPO	2122003	0.5	12.2	0

[a] Reaction conditions: BPO/St = 4.0% (wt %); preswelling time: 1 h; reaction time: 2 h; temperature: 120°C.
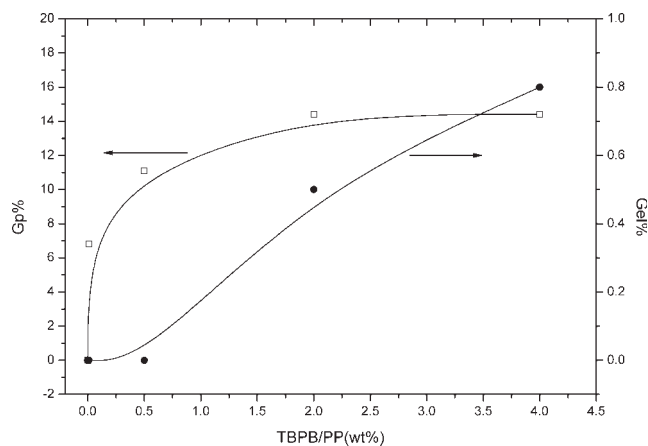

Figure 7 Effect of the initiator concentration on the grafting degree and the content of gel (graft copolymerization of styrene and PPR for 2 h at 120°C).

termination or disproportionate termination of macromolecule free radicals. But the half-life of TBPB is longer than that of BPO at the same temperature. During the period of polymerization, there is always macromolecule free radicals formed, which are initiated by TBPB·. Because of the relatively low concentration of macromolecule free radicals, there is enough time for them to diffuse to meet with styrene monomer with relatively lower couple termination or disproportionate termination. Hence, the grafting degree of the polymerization initiated by TBPB was higher than that initiated by PBO. At the same time,

there was more gel formed in the polymerization initiated by TBPB than that initiated by PBO.

Gelation mechanism in the solid-state graft copolymerization of styrene and spherical polypropylene granules

It has been found that the radical grafting of a monomer onto PP in the presence of a peroxide initiator is often accompanied by severe degradation of the PP backbone. As shown in Scheme 2, it has been well established that a free-radical grafting process starts with the formation of macroradicals (shown as radical I in of Scheme 2) along the PP chains by a so-called hydrogen abstraction mechanism. These macroradicals may subsequently follow two competing pathways. They can either initiate grafting of the styrene monomers to form grafting copolymer or radical II or undergo chain scission to form radical III, which is the main side reaction during the process. Then radical I meets with each other and couples to form gel I. Radical II combines with radical I or couple to form gel II. Subsequently gel I and gel II interact with free-radical to form new style macroradicals, radical IV and radical V. Radical IV interact with styrene monomer and then combine with each other to form gel III. Radical V combine with each other and also form gel III. During the cross-link reaction process, both styrene and free-radical participate into the reaction that discloses the reason of the increment of gel with the increment of styrene consumption or initiator consumption, as shown in Figures 5 and 7.

Scheme 2 The hypothetic cross linking reactions of the radical grafting of St onto PP or PPR by TBPB.

CONCLUSIONS

By free-radical initiated solid phase graft copolymerization, a high level of styrene (3.8–25.2 wt %, based

on the grafting product) can be grafted to PP spherical granules. This reaction utilized no solvent and interfacial agent and can be performed at relatively low temperature (120°C) and at atmospheric pressure. But in the copolymerization some gel formed as a by-product.

By studying the effects of reaction conditions on grafting degree and the gelation, it is found that the amount of the free-radical initiator, the species of the free-radical initiator, feed ratio of the styrene monomer, and the composition of the polyolefin are all the key factors influencing the grafting degree and the gelation. High initiator amount, high feed ratio of styrene, and random copolymer chain structure are favorable to the grafting reaction and the gelation. Under the suitable conditions, grafting degree as high as 25.2 wt % can be reached; however, the content of gel in the grafting product is as high as 15.0 wt %. Both styrene and free radical participate into the cross-link reaction. To reduce the amount of gel efficiently while preserving the graft efficiency, the amount of TBPB should be less than 1 wt % or use BPO as free radical initiator.

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