

Influence of an Annealing Treatment on the Solid-State Grafting of Styrene onto Spherical Isotactic Polypropylene Granules

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ABSTRACT: The main place of solid-state graft polymerization in polypropylene (PP) granules has been believed to be the amorphous region of PP. In this work, the solid-phase morphology of nascent spherical PP (N-PP) granules was found to be markedly changed by an annealing treatment. The crystallinity of PP granules was almost doubled after annealing at 150°C for 12 h, whereas the porosity of the granules was unchanged. Solid-state grafting polymerizations of styrene initiated by *tert*-butyl perbenzoate in both N-PP and annealed polypropylene (A-PP) granules were compared under different reaction conditions. The formation of gel in the product could be completely depressed at a low concentration of the initiator when A-PP granules were used as the matrix and

graft-polymerized at 120°C. Both the introduction of styrene and the annealing treatment of the PP granules led to a depression of polymer degradation in the process of the grafting reaction. However, using A-PP as the matrix caused an increase in the grafting degree at a relatively high concentration of the initiator. A reduction in the amorphous phase in the PP granules was thought to be the main reason for the effects of the annealing treatment on the structure of the graft polymerization products. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1990–1996, 2008

Key words: annealing; graft copolymers; poly(propylene) (PP); polystyrene; solid-state polymerization

INTRODUCTION

Although polypropylene (PP) is prepared on an enormous scale, its applications are limited in several technologically important fields by its low surface energy, lack of reactive groups, and poor compatibility with polar synthetic polymers.^{1–3} In fact, large amounts of PP are used in blends (or alloys), so the effective preparation of PP blends with other kinds of polymers often requires the addition of PP block or graft copolymers to prevent macrophase separation.^{2,4,5} In the past decades, many efforts have been made to prepare functionalized PP copolymers through postfunctionalization of PP by different methods, such as solution grafting and melt grafting of functional monomers onto PP chains.^{5,6} The modification of PP by free-radical-

initiated solid-state grafting^{7–9} has been developed since the 1990s and has attracted much attention because in this kind of process the degradation of PP through a β -scission reaction is greatly depressed in comparison with the melt-grafting process. The use of a solvent in the solution process can also be avoided in solid-state grafting.

In the early 1990s, Montell Co.¹⁰ developed the so-called Hivalloy resins, which were produced by solid-state grafting of vinyl monomers in PP granules synthesized with spherical Ziegler–Natta catalysts. It has been found that nascent polypropylene (N-PP) granules synthesized with a spherical Ziegler–Natta catalyst are in the form of regular spheres (usually 1–5 mm in size) and are highly porous. This kind of solid-phase structure of PP is especially beneficial to the solid-state grafting copolymerization of a second monomer in the granules. The specific external surface area of the spherical granules is much smaller than that of irregular fine PP particles (usually <1 mm in size) produced with conventional nonspherical catalysts, and this lowers the risk of particle coagulation when a high loading of the graft monomer is adopted.

As is well known, grafting reactions initiated by free-radicals are always accompanied by side reactions such as the homopolymerization of the mono-

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mer, degradation, and crosslinking of the matrix polymer.^{9,11} Degradation is often serious in PP grafting reactions, especially in the melt-grafting process, which changes the molecular weight distribution and ultimate properties of the functionalized polymers.^{6,12} Significant degradation will diminish the mechanical properties of the material, and extensive crosslinking will ruin its processability. Consequently, the development of new methods for the grafting polymerization of PP, which can largely depress the degradation and crosslinking, would allow the preparation of functionalized PP with good properties.^{13–15} As it is well known that the solid-state grafting reaction takes place only in the amorphous region of PP,^{8,16} changes in the phase morphology of the PP matrix may influence the grafting reaction. In this work, we increased the crystallinity of N-PP granules through an annealing treatment and prepared styrene (St)-grafted PP through the solid-state grafting of St in the treated PP granules. The influence of the annealing treatment on the grafting reaction was studied.

EXPERIMENTAL

Materials

St was distilled under reduced pressure after being washed with a 10% NaOH solution. *tert*-Butyl perbenzoate (TBPB; Aldrich, Tianjin, China) was used as an initiator without treatment. Spherical N-PP granules with a porosity of about 15% and diameter of 1.4–2.5 mm were kindly provided by Sinopec (Shandong, China). In most experiments, the PP granules were annealed for 12 h at 150°C under an N₂ atmosphere before the grafting copolymerization.

Grafting copolymerization

The grafting reaction was carried out in a Schlenk flask equipped with a mechanical stirrer. About 10 g of PP granules was charged into the reactor, and the flask was then evacuated. A solution of St containing the designated initiator (TBPB) was injected into the reactor by a syringe and then pressurized with nitrogen. Subsequently, the mixture was stirred for 60 min at 60°C and then was quickly heated to the designated temperature under stirring and maintained there for 2 h. A mixture of ethanol and *n*-pentane was then used to stop the reaction and remove the residual St in the granules. The product was dried *in vacuo* for 12 h at 50°C.

Determination of the gel content

About 1 g of the dried graft product was wrapped in a 150-mesh stainless steel mesh and extracted in boiling xylene for over 30 h. Butylated hydroxy tolu-

ene was added as an antioxidant to depress oxidation. After the extraction, residual polymer in the mesh was considered to be gel and separated from the soluble graft copolymer and St homopolymer. The xylene solution was then concentrated in a rotary evaporator. About 100 mL of ethyl acetate was added to the concentrated solution to precipitate the graft copolymer, and the St homopolymer in the remaining solution was separated from the graft copolymer by filtration. The gel content was defined as follows:

$$\text{Gel (\%)} = [w_{\text{gel}} / (w_{\text{gel}} + w_{\text{graft}})] \times 100$$

where w_{gel} is the weight of the gel and w_{graft} is the weight of the graft copolymer.

Measurements

Differential scanning calorimetry (DSC) curves of samples were recorded with a PerkinElmer Pyris 1 DSC instrument (Wellesley, MA) at a constant heating rate of 10°C/min in the temperature range of 50–190°C under a nitrogen atmosphere. The crystallinity percentage of the polymer samples was calculated on the basis of the heat of fusion of 100% crystalline PP, that is, 50 cal/g.¹⁷

Fourier transform infrared spectra of the graft copolymer separated from polystyrene (PS) were recorded with a Bruker Vector 22 spectrometer (Ettlingen, Germany). Thin films of samples were prepared by hot-compression molding between steel plates at 170°C for about 10 s under a pressure of 20 MPa. The grafting degree (GD) is defined as follows:

$$\text{GD (\%)} = [m_{\text{St}} / (m_{\text{St}} + m_{\text{PP}})] \times 100$$

where m_{St} is the weight of styrene in the graft copolymer (including the styrene incorporated into the gel when the gel is formed) and m_{PP} is the weight of polypropylene. GD was calculated according to a calibration equation obtained in our previous work:¹⁸

$$y = -1.60 + 77.05x$$

where y is the ratio of the peak areas of the bands at 700 (assigned to the out-of-plane bending mode of the aromatic C–H) and 808 cm⁻¹ (assigned to the CH₂ and CH rocking of PP)^{19,20} and x is the ratio of the weight of polystyrene to that of polypropylene.

The molecular weight and molecular weight distribution of the graft copolymer were measured with a gel permeation chromatograph (PL-220) at 150°C with 1,2,4-trichlorobenzene as the eluent. The porosity of N-PP and annealed polypropylene (A-PP) granules was measured with a mercury porosimeter (Autopore IV 9500) (Norcross, MA) with an approximately 1-g sample each time.

TABLE I
Thermal Analysis and Porosity Results of N-PP and A-PP

Run	Annealing temperature (°C)	Onset temperature (°C)	Melting peak (°C)	ΔH (J/g)	Crystallinity (%)	Porosity (%)
1	—	119.2	164.6	40.8	19.5	15.2
2	110	120.6	164.9	52.6	25.2	14.3
3	130	134.4	164.0	62.8	30.1	15.5
4	150	153.6	164.8	79.1	37.9	15.8

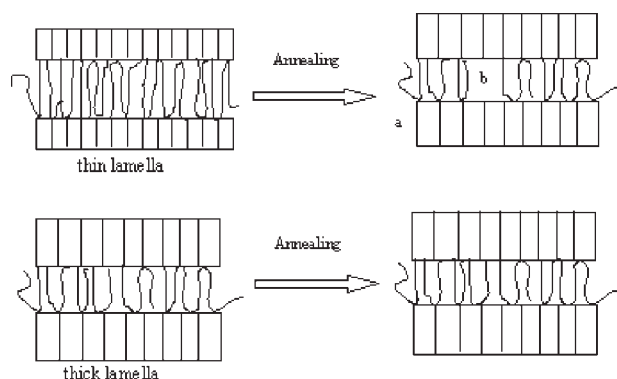
ΔH , enthalpy of fusion.

RESULTS AND DISCUSSION

Annealing treatment of N-PP granules

As isotactic PP is a semicrystalline polymer, its phase morphology will be affected by the thermal history. In this work, three batches of the same N-PP granules were annealed at 150, 130, and 110°C for 12 h. This demonstrated that there were distinct differences between N-PP and A-PP. The results of thermal analysis are listed in Table I. The range of the melting peaks of the PP annealed at 150°C is much narrower than that of N-PP. The crystallinity of A-PP is higher than that of N-PP and increases with the annealing temperature. The PP annealed at 150°C has crystallinity almost double that of N-PP. However, as the annealing temperature of 150°C is still lower than the melting peak temperature of N-PP (ca. 165°C), the morphology of PP granules was almost intact after the annealing treatment because the porosities of the N-PP and A-PP granules were almost the same (see Table I).

The changes in the crystalline morphology after the annealing treatment are schematically depicted in Scheme 1. The annealing treatment has a remarkable influence on the morphology and lamellar size of the PP matrix, leading to the increase in the crystallinity of the PP matrix through melting and recrystallization of the poorly crystallized region in N-PP granules (as shown in Scheme 1). Then, the

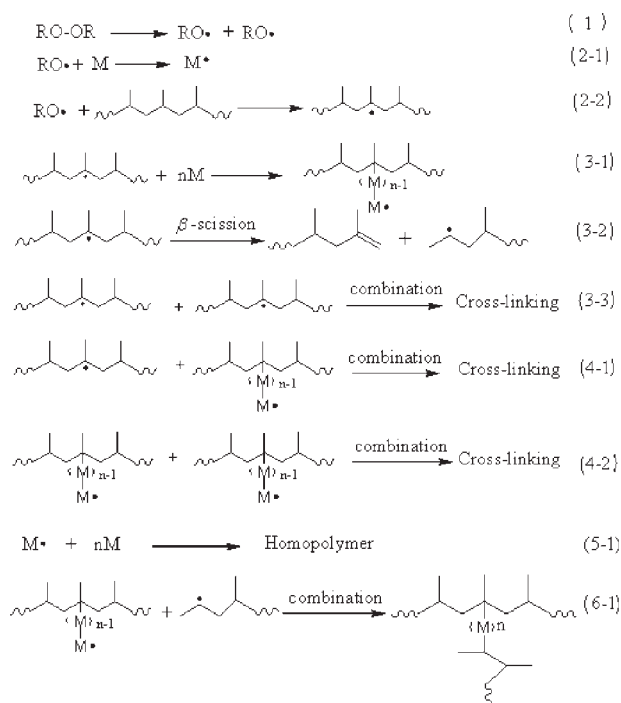


Scheme 1 Simplified model for the influence of annealing treatment on the phase morphology: (a) crystalline lamellae and (b) amorphous region.

volume percentage of the amorphous region becomes much lower. Because the amorphous region of PP is the main place for grafting copolymerization,^{8,16} changes in the solid-phase morphology of the matrix polymer may influence the result of the grafting reaction. Therefore, the PP granules annealed at 150°C were used as the matrix of solid-state grafting polymerization in the following experiments because they had differed the most from N-PP with respect to the crystalline structure. Through the comparison of grafting polymers from A-PP with those from the N-PP granules, the influence of PP's crystalline structure on the polymerization behaviors and structures of the products can be discovered.

Formation of gel

Possible reactions in the process of solid-state grafting polymerization initiated by free radicals are illustrated in Scheme 2. As shown in Scheme 2, grafting reactions initiated by free radicals are always accom-



Scheme 2 Possible reactions in the process of solid-state grafting polymerization initiated by free radicals.

panied by side reactions, among which degradation (3-2) and crosslinking (3-3, 4-1, and 4-2) of the matrix polymer are the main ones. Crosslinking will lead to the formation of gel. According to the literature,^{8,21} reaction conditions such as the reaction temperature, amount of the monomer, and initiator concentration will affect the formation of gel in the solid-state grafting polymer. As shown by a DSC analysis of the PP samples, the main part of the melting peak of N-PP begins at about 130°C, and that of PP annealed at 150°C begins at over 150°C. This means that the PP granules will be in the solid state at 130°C or a lower temperature, and grafting reactions at these temperatures still belong to solid-state grafting.

In this work, we first studied the effect of the initiator concentration on gel formation at different reaction temperatures, namely, 130, 120, 110, and 100°C. In a wide range of TBPB concentrations (0–6.2 wt %; weight percentage ratio of TBPB to PP) at 110 and 100°C, no gel formed in the obtained products. On a further increase in the reaction temperature (120 and 130°C), gel was formed in the obtained products. This experimental result can be explained as follows: the increase in the reaction temperature facilitates the decomposition of the initiator and leads to the increase in the free-radical concentration,²¹ resulting in crosslinking and the formation of gel.

Figure 1 shows the variation of the gel content with the TBPB concentration at reaction temperatures of 130 and 120°C with N-PP granules and A-PP granules as the matrix. For the grafting reaction at 130°C, the gel content of products based on N-PP and A-PP gradually increased with the TBPB concentration. When the TBPB concentration was lower than 0.5 wt %, there was almost no gel formed. At a higher range of TBPB concentrations, there was little difference in the gel content in the samples. On the other hand, when the temperature of the grafting reaction was reduced to 120°C, the gel content also increased with an increase in the TBPB concentration. However, the difference in the gel content between the samples with N-PP and A-PP granules as the matrix was more remarkable. As shown in Figure 1(b), with N-PP granules as the matrix, the grafted products already contained gel when the TBPB concentration was higher than 1.0 wt %. However, there was no gel formed until the concentration of TBPB was higher than 2 wt % with A-PP granules as the matrix. According to these experimental results, it may be concluded that gel formation can be depressed at a relatively low concentration of TBPB. The depression of gel formation is more notable at lower temperatures.

As these parallel reactions were conducted under the same conditions, the difference in gel formation should be attributed to the change in the phase mor-

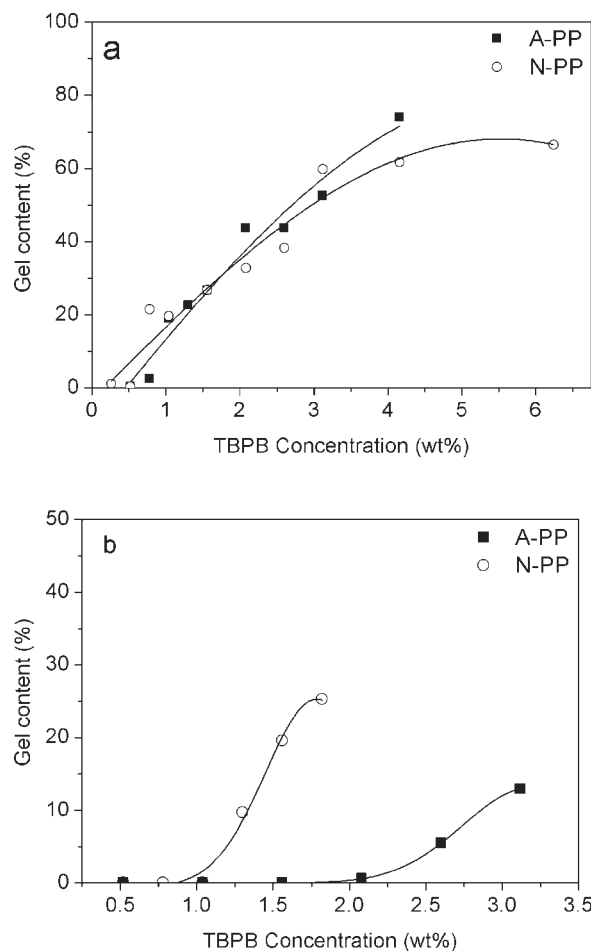


Figure 1 Variation of gel content with initiator concentration at grafting polymerization temperatures of (a) 130 and (b) 120°C with N-PP and A-PP granules as matrices, respectively [reaction time = 2 h, St/PP (w/w) = 45.5%].

phology with the annealing treatment. At a relatively low initial concentration of TBPB, the amount of initiator is low for the matrix of N-PP and A-PP. As the size of the amorphous domains in N-PP is larger than that of A-PP, the average number of initiator molecules in a single amorphous region of N-PP will be higher than that of A-PP. This will increase the probability of crosslinking, leading to more gel formation in the former matrix. However, at a high initial concentration of TBPB, the amorphous region in both N-PP and A-PP can absorb plenty of the initiator, and the number of macroradicals in both matrices will be high enough to induce crosslinking. Therefore, there is little difference in their gel formation. For the remarkable difference in gel formation at 120 versus 130°C, besides the influence of the morphology, the difference in the polymer chain mobility at different reaction temperatures should also be considered. It is likely that the lower mobility of chains at 120°C makes their crosslinking reactions more sensitive to changes in the radical concentration.

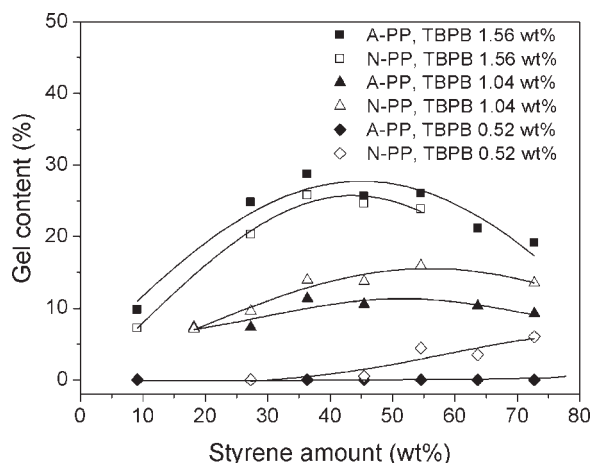


Figure 2 Variation of gel content with St concentration at different concentrations of TBPB (reaction temperature = 130°C).

In a previous work,²² we found that the grafting monomer St takes part in the formation of gel. Therefore, the amount of St is also a factor that influences the formation of gel. Figure 2 shows the variation of the gel content with the concentration of St in grafting reactions conducted at 130°C. The gel content in the samples with N-PP and A-PP as the matrix first increased and then dropped with an increase in the St concentration. The trend of the gel content with the St amount can be understood because St takes part in the formation of the cross-linking structure (4-1 and 4-2). At a low concentration of St, it might be assumed that most of the primary radicals could effectively attack the PP chain and form alkyl radicals; then, the St unit is grafted onto the alkyl radicals to form more stable styryl radicals. This facilitates the combination reactions among macroradicals, leading to gel formation. With the increase in the St concentration, longer PS side chains also may be formed, which can reach other PS radicals or PP radicals more easily to form cross-links, which also result in an increase in the gel content. However, with the St concentration further increasing, there is an excess of monomer competing for the initiator, leading to the homopolymerization of St (5-1) and a decrease in the gel content. In comparison with the gel formation with the St concentration at three levels of TBPB concentration based on N-PP and A-PP, some discrepancy also exhibits. When the TBPB concentration was 1.56 wt %, there was little difference in the gel content in the samples. With a decrease in the TBPB concentration to 1.04 wt %, the gel content in the samples based on A-PP, however, was lower than that in the samples based on N-PP with an initial St concentration higher than 30 wt %. The gel content that formed at 1.56 wt % TBPB was much higher than the gel content that formed at 1.04 wt % TBPB, and the maxi-

imum level of gel content appeared at a lower St concentration in comparison with the reactions with 1.04 wt % TBPB. With a further decrease in the TBPB concentration to 0.52 wt %, there was no gel formed in the samples with A-PP as the matrix, but there was still a small amount of gel that formed in the samples with N-PP as the matrix when the St concentration was higher than 45 wt %. In summary, the influence of the St concentration on gel formation with different levels of TBPB is consistent with the former experimental results showing that gel formation is depressed by the use of A-PP granules as the matrix at a relatively low concentration of TBPB. The difference should also arise from the change in the phase morphology after the annealing treatment.

Influence of the reaction conditions on GD

Figure 3 shows the variation of GD with the initiator concentration at different reaction temperatures. GD increased with the increase in the reaction temperature, and GD in all reactions first increased with the increase in the TBPB concentration and then dropped. This trend can be explained by the fact that the number of free radicals generated increases with the temperature and/or initial TBPB concentration increasing, and this results in the increase in grafting. However, at a TBPB concentration higher than a certain level, there would be a tendency for the chain transfer to the monomer to be more pronounced, facilitating the homopolymerization of St and a decrease in GD. In the grafting reactions carried out at 100 and 110°C, GD of the samples with A-PP as the matrix was much lower than that for the grafting reactions carried out at 120 and 130°C, and this was undesirable. Therefore, a comparison of GD values for the products based on N-PP and A-PP was made only for reaction temperatures of 120

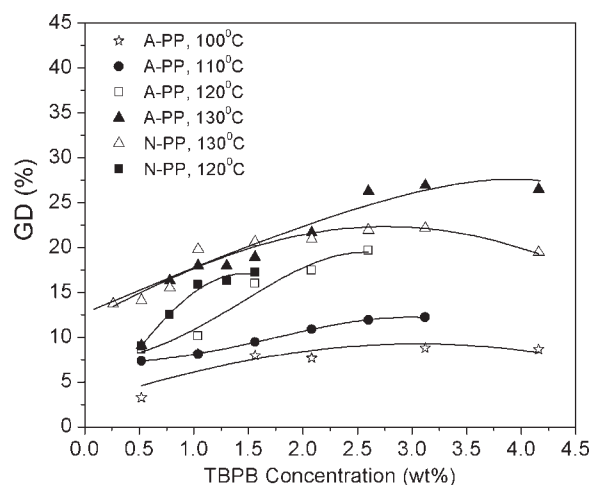


Figure 3 Variation of GD with TBPB concentration at different reaction temperatures (St/PP = 45.5 wt %).

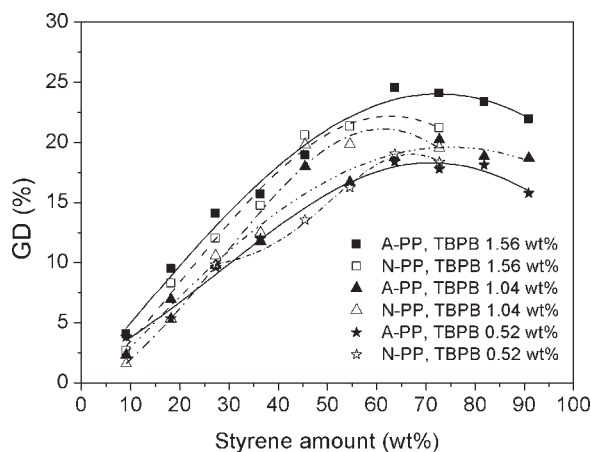


Figure 4 Variation of GD with St concentration at different concentrations of TBPB (reaction temperature = 130°C).

and 130°C. In the studied range of initiator concentrations, GD of the samples prepared at 120°C with N-PP as the matrix was higher than that of samples with A-PP as the matrix. However, GD at 130°C showed a different tendency. At a low concentration of the initiator (<2 wt %), the GD values of the samples based on N-PP and A-PP were almost the same. At a high concentration of TBPB, GD of samples with N-PP as the matrix was inversely a little lower than that of samples based on A-PP. It can be hypothesized that, as the amorphous domains in A-PP are smaller than those in N-PP, PS branches in the former may tend to stretch out from the amorphous domains and couple with the PS chain radicals formed in the voids of PP granules, forming longer PS branches. This means that GD at a low level of TBPB shows little difference, although at a high level of TBPB, samples based on A-PP exhibit higher GD than samples based on N-PP.

Figure 4 shows the variation of GD with the concentration of St at three levels of TBPB concentration at 130°C. As shown in Figure 4, the GD values of the samples based on N-PP or A-PP all increased with the St concentration at first and then leveled off at a

high St concentration. However, the GD values of samples based on N-PP and A-PP at the same level of TBPB concentration showed little difference. This experimental result can be explained as follows. As the concentration of St increases up to a certain level, the amount of St in the grafting chains increases, and this results in an increase in GD. However, on a further increase in the St concentration, there is excess St competing for the initiator, facilitating the St-homopolymerization and leading to a decrease in GD.

Degradation of the polymer

As shown in Scheme 2, β -scission of alkyl free radicals is the main reaction resulting in the degradation of the polymer. In this work, we also studied the influence of the annealing treatment on the molecular weight of the grafting product through two series of parallel experiments in which all the products contained no gel. The results of the gel permeation chromatography analysis are shown in Table II. The number-average molecular weights (M_n 's) of the products all decreased in comparison with that of the PP feedstock, and this implied that degradation occurred in all these grafting reactions. However, the weight-average molecular weights (M_w 's) of samples 2 and 5 prepared with N-PP as the matrix were lower than that of the original PP, but the M_w values of samples 4 and 7 prepared with A-PP as the matrix were higher than that of N-PP. Moreover, samples 3 and 6 were also based on A-PP but with no or a small amount of St. Their M_w values exhibited a different magnitude of decrease in comparison with those of N-PP and samples 4 and 7. In particular, the reduction of M_w in sample 3 was quite remarkable; it contained no St as the graft monomer. This means that, without St, the degradation is very serious with A-PP as the matrix. From these experimental results, we can draw the conclusion that either the annealing treatment of N-PP or the introduction of St can lead to the depression of the degradation of PP chains in the grafting copolymerization pro-

TABLE II
Molecular Weight of the Grafting Products Based on N-PP and A-PP

Run	Matrix	Reaction temperature (°C)	TBPB/PP (wt %)	St/PP (wt %)	$M_n \times 10^{-3a}$	$M_w \times 10^{-3a}$
1	N-PP	—	—	—	66	298
2	N-PP	130	0.52	45.5	50	247
3	A-PP	130	0.52	0	41	195
4	A-PP	130	0.52	45.5	55	310
5	N-PP	120	0.52	63.6	33	261
6	A-PP	120	1.56	9.1	46	281
7	A-PP	120	1.56	63.6	60	318

^a Molecular weight of the grafting products measured by GPC. The St homopolymer in the products was removed, as described in the Experimental section.

cess. This result can be explained in two ways. On the one hand, the depression of degradation can be ascribed to the decrease in the amorphous volume ratio in the PP matrix after the annealing treatment, resulting in a decrease in chains that can be attacked by radicals. Also, because the styryl free radical is much more stable than the alkyl free radical, further β -scission of the alkyl free radical is reduced, and this leads to the decrease in degradation. On the other hand, the increase in M_w for products based on A-PP can be explained as follows: a reduction in the size of the amorphous regions may increase the probability of combination reactions between PP \cdot and/or PP-g-PS \cdot radicals in the amorphous regions and PS \cdot radicals located in the voids, and longer branches are formed. Because of these combination reactions, another expectable result is the formation of long-chain-branch structures similar to those formed in the process of electron-beam irradiation of PP^{23,24} when the crosslinking is not serious enough to form gel.

CONCLUSIONS

The solid-phase morphology of spherical N-PP granules can be effectively changed by an annealing treatment. The crystallinity of PP granules can be greatly increased by annealing at 110–150°C for 12 h, with the granule porosity kept unchanged. In the solid-state grafting polymerization of St onto PP, the formation of gel in the product can be completely depressed at a low concentration of the initiator when A-PP granules are used as the matrix and graft-polymerized at 120°C. Both the introduction of St and an annealing treatment of the N-PP granules lead to depression of polymer degradation in the process of the grafting reaction.

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