Macromolecules **2001,** *34,* 2089−2094

Well-Defined Polystyrene Grafted to Polypropylene Backbone by "Living" Radical Polymerization with TEMPO

Youhei Miwa,[†] Katsuhiro Yamamoto,[†] Masato Sakaguchi,[‡] and Shigetaka Shimada*,[†]

Department of Material Science & Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan, and Ichimura Gakuen College, 61 Uchikubo, Inuyama, 484-8503, Japan

Received August 17, 2000

ABSTRACT: A stable free radical (2,2,6,6-tertamethylpiperidinyl-1-oxy, TEMPO) polymerization technique was applied to a graft polymerization of styrene (ST) to polypropylene (PP). PP peroxides produced by γ-irradiation (7.2, 12, and 35 kGy) in air were used as macromolecular initiators for grafting. Grafted polystyrene (PS_{graft}) was cleaved from the main PP chain by reaction with trifluoroacetic acid. The molecular weight (M_n) and polydispersity of the PS_{graft} and the free (nongrafted) polystyrene (PS_{free}) were determined by GPC. These PS's have almost the same M_n (nearly theoretical M_n) and narrow polydispersity. Nitroxide-terminated PS grafted to the PP was chain extended by sequential activation of the dormant chain ends in the presence of additional ST monomer. The polydispersity of the extended PS_{graft} remained narrow. A controlled random graft copolymer of PP with ST and *n*-butyl methacrylate was also synthesized using this technique.

Introduction

Chemical modification of polyolefins[1] (e.g., polyethylene (PE) and polypropylene (PP)) has long been a scientific challenge. This is an important research area for industry because it serves as a route to expand polyolefin applications into polymer blends and composites. Among polyolefins, isotactic PP is the most desirable but also the most difficult to modify. New catalysts were recently discovered for the polymerization of olefins to produce polymers with defined regio- and stereochemistry.[2,3] However, their function is limited, especially where adhesion or compatibility with polymers, metal, or glass is desired. Although block or graft copolymers can be used to improve the compatibility of immiscible polymer,[4−6] a primary method for the synthesis of olefin-based polymers is based on transition metal catalysts (Ziegler−Natta and metallocene), which do not readily yield block and graft copolymers with other monomers.[7]

For a better understanding of the compatibilization process and the influence of molecular parameters of the compatibilizer on morphology and mechanical properties of the blends, well-defined structures must be used as compatibilizing agents.[8] Recently "living" polymerizations, including anionic[9] and cationic[10] polymerization, have been used to obtain graft copolymers with well-controlled structures.[11−19] Much attention also has been focus on controlled grafting from a solid surface.[20−23] Besides the stringent conditions required for ionic polymerizations, e.g., complete absence of water, they are limited by the scope of monomers that can be used. In contrast, controlled free radical polymerizations combine ease of polymerization and a large number of monomers capable of reaction. Chung has developed an interesting approach to polyolefin/poly(methyl methacrylate) graft copolymers by careful introduction of oxygen to a borane-functionalized polyolefin.[11−14] Hawker reported a synthesis of PP-*graft*-PS by a combination of metallocene and stable free radical polymerization (SFRP), in which the molecular weight (M_n) and polydispersity were controlled.[15] Ying reported a synthesis of ethylene−propylene−diene terpolymer/poly(methyl methacrylate) graft copolymers with well-defined structure by atom transfer radical polymerization (ATRP).[16]

We previously reported a synthesis of PP-*g*-PS by a combination of radiation-induced graft and SFRP techniques.[17] However, detailed characterizations of the grafted PS were pending. This paper reports a controlled graft polymerization of ST and a controlled random-graft polymerization of ST and *n*-butyl methacrylate to a commercially available PP by the SFRP technique and also reports characteristics of the grafted chains.

Experimental Section

Material. Isotactic PP ($M_v = 400$K) was obtained from Mitsubishi Chemical Co., Ltd., dissolved in boiled toluene, cooled to room temperature, filtered, and dried in a vacuum. This procedure was repeated three times. Styrene (Reagent, Nacalai Tesque Co., Ltd.) and *n*-butyl methacrylate (BMA) (Extra Pure Reagent, Tokyo Chemical Co., Ltd.) were distilled under reduced pressure. Benzoyl peroxide (Reagent, Nacalai) was dissolved in chloroform, precipitated into methanol, and recrystallized. TEMPO (99%) and trifluoroacetic acid (99%) were obtained from Aldrich Chemical Co., Ltd., and used as received. Tetrahydrofuran, methanol, toluene, and chloroform were obtained from Nacalai Tesque Co., Ltd. (Extra Pure Reagent), and used as received.

Gel Permeation Chromatography. The M_n and polydispersity of the PS_{graft}, PS_{free} and the random copolymer were determined by gel permeation chromatography (GPC) in THF (1 mL/min) at 313 K on four polystyrene gel columns (Tosoh TSK gel GMH (beads size is 7 μm), G4000H, G2000H, and G1000H (5 μm)) that were connected to a Tosoh CCPE (Tosoh) pump and a ERC-7522 RI refractive index detector (ERMA Inc.). The columns were calibrated against standard polystyrene (Tosoh) samples.

NMR Measurement. Nuclear magnetic resonance was performed on a Bruker AVANCE 200 spectrometer using deuterated chloroform at 25 °C with tetramethylsilane as an internal reference.

[†] Nagoya Institute of Technology.

[‡] Ichimura Gakuen College.

10.1021/ma001449f CCC: $20.00

Grafting Ratio. The grafting ratio was defined as follows:

$$\text{grafting ratio (wt \%)} = (W_{\text{graft}} - W_{\text{PP,ini}})/W_{\text{PP,ini}} \times 100$$

Here W_{graft} is weight of the sample after grafting, and $W_{\text{PP,ini}}$ is the initial weight of the irradiated the PP. The grafting ratio was estimated by the FT-IR (IMPACT400D, Nicolet Instrument Co.; KBr) method because of a large experimental error involved in measuring a weight increase after grafting. Grafting ratios were calculated from the ratio of the IR absorbance of the PS (700 cm^{-1}) to that of the PP (810 cm^{-1}), where the absorption of 700 cm^{-1} is assigned to the CH bending vibration of a PS benzene ring and that of 810 cm^{-1} is assigned to the CH_2 and CH rocking vibration of the PP.[24] In advance, some mixtures of PS and PP were prepared to make a calibration curve of the grafting ratio (weight ratio of the mixture) against the absorbance ratio.

"Living" Radical Graft Polymerization of Styrene to Polypropylene with TEMPO. The PP powder was ^{60}Co γ-irradiated (the total doses were ca. 7.2, 12, and 35 kGy at a dose rate of 0.10, 0.17, and 0.20 kGy/h, respectively) in air. The typical grafting reaction is as follows: The γ-irradiated PP (0.2 g, 12 kGy), ST (1.50 mL, 13.0 mmol), and TEMPO (4.05 mg, 2.59×10^{-2} mmol) were placed in a glass ampule. After degassing by a freeze−pump−thaw method, the ampule was sealed in a vacuum. The sealed ampule was heated at 368 K for 5 h, and then the polymerization was carried out at 398 K. During polymerization, the PP powder became completely soluble in ST, the solution became transparent and colorless, and its viscosity increased substantially. The reactions were terminated by quenching to liquid nitrogen temperature. Percent conversions of ST were calculated from the weight of the reaction mixture which included PP-*g*-PS and PS_{free} after residual ST monomer was completely evacuated in a vacuum at 353 K for 24 h. After that, the sample was immersed into THF to extract PS_{free} from the grafted PS. The PS_{free} was precipitated from THF solution into methanol and dried in a vacuum at 343 K for 24 h. The monomer conversion was 20.9%, and the grafting ratio of PP-*g*-PS was 18.6 wt % after polymerizing for 9 h. The sample of the PS grafted to PP was washed by a Soxhlet extraction with THF for 24 h and dried in a vacuum at 343 K for 24 h. Although the further Soxhlet extraction for 24 h was carried out, there was no change in a grafting ratio before and after the second extraction.

Cleavage of the Polystyrene Grafted to Polypropylene. The PS_{graft} was cleaved from the PP main chain by reaction with trifluoroacetic acid. As a typical reaction, the sample of the PS grafted to PP (grafting ratio = 24.1 wt %, ca. 0.2 g) in trifluoroacetic acid (1.5 mL) and toluene (1.5 mL) mixture was allowed to stand at room temperature for a couple of days and then was evaporated in a vacuum. The dried sample was immersed into THF, and the PS_{graft} was extracted; thus, the PS_{graft} and the PP main chain were separated. The extracted PS_{graft} was precipitated in methanol, filtered, and dried in a vacuum. The yield of the PS_{graft} was ca. 1 mg.

Controlled Random Graft Copolymerization of Styrene and *n*-Butyl Methacrylate to PP. As a typical example, the ^{60}Co γ-irradiated (the total doses were ca. 7.2 kGy at a dose rate of 0.10 kGy/h) PP (0.4 g), ST (3.20 mL, 27.7 mmol), BMA (0.8 mL, 5.06 mmol), benzoyl peroxide (20.3 mg, 8.38×10^{-2} mmol), and TEMPO (17.1 mg, 0.11 mmol) were placed in an ampule. After degassing by a freeze−pump−thaw method, the ampule was sealed in a vacuum. The sealed ampule was heated at 368 K for 5 h, and then the polymerization was carried out at 398 K. The reactions were terminated by quenching to liquid nitrogen temperature. Percent conversions of monomer were calculated from the weight of the reaction mixture after residual monomers were completely evacuated in a vacuum at 353 K for 24 h. The conversion was 25.9% after polymerizing for 5 h. In this case, benzoyl peroxide was added as a free initiator to control the polymerization. This reaction system also resulted in yielding free (nongrafted) copolymer. The grafted copolymer and the free copolymer were immersed into THF to extract free copolymer from the grafted copolymer. The free copolymer was precipitated from THF solution into methanol and dried in a vacuum at 343 K for 24 h. The sample of the random copolymer grafted to the PP was washed by a Soxhlet extraction with THF for 24 h and dried in a vacuum at 343 K for 24 h. The graft polymerization of poly(ST-*ran*-BMA) to PP was identified by FT-IR (1725 cm^{-1} for carbonyl, 700 cm^{-1} for phenyl ring). The grafted copolymer was cleaved from the PP main chain by reaction with trifluoroacetic acid.

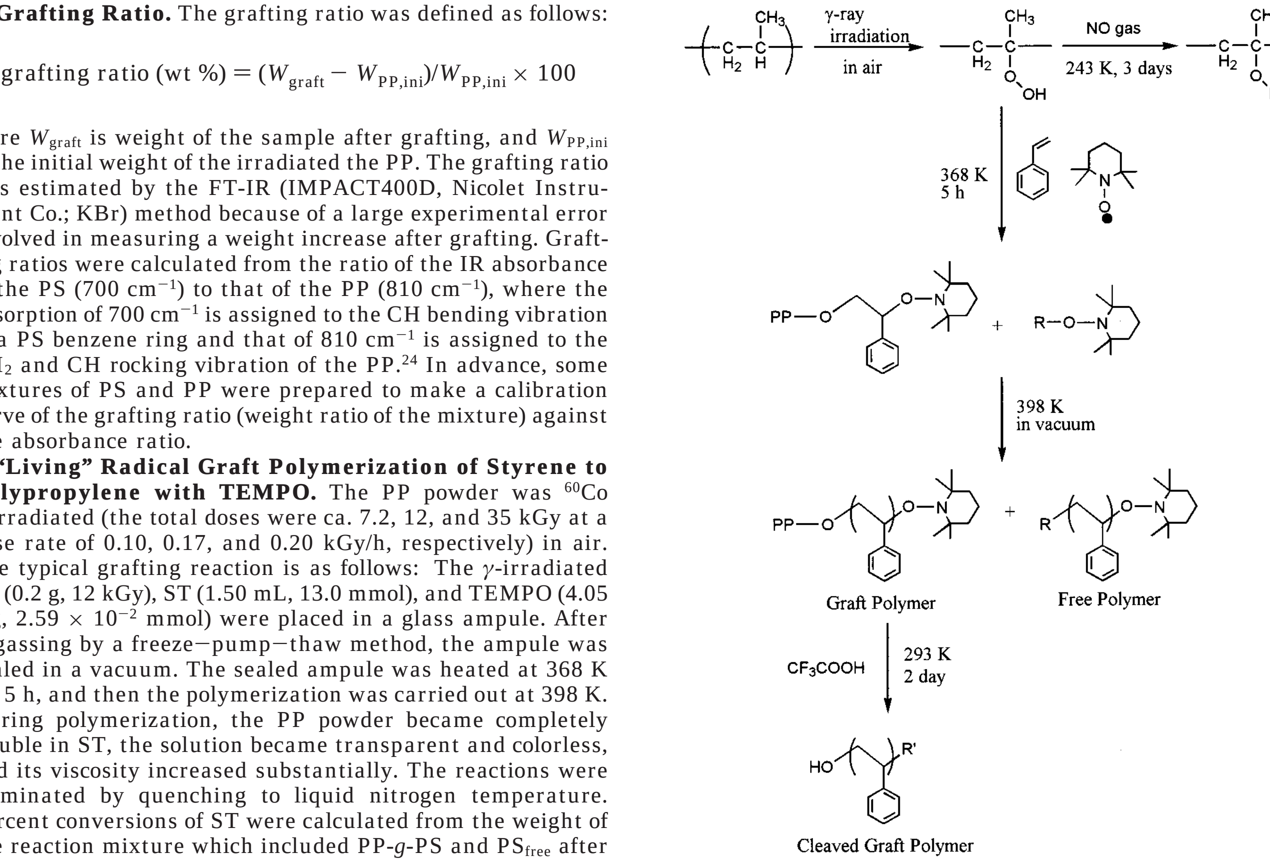

Figure 1. Reaction scheme of graft polymerization of styrene to PP. The most likely end structures R are groups generated through Diels−Alder reaction of ST and hydroxy group generated by decomposition of the PP-peroxide. The most likely end group R′ of the cleaved PS_{graft} is a hydroxy and/or TEMPO moiety.

Chain Extension of PS_{graft}. The PP-*g*-PS (grafting ratio = 6.1 wt %, $M_{\text{n,graft}} = 1.42 \times 10^4$, $M_{\text{w}}/M_{\text{n}} = 1.16$, 0.4 g), ST (3 mL, 25.92 mmol), TEMPO (8.10 mg, 5.19×10^{-2} mmol), and benzoyl peroxide (6.30 mg, 2.60×10^{-2} mmol) were placed in an ampule. After degassing by a freeze−pump−thaw method, the ampule was sealed in a vacuum. The sealed ampule was heated at 368 K for 3.5 h, and then the polymerization was carried out at 398 K. The reactions were terminated by quenching to liquid nitrogen temperature. The monomer conversion was 14%, and the grafting ratio increased to 10.5 wt % after polymerizing for 5 h.

Results and Discussion

"Living" Radical Graft Polymerization Behavior of Styrene to PP. Benzoyl peroxide has generally been used as the initiator in SFRP, with TEMPO added to control the polymerization. In this work, PP peroxides produced by γ-irradiation in air were used as macromolecular initiators of grafting instead of benzoyl peroxide. γ-Irradiation to PP in air produces mainly peroxides,[25] which can effectively initiate radical polymerization.[26] Figure 1 shows a reaction scheme for the grafting. Reaction of the peroxide with nitrogen mon-

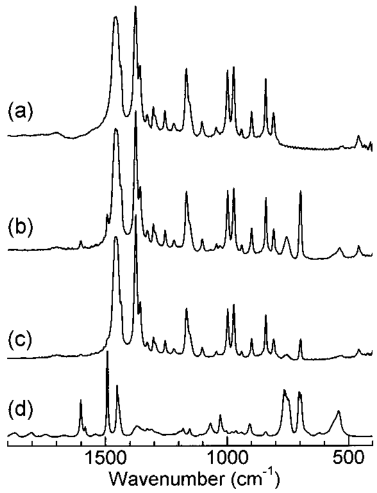

Figure 2. FT-IR spectra of irradiated PP (12 kGy) (a), PP-*g*-PS (b), PP-*g*-PS after cleaving (d), and cleaved PS$_{graft}$ (d).

oxide results in a nitrate. Carlsson et al.[25] quantified the amount of nitrates (1276 and 860 cm^{-1} for primary, 1276 and 867 cm^{-1} for secondary, and 1302, 1290, and 860 cm^{-1} for tertiary) by FT-IR and then quantified the peroxides. We estimated the concentration of PP peroxides by their method. The concentrations of the peroxides for the PP samples with total doses of 7.2, 12, and 35 kGy were 1.17, 1.78, and 2.35 × 10^{-5} (mol/g (PP)), respectively. The molar ratio of PP-peroxide:ST:TEMPO was 1:5500:11 for PP sample with total dose of 7.2 kGy, for example. If the concentration of TEMPO were comparable with that of the peroxides, the former was too small to control the grafting. Thus, a large amount of TEMPO compared to that of PP-peroxide must be introduced. In a typical SFRP with benzoyl peroxide and TEMPO, the concentration of growing polymer is determined not by the concentration of benzoyl peroxide but by that of nitroxyl radical.[27] The excess of TEMPO molecules to the PP-peroxides is consumed by free radicals generated through Diels–Alder reaction autopolymerization[28,29] between two molecules of ST and by hydroxy radicals from homolytic cleavage of PP-peroxides. This reaction system results in PS$_{free}$ simultaneously with PS$_{graft}$ in our system.

Figure 2 shows FT-IR spectra of irradiated PP (a) and PP-*g*-PS (b). The peak of 700 cm^{-1} was clearly observed, indicating the grafting of ST. Figure 3 shows the relationships between the grafting ratio and the reaction time in the presence and absence of TEMPO. TEMPO suppressed the grafting rate considerably and controlled the grafting ratio of ST. The grafting ratio increased with increasing irradiation dose. No grafting was obtained for the nonirradiated PP. The increase in the grafting ratio with increasing irradiation dose is due to the higher concentration of PP peroxide.[17]

To further understand the characteristics of the grafted PS prepared by TEMPO-mediated graft polymerization, the PS$_{graft}$ was cleaved with trifluoroacetic acid from the PP-*g*-PS (irradiation dose of 12 kGy) at their point of attachment. The reaction cleaved the ether group. FT-IR spectra c and d in Figure 2 were the PP-*g*-PS after cleaving and cleaved PS$_{graft}$, respectively. The cleaved PS$_{graft}$ had a hydroxy end group (3.6 ppm, HO–C*H*$_2$–). The decrease in peak intensity of 700 cm^{-1} in spectrum c and NMR result indicated successful cleaving reaction. The cleaved PS$_{graft}$ then analyzed by GPC. Figure 4 shows the M_n and M_w/M_n of the cleaved PS$_{graft}$.

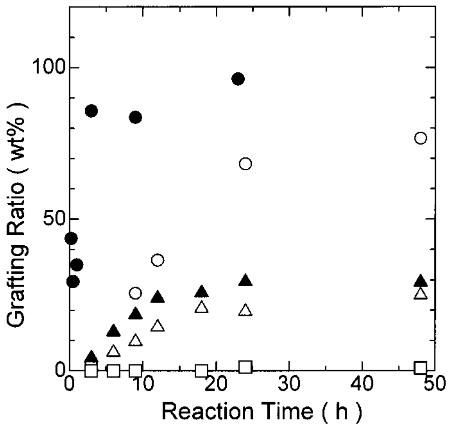

Figure 3. Grafting ratio of styrene to isotactic polypropylene vs graft polymerization time: irradiated PP (35 kGy) in the absence of TEMPO (solid circles); irradiated PP with 35 kGy (open circles), 12 kGy (solid triangles), 7.2 kGy (open triangles), and nonirradiated PP (open squares) in the presence of TEMPO. Irradiated PP = 0.2 g, ST = 13 mmol, and TEMPO = 2.59 × 10^{-2} mmol.

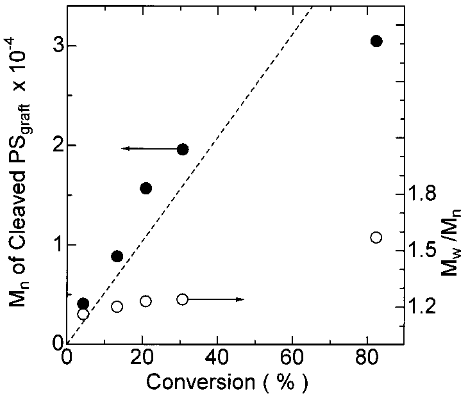

Figure 4. M_n and M_w/M_n of the cleaved PS$_{graft}$ prepared with irradiated PP (12 kGy, 0.4 g), TEMPO (2.59 × 10^{-2} mmol), and ST (13 mmol) at 398 K. The broken line indicates the theoretical M_n.

The M_n of the PS$_{graft}$ is proportional to the percent conversion of ST, and the polydispersity is narrow. Moreover, ln([M]$_0$/[M]) increased linearly with polymerization time, and the M_n of the PS$_{graft}$ is close to the theoretical value expected from the molar ratio of styrene to TEMPO, indicating that the radical graft polymerization of styrene from the γ-irradiated PP is a controlled process. The M_n of free and grafted PS deviated from the expected M_n at higher conversion, indicating poorly controlled. The reaction system was heterogeneous, and the termination occurred. The conversion, grafting ratio, weight ratio of PS$_{free}$ to PS$_{graft}$, M_n, and M_w/M_n of the PS$_{graft}$ and the PS$_{free}$ are listed in Table 1 for samples with irradiation dose of 12 kGy. The weight ratio was almost constant at lower conversion but increased at higher conversion. The same tendency was obtained for samples with irradiation dose of 7.2 kGy. (The ratio increased from 11 for 3 h to 23 for 48 h.) The weight ratio of PS$_{free}$ to PS$_{graft}$ for samples with 35 kGy was constant through grafting (the ratio = 5.6 ± 0.7). Since each concentration of grafts along the PP chain calculated from the grafting ratio and M_n of PS$_{graft}$ was almost constant (as shown later in Figure 6), the increase in the weight ratio showed an increase in the concentration of PS$_{free}$ (not propagation end). When some dead PS (graft and free) was generated as grafting advanced, new PS$_{free}$ can be regenerated by autopoly-

Table 1. Stable Free Radical Polymerization of Styrene to PP (Irradiation Dose of 12 kGy)

grafting time (h)	conv (%)	grafting ratio[a]	weight ratio[b]	$M_n{}^c \times 10^{-3}$ PS cleaved[d]	$M_w/M_n{}^c$	$M_n{}^c \times 10^{-3}$ PS free	$M_w/M_n{}^c$
3	4.3	4.3	5.9	4.07	1.16	3.38	1.27
6	13.3	12.8	6.0	8.86	1.20	8.12	1.18
9	20.9	18.6	6.6	15.7	1.23	12.9	1.20
12	30.7	24.1	7.6	19.6	1.24	17.4	1.24
48	82.4	29.3	18.0	30.5	1.57	27.1	1.37

[a] Percent ratio of weight of PS_{graft} to PP. [b] Weight ratio of PS_{free} to PS_{graft}. [c] By GPC. [d] Identified by FT-IR and NMR.

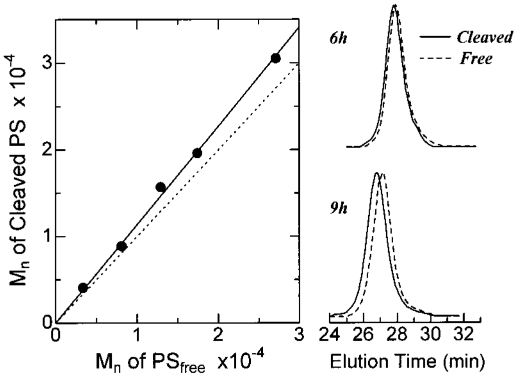

Figure 5. Relationship between M_n of the PS_{graft} and that of the PS_{free}, and GPC curves of the PS_{graft} (solid) and PS_{free} (dashed) which were prepared with irradiated PP (12 kGy, 0.4 g), TEMPO (2.59 × 10^{-2} mmol), and ST (13 mmol). The dotted line indicates identical M_n for the PS_{free} and PS_{graft} in the plot.

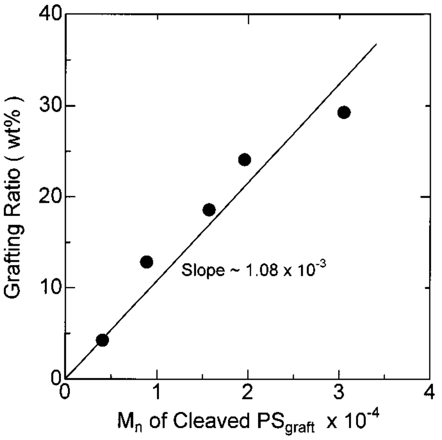

Figure 6. Grafting ratio vs M_n of the cleaved PS_{graft} prepared with irradiated PP (12 kGy, 0.4 g), TEMPO (2.59 × 10^{-2} mmol), and ST (13 mmol). The slope corresponds to the concentration of grafts along the PP main chain.

merization of ST. On the other hand, new PS_{graft} is never formed essentially, which was consistent with the constant concentration of the grafts.

Figure 5 shows the relationship between the M_n of the PS_{graft} and that of the PS_{free} formed simultaneously during grafting. The M_w/M_n of the PS_{graft} corresponds very closely to that of the PS_{free} and is also narrow. The difference between M_n of the PS_{graft} and PS_{free} increased as the polymerization advanced; i.e., the M_n of the PS_{graft} is slightly higher (ca. 10%) than the M_n of the PS_{free}. In addition, the GPC peak for the PS_{graft} shifted slightly to high molecular weight for all samples as compared to that for the PS_{free}. These results suggest that the propagation rate of the PS_{graft} might be larger than that of the PS_{free}.

Figure 6 shows the grafting ratio vs the M_n of PS_{graft}, and the linear relationship indicates that grafting is controlled. The slope in Figure 6 corresponds to the average concentration of grafts along the PP main chain. For the PP-*g*-PS, where the PP was irradiated with a dose of 12 kGy, the concentration of grafts is approximately 1.08 × 10^{-5} (mol/g(PP)). This value is about 61% smaller than the concentration of PP peroxide sites (1.78 × 10^{-5} mol/g(PP)). The average concentration estimated for four points at lower M_n where is well-controlled was about 1.23 × 10^{-5} (mol/g(PP)) and 69% smaller than that of the peroxides. Since the cleaving reaction for PP-*graft*-PS samples using peroxides γ-irradiated with 7.2 and 35 kGy was not conducted, the concentrations of the grafts of two cases were not obtained. Assuming that M_n of the PS_{graft} for each sample was identical with that of PS_{free}, the concentrations of the grafts along the PP chains can be estimated. The estimated concentration of the grafts was about 70% lower than the peroxide concentration of PP. Smaller values were obtained for all of the PP-*g*-PS samples with various irradiation doses (7.2, 12, and 35 kGy). Thus, the initiation efficiency of grafting was approximately 60−70%.

A typical molar ratio of nitroxide to initiator of 1.1−1.3 was used for the styrene/TEMPO/benzoyl peroxide (SFRP) system.[30] The number of the growing PS chains did not correspond to $2[ST]_0/[\text{benzoyl peroxide}]_0$ but $[ST]_0/[TEMPO]_0$. That is, the initiation efficiency of benzoyl peroxide was not 100%. Nitroxide induces the decomposition of benzoyl peroxide, forming one benzoyloxy radical and benzoic acid.[31] The reaction of TEMPO with benzoyl peroxide is rapid compared to thermal decomposition of benzoyl peroxide.[32] The similar reaction was considered in our system. Thus, all the PP peroxides were decomposed after heating at 385 K before grafting. Some PP peroxides were consumed without initiating graft polymerization.

Chain Extension of PS_{graft}. The PP-*g*-PS samples prepared by the "living" radical graft polymerization should be terminated with TEMPO moieties at the chain ends of the PS_{graft}. The nitroxide-terminated PS grafted to PP can be used as a macroinitiator for a chain extension polymerization using the SFRP initiation system. The chain extension polymerization of ST with the PP-*g*-PS ($M_{n,graft}$ = 1.42 × 10^4; M_w/M_n = 1.16) as the initiator was carried out. After chain extension for 5 h, the M_n of the chain-extended PS_{graft} increased to 2.01 × 10^4 with essentially the same polydispersity of 1.19. The increase in the molecular weight of the PS is clearly demonstrated in the GPC curves as shown in Figure 7. Figure 8 shows grafting ratio plotted against the M_n of the PS_{free}, which was almost identical with the M_n of the PS_{graft}. The PP-*g*-PS sample with grafting ratio of 6.1 wt % was used for the chain extension polymerization. The grafting ratio increased linearly with the M_n of the PS_{free} in both the first step (solid circles) and second step (open circles) (chain extension) polymerizations. These results show that the chain extension of the PS_{graft} was successful and controlled.

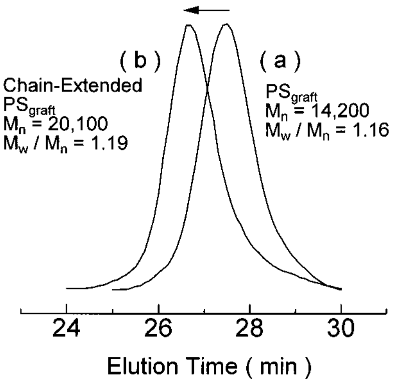

Figure 7. GPC curves of the cleaved PS_{graft} before (a) and after the chain extension (b). The PP-*g*-PS (grafting ratio = 6.1 wt %, 0.4 g), ST (25.92 mmol), TEMPO (5.19×10^{-2} mmol), and benzoyl peroxide (2.60×10^{-2} mmol) were used for the chain extension.

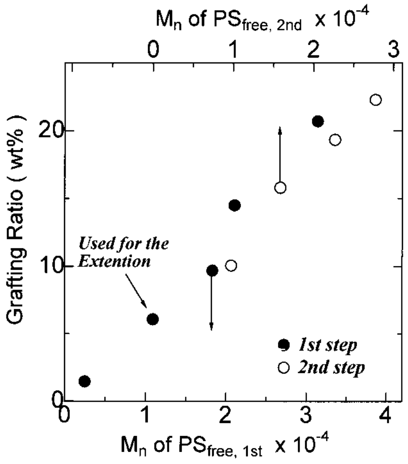

Figure 8. Grafting ratio vs $M_{n,1st}$ or $M_{n,2nd}$ of the PS_{free}. Irradiated PP (12 kGy, 0.4 g), TEMPO (2.59×10^{-2} mmol), and ST (13 mmol) were used for first grafting. The PP-*g*-PS (12 kGy, grafting ratio = 6.1 wt %, 0.4 g), ST (25.92 mmol), TEMPO (5.19×10^{-2} mmol), and benzoyl peroxide (2.60×10^{-2} mmol) were used for the chain extension polymerization.

"Living" Radical Graft Polymerization of Poly(styrene-*ran*-*n*-butyl methacrylate) to PP. The number of monomers whose homopolymerizations have been successfully controlled by SFRP is limited to date. Acrylonitrile, methyl and ethyl acrylates, 9-vinylcarbazole, and BMA gave no polymer (or poorly defined polymer) under the conditions used successfully to polymerize ST with benzoyl peroxide initiator and TEMPO.[33] However, the random copolymerization of ST with an SFRP-uncontrollable monomer proceeded in a "living" fashion.[28,34,35]

The ability to form well-defined random copolymers from simple monomer mixtures is one of the advantages of "living" free radical procedures when compared to other living polymerizations such as anionic and cationic processes.[36] This feature can be exploited in the design of random graft copolymer chains. We performed a controlled random graft polymerization of ST with BMA to PP.

The M_n of the free copolymer (nongrafted) formed simultaneously during grafting increased linearly with monomer conversion, and PS_{free} had a narrow polydispersity. The M_n and M_w/M_n of the cleaved graft copolymer are plotted with the percent monomer conversion in Figure 9. The M_n of the cleaved graft copolymer increased linearly with conversion, and the copolymer had a narrow polydispersity. This indicates that the polymerization has proceeded without chain transfer. The GPC peak top of the cleaved graft copolymer was of slightly higher molecular weight compared to the free copolymer. This is similar to the ST grafting.

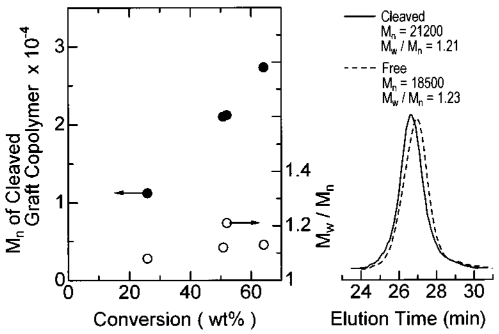

Figure 9. M_n, M_w/M_n, and GPC curves of the cleaved graft poly(ST-*ran*-BMA) (solid symbols, line) and the free poly(ST-*ran*-BMA) (open symbols, dashed line). GPC columns were calibrated with standard polystyrene samples. Irradiated PP (7.2 kGy) = 0.4 g, ST = 27.7 mmol, BMA = 5.06 mmol, benzoyl peroxide = 8.38×10^{-2} mmol, and TEMPO = 0.11 mmol.

Free poly(ST-*ran*-BMA) was characterized by NMR. The molar composition of PS:PBMA was 70:30. The amount of cleaved poly(ST-*ran*-BMA) was too small to analyze its composition by NMR. From FT-IR spectra for PP-*graft*-poly(ST-*ran*-BMA) and free poly(ST-*ran*-BMA), the ST composition in the grafted poly(ST-*ran*-BMA) was slightly smaller than that in the free one. The reproducibility about this result is important. The composition data for various samples need to be accumulated. We will analyze quantitatively the composition in the future. If it was true that the ST composition in the poly(ST-*ran*-BMA) was slightly smaller than that in the free one, the likely reason is as follows: Isotactic PP is not dissolved in BMA but ST monomer at high temperature (polymerization temperature). It was likely that the concentration of BMA around the grafted polymer chains was lower than that around free polymer chains, resulting in different composition for both polymers.

Conclusions

ST was successfully grafted to PP by the combination of radiation-induced graft and SFRP techniques. The PS_{free} and PS_{graft} which was cleaved from PP main chain had almost the same M_n and M_w/M_n. The nitroxide-terminated PS grafted to the PP can be used as a macroinitiator for chain extension polymerization using the SFRP initiation system. The M_n of the PS_{graft} increased and the copolymer had narrow polydispersity. The graft polymerization of poly(ST-*ran*-BMA) to the PP also proceeded without evidence of chain transfer.

References and Notes

(1) Chung, T. C. *Macromolecules* **1988**, *21*, 865. (b) Chung, T. C. *Chem. Technol.* **1991**, *27*, 496. (c) Mulhaupt, R.; Duschek, T.; Rieger, B. *Makromol. Chem. Macromol. Symp.* **1991**, *48/49*, 317. (d) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679.
(2) Brintzinger, H. H.; Fischer, D.; Muelhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.
(3) Boor, J. J. *Ziegler–Natta Catalysts and Polymerizations*; Academic Press: New York, 1979.
(4) Aggarval, S. L. *Block Copolymers*; Plenum Press: New York, 1970.

(5) Riess, G.; Periard, J.; Banderet, A. *Colloidal and Morphological Behavior of Block and Graft Copolymers*; Plenum Press: New York, 1971.

(6) Lohse, D. J.; Datta, S.; Kresge, E. N. *Macromolecules* **1991**, *24*, 561.

(7) Chung, T. C.; Lu, H. L.; Ding, R. D. *Macromolecules* **1997**, *30*, 1272.

(8) Arnold, M.; Knorr, J.; Koller, F.; Bornemann, S. *J. Macromol. Sci., Pure Appl. Chem.* **1999**, *A36* (11), 1655.

(9) Chung, T. C.; Lu, H. L. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4176.

(10) Kennedy, P.; Vidal, A. *J. Polym. Sci.* **1975**, *13*, 1765.

(11) Chung, T. C.; Jiang, G. J. *Macromolecules* **1992**, *25*, 4816.

(12) Chung, T. C.; Rhubright, D.; Jiang, G. J. *Macromolecules* **1993**, *26*, 3467.

(13) Chung, T. C.; Janvikul, W.; Bernard, R.; Jiang, G. J. *Macromolecules* **1994**, *27*, 26.

(14) Chung, T. C.; Janvikul, W.; Bernard, R.; Hu, R.; Li, C. L.; Lie, S. L.; Jiang, G. J. *Polymer* **1995**, *36*, 3565.

(15) Stehling, U. M.; Malmstrom, E. E.; Waymouth, R. W.; Hawker, C. J. *Macromolecules* **1998**, *31*, 4396.

(16) Ying, S. K.; Wang, X. S.; Luo, N. *Polymer* **1999**, *40*, 4515.

(17) Miwa, Y.; Yamamoto, K.; Sakaguchi, M.; Shimada, S. *Macromolecules* **1999**, *32*, 8234.

(18) Hawker, C. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1456.

(19) Beers, K. L.; Gaynor, S. G.; Matyjaszewski, K.; Sheiko, S. S.; Möller, M. *Macromolecules* **1998**, *31*, 9413.

(20) Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **1998**, *31*, 5934. Yamamoto, S.; Ejaz, M.; Tsujii, Y.; Matsumoto, M.; Fukuda, T. *Macromolecules* **2000**, *33*, 5602. Yamamoto, S.; Ejaz, M.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2000**, *33*, 5608. Yamamoto, S.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2000**, *33*, 5995.

(21) Husseman, M.; Malmström, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32*, 1424.

(22) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokula, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716.

(23) Haung, X.; Wirth, M. J. *Anal. Chem.* **1997**, *69*, 4577. Haung, X.; Wirth, M. J. *Macromolecules* **1999**, *32*, 1694.

(24) *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1989.

(25) Lacoste, J.; Vaillant, D.; Carlsson, D. J. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 715.

(26) Mukherjee, A. K.; Gupta, B. D. *J. Macromol. Sci., Chem.* **1983**, *A19* (7), 1069.

(27) Yoshida, E.; Okada, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3631.

(28) Devonport, W.; Michalak, L.; Malmström, E. E.; Mate, M.; Kurdi, B.; Hawker, C. J. *Macromolecules* **1997**, *30*, 1929.

(29) Mayo, F. R. *J. Am. Chem. Soc.* **1968**, *90*, 1289.

(30) MacLeod, P. J.; Veregin, R. P. N.; Odell, P. G.; Georges, M. K. *Macromolecules* **1997**, *30*, 2207.

(31) Moad, G.; Rizzardo, E.; Solomon, D. H. *Tetrahedron Lett.* **1981**, *22*, 1165.

(32) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316.

(33) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.

(34) Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T.; Shimizu, Y. *Macromolecules* **1996**, *29*, 3050.

(35) Hawker, C. J.; Elce, E.; Dao. J.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686.

(36) Mansky, P.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576.

MA001449F