

“Living” Radical Graft Polymerization of Styrene to Polyethylene with 2,2,6,6-tetramethylpiperidine-1-oxyl

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ABSTRACT: A stable free radical (2,2,6,6-tetramethylpiperidine-1-oxyl, TEMPO) polymerization technique was applied to a graft polymerization of styrene (ST) to polyethylene (PE). PE peroxides produced by γ -irradiation in air were used as macromolecular initiators for grafting. Grafted polystyrene (PS_{graft}) was cleaved from the PE main chains by reaction with hydroiodic acid. The molecular weight (M_n) and polydispersity of the PS_{graft} and free (nongrafted) polystyrene (PS_{free}) were determined by GPC. These PS's have almost the same M_n in low conversion and narrow polydispersity. Nitroxide-terminated PS grafted to the PE was chain extended by sequential activation of the dormant chain ends in the presence of additional ST monomer. The grafting (weight) ratio of PS to PE was increased linearly with increasing M_n of PS_{graft}.

KEY WORDS Living Radical Graft Polymerization / Polyethylene / Styrene / 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) / Radiation Induced Grafting /

Living radical polymerization (LPR) is now one of the most extensively researched subjects in precise controlled polymerization.^{1–4} The one of the most advantages of LPR was dispensability for a stringent condition compared to anionic system. In addition, LPR has been applied to block and graft polymerizations to design multifunctional polymers.^{5–13} Much attention also has been focus on controlled grafting from a solid surface.^{14–20}

In LPR field, both atom transfer radical polymerization (ATRP)^{7,8} and stable free radical polymerization (SFRP)^{6,9–11} have been used to prepared polyolefin graft copolymer. Polyolefins form the largest class of thermoplastic polymers. Polyethylene and polypropylene are often used in blends with other polymer in order to improve their physical properties. However, since polyolefins are incompatible with almost all other polymers due to their low surface free energy, compatibilizing agents are required to avoid macrophase separation. The compatibilizer is ordinary block or graft copolymers with a polyolefin segment. Block and graft copolymers have been used to improve the compatibility of immiscible polymers.^{21,22} For a better understanding of the influence of molecular parameters of the compatibility or adhesion on morphology and mechanical properties of the polymer alloy, well-defined structures must be required.

This paper reports a controlled grafting of styrene to commercially available high-density polyethylene by a

combination of radiation-induced graft polymerization and SFRP technique.

EXPERIMENTAL

Materials

High density polyethylene (PE, HJ560 W, $M_n = 1.3 \times 10^4$, $M_w = 8.0 \times 10^4$) 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.) was distilled under reduced pressure. Benzoyl peroxide (Reagent, Nacalai) was dissolved in chloroform, precipitated into methanol, and recrystallized. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (99%) was purchased from Aldrich and used as received. Tetrahydrofuran, toluene, chloroform, methanol (Extra Pure Reagent) and hydroiodic acid (Guaranteed Reagent) were purchased from Nacalai and used as received.

Gel Permeation Chromatography (GPC)

The M_n and polydispersity of the PS_{graft} and PS_{free} were determined by GPC in THF (1 mL min⁻¹) at 313 K on four polystyrene gel columns (Tosoh TSK gel GMH (beads size is 7 μ m), G4000 H, G2000 H, and G1000H (5 μ m)) that were connected to an online degasser (SD-8022 Tosoh), a Tosoh CCPE (Tosoh) pump and a ERC-7522 RI refractive index detector (ERMA Inc.). The columns were calibrated against standard

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polystyrene (Tosoh) samples.

Grafting Ratio

The grafting ratio was defined as follows:

$$\text{grafting ratio (wt\%)} = 100 \times (W_g - W_0)/W_0$$

Here W_g is weight of the sample after grafting, and W_0 is the initial weight of the irradiated the PE. 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 (540 cm^{-1}) to that of the PE (1470 cm^{-1}). The absorptions of 540 cm^{-1} and 1470 cm^{-1} are assigned to the C–C bending vibration in a phenyl ring plane and the CH₂ bending (scissoring) vibration, respectively. In advance, some mixtures of PE and PS 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 Polyethylene with TEMPO

The PE powder was ⁶⁰Co γ -irradiated (the total doses were *ca.* 29, 37, 56, and 62 kGy) in air. The typical grafting reaction is as follows: The γ -irradiated PE powder (0.20 g, 56 kGy), ST (1.50 mL, 13 mmol), TEMPO (4.0 mg, 2.56×10^{-2} mmol), and benzoyl peroxide (3.1 mg, 1.28×10^{-2} mmol) were placed in glass tube. After degassing by freeze-pump-thaw method, the tube was sealed in a vacuum. The sealed tube was heated at 368 K for 3.5 h, and then the polymerization was carried out at 398 K. During polymerization, the PE powder became completely soluble in ST, the solution became transparent and colorless. The reaction was terminated by quenching to liquid nitrogen temperature. Percent conversion of ST was calculated from the weight of the reaction mixture which include PE-*graft*-PS and PS_{free} after the residual ST monomer was completely evacuated in a vacuum at 353 K for 24 h. After that, the sample was immersed in 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 33%, and the grafting ratio of PE-*graft*-PS was 22 wt% after polymerization for 7 h. The sample of the PE-*graft*-PS 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 extraction for 24 h was carried out, there was no change in a grafting ratio before and after the second extraction.

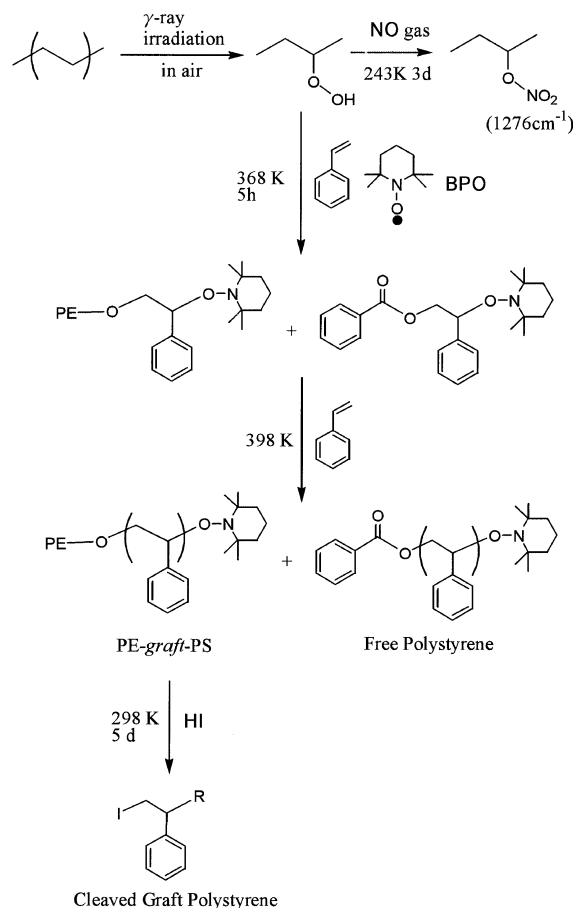


Figure 1. Reaction scheme of graft polymerization of styrene to PE. The most likely end group R of the cleaved PS_{graft} is a hydroxy and/or TEMPO moiety.

Cleavage of the Polystyrene Grafted to Polyethylene

The PS_{graft} was cleaved from the PE main chains by reaction with hydroiodic acid. The sample of the PE-*graft*-PS (grafting ratio = 18 wt%, 56 kGy, *ca.* 0.2 g) in a hydroiodic acid was vigorously stirred at room temperature for 3 days. The reaction mixture was diluted by addition of distilled water, filtered, and dried in a vacuum for 24 h. The dried sample was immersed in THF and stirred at room temperature for 24 h. The cleaved PS_{graft} was soluble in THF and precipitated into methanol, filtered, and dried in a vacuum. The yield of the PS_{graft} was *ca.* 1 mg.

Quantification of the PE Peroxide^{23, 24}

The PE peroxide was quantified by means of FT-IR method. Reaction of PE peroxides (*sec*-hydroperoxide) with nitrogen monoxide results in a nitrate (1276 cm^{-1}) as shown in Figure 1. The irradiated PE film (56 kGy, 0.015 g, 44 μm thickness) was placed in glass tube (40 cm^3) and evacuated. And then, nitrogen monoxide gas (410 torr) was introduced into the tube. The reaction was conducted at 243 K for 3 days. The concentration of the peroxides was estimated at $1.56 \times 10^{-5}\text{ mol g}^{-1}$.

Chain Extension of PS_{graft}

The PE-*graft*-PS (grafting ratio = 20 wt%, 30 kGy, $M_{n,\text{free}} = 3.7 \times 10^4$, $M_w/M_n = 1.16$, 0.3 g), ST (2.25 mL, 19.5 mmol), TEMPO (6 mg, 3.84×10^{-2} mmol), and benzoyl peroxide (4.65 mg, 1.92×10^{-2} mmol) were placed in a glass tube. After degassing by a freeze-pump-thaw method, the tube 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 for 5 h. The reaction were terminated by quenching to liquid nitrogen temperature.

RESULT AND DISCUSSION

“Living” Radical Graft Polymerization Behavior of Styrene to PE

In our previous work, we have clarified that peroxides generated in polypropylene backbone by γ -irradiation was used as an initiator of stable free radical polymerization (SFRP) of ST with TEMPO.^{10,11} In this report, the polyethylene peroxides were used as macroinitiators of grafting. Figure 1 shows a reaction scheme for the grafting. The secondary peroxide in PE was mainly generated by irradiation in air.^{23,24} The concentration of TEMPO was larger than that of the PE peroxides because the concentration of TEMPO was too small to control the grafting. In a typical SFRP with benzoyl peroxide and TEMPO, the concentration of growing chain is determined not from the concentration of benzoyl peroxide but from that of nitroxyl radicals.²⁵ The excess of TEMPO molecules to the PE peroxide is consumed by styryl radical generated through a reaction of ST with benzoyl peroxide and by hydroxyl radicals from homolytic cleavage of PE peroxides. This reaction system produces simultaneously both PS_{free} and PS_{graft} . The PS_{free} has been confirmed to be a good index of PS_{graft} in PP-*graft*-PS system.¹¹

Figure 2 shows FT-IR spectra of irradiated PE (a) and PE-*graft*-PS (b, c, and d). The characteristic peaks of PS (540, 698, 756, 1493, and 1600 cm^{-1}) was clearly observed in b, c, and d, indicating the grafting of ST. The peak intensity arising from PS_{graft} increased with reaction time. Figure 3 shows the relationship between the grafting ratio and the reaction time in the presence and absence of TEMPO. In absence of TEMPO, the grafting was conducted at 398 K without preheating at 368 K. The grafting ratio reached to plateau level for a few hours. On the other hand, in presence of TEMPO, TEMPO suppressed the grafting rate considerably and controlled the grafting ratio of ST. The increase in the grafting ratio with increasing irradiation dose. No grafting was observed for the nonirradiated PE. The increase in the grafting ratio with increasing

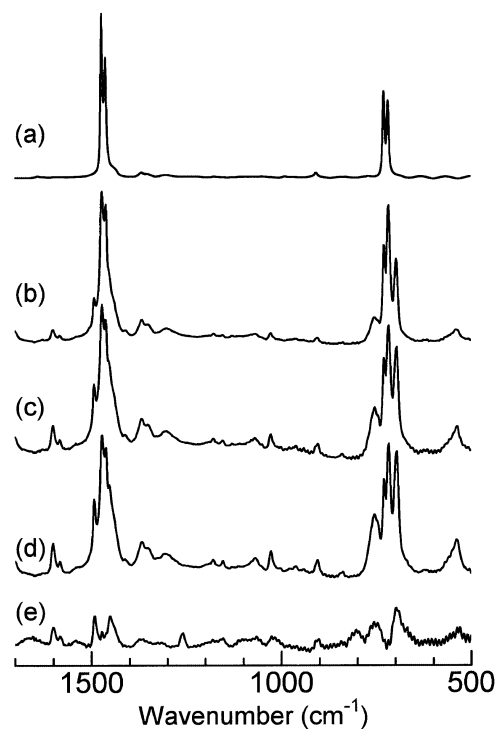


Figure 2. FT-IR spectra of irradiated PE (a), PE-*graft*-PS (b, c, and d) and cleaved PS_{graft} (e). Irradiation dose for samples was 56 kGy. Graft polymerization times for PE-*graft*-PS b, c, and d were 4, 7, and 14 h, respectively. Irradiated PE = 0.2 g. ST = 13 mmol, and TEMPO = 2.56×10^{-2} mmol, and benzoyl peroxide = 1.28×10^{-2} mmol.

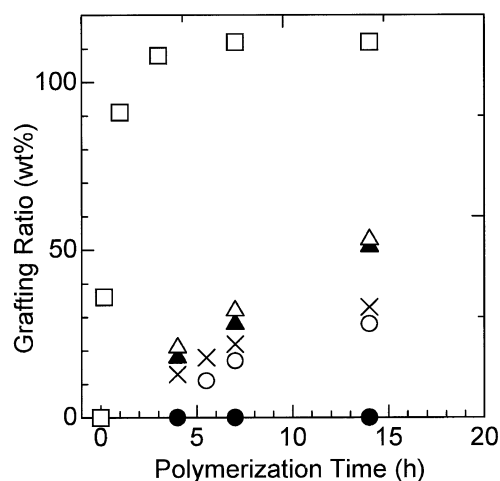


Figure 3. Grafting ratio of styrene to high density polyethylene vs. graft polymerization time: irradiated PE (37 kGy) in the absence of TEMPO (squares); irradiated PE with 62 kGy (open triangles), 56 kGy (solid triangles), 37 kGy (cross), 29 kGy (open circles), and nonirradiated PE (solid circles) in the presence of TEMPO. Irradiated PE = 0.2 g. ST = 13 mmol, and TEMPO = 2.56×10^{-2} mmol, and benzoyl peroxide = 1.28×10^{-2} mmol.

irradiation dose is due to the higher concentration of PE peroxide. The concentration of PE peroxide was confirmed to increase linearly with irradiation dose.

To further understand the characteristics of the grafted PS prepared by TEMPO-mediated graft poly-

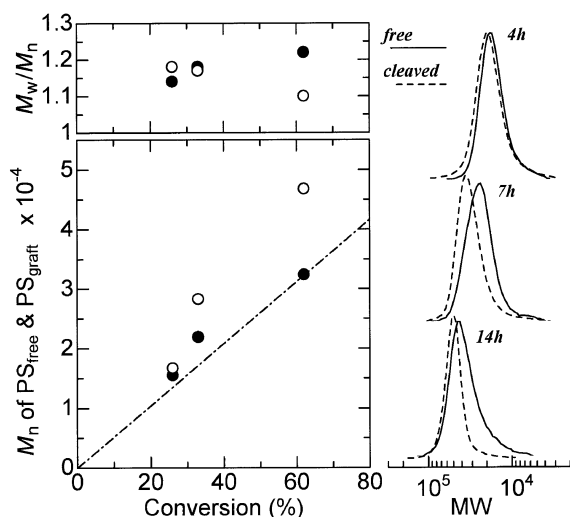


Figure 4. M_n , M_w/M_n , GPC curves of the PS_{free} (solid symbols and lines) and cleaved PS_{graft} (open symbols and broken lines) prepared with irradiated PE (56 kGy). The dot-dashed line indicates the theoretical M_n .

merization, the PS_{graft} was cleaved with hydroiodic acid from PE-*graft*-PS (irradiation dose of 56 kGy) at their point of attachment. The reaction cleaved the ether bond. FT-IR spectrum e in Figure 2 was cleaved PS_{graft} which was identical with the PS_{free} . Figure 4 shows M_n and M_w/M_n of the PS_{free} (solid) and PS_{graft} (open) produced in presence of TEMPO. The M_n of PS_{graft} deviated from the theoretical value ($M_{n,\text{th}}$), which is expected from the molar ratio of styrene to TEMPO, toward high molecular weight range, while the M_n of PS_{free} is close to the ($M_{n,\text{th}}$). However, both M_n are almost proportional to the percent conversion of ST, and the polydispersities are narrow. In addition, Semilogarithmic plots of monomer conversion vs. polymerization time is nearly linear (Figure 5). On the other hand, in absence of TEMPO, the M_n and M_w/M_n of the PS_{free} after grafting for 4 h (irradiation dose of 37 kGy) were 6.35×10^4 and 3.78, respectively. In addition, the M_n and M_w/M_n of the cleaved PS_{graft} were 1.48×10^5 and 2.77, respectively (Table I). The M_n of PS_{free} and PS_{graft} were independent of time in non-living system. The difference between M_n of PS_{free} and PS_{graft} was considerably large and the M_w/M_n of these PS chains was fairly broad. The grafting without TEMPO was not controlled process as expected. Therefore, these results indicated that the graft polymerization of styrene with TEMPO from γ -irradiated PE is a controlled process.

The M_n of PS_{graft} was higher than that of PS_{free} . The GPC peak for the PS_{graft} shifted to higher molecular weight for all samples as compared to that for PS_{free} . The difference between M_n of PS_{graft} and PS_{free} increased as the polymerization advanced. This tendency was observed in the case of living radical grafting of ST to isotactic polypropylene.¹¹ The likely reason for the

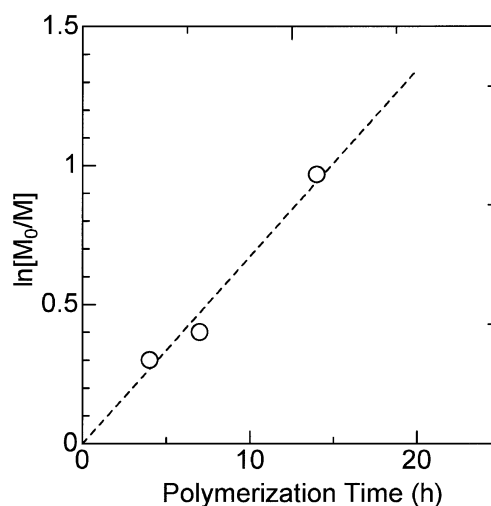


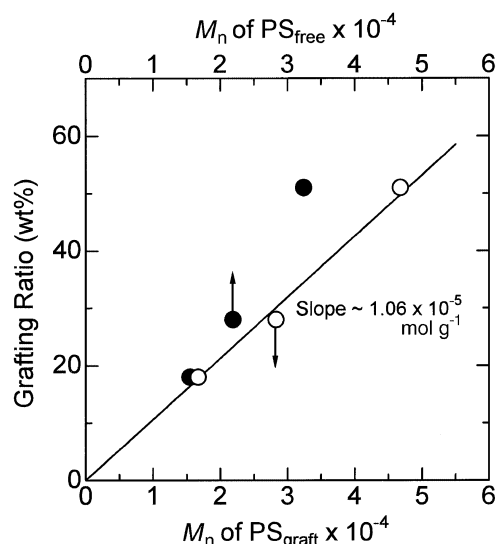
Figure 5. Semilogarithmic plots of monomer conversion vs. polymerization time: γ -irradiated PE (0.20 g, 56 kGy), ST (13 mmol), TEMPO (2.56×10^{-2} mmol), and benzoyl peroxide (1.28×10^{-2} mmol).

higher M_n of PS_{graft} is as follows: Polyolefins such as polyethylene and polypropylene are soluble in styrene monomer at 398 K but incompatible with polystyrene. At early stage of the grafting, both PE-*graft*-PS and PS_{free} can be soluble in ST. When the grafting proceeded, ST monomer decreased due to converting to PS_{graft} and PS_{free} . At higher conversion, a macroscopic phase separation of PE-*graft*-PS and PS_{free} was observed. The PE-*graft*-PS and PS_{free} rich phases could be present in ST monomer during the grafting. It was likely that the concentrations of the propagating radical of PS_{free} and PS_{graft} to ST monomer were different. The molecular weight of PS for nitroxide-mediated living polymerization is consistent with initial concentration of TEMPO to ST monomer. The number of TEMPO molecules is identical with that of propagating ends.²⁵ In this study, since PS chains are incompatible with PE chains, it is difficult for PS_{free} to mix into PE-*graft*-PS rich phase. As a result, the concentration of the propagating end of PS_{graft} to ST became lower than that of the PS_{free} and the M_n of PS_{graft} was higher than that of PS_{free} . As shown in GPC curves and Table I, the polydispersity of PS_{graft} tended to be narrow as compared to that of PS_{free} at high conversion. When some dead PS (graft and free) was generated as grafting advanced, new PS_{free} can be regenerated by autopolymerization²⁶ of ST. On the other hand, new PS_{graft} is never formed essentially. The autopolymerization of ST made the polydispersity broader. Therefore, it can be considered that the polydispersity of PS_{graft} was narrower than that of PS_{free} . Additionally, the autopolymerization was also responsible for reducing M_n of free chains.

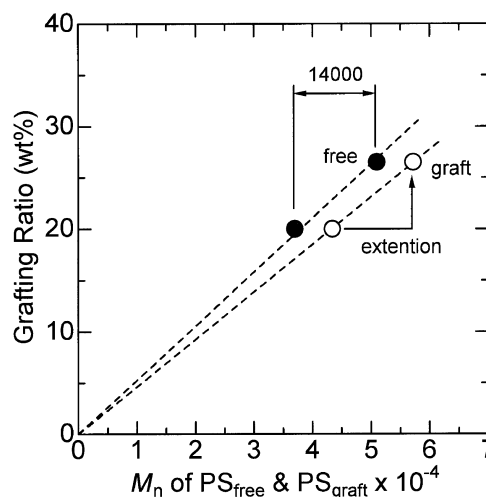
Figure 6 shows the grafting ratio vs. the M_n of PS_{graft} (open) and PS_{free} (solid). The linear relationship for the

Table I. Stable free radical graft polymerization of styrene to PE (irradiation dose of 56 kGy)

run	Grafting time h	Conv %	Grafting ratio wt%	$M_n \times 10^{-3}$ PS _{free}	M_w/M_n PS _{free}	$M_n \times 10^{-3}$ PS _{graft}	M_w/M_n PS _{graft}
1	4	26	18	15.5	1.14	16.7	1.18
2	7	33	28	21.9	1.18	28.3	1.18
3	14	62	51	32.4	1.22	46.8	1.10
4 ^a	4	65	109	63.5	3.78	148	2.77

^aWithout TEMPO or BPO, irradiation dose of 37 kGy.**Figure 6.** Grafting ratio vs. M_n of the PS_{free} (solid) and PS_{graft} (open) prepared with irradiated PE (56 kGy). The slope for the PS_{graft} corresponds to the concentration of grafts along the PE main chains.

PS_{graft} indicates that grafting is controlled. The slope for the PS_{graft} in Figure 6 corresponds to the average concentration of grafts along to PE main chain. For the PE-*graft*-PS, where the PE was irradiated with a dose of 56 kGy, the concentration of grafts is about 1.06×10^{-5} mol per PE of one gram. This concentration value was comparable to that obtained concentration for PP-*graft*-PS specimens which was subjected to irradiation of 12 kGy in air (1.08×10^{-5} mol per gram (PP)). Despite the higher irradiation dose (56 kGy) for PE-*graft*-PS sample, the comparable concentration of the grafts for both cases is caused by a difference of formation amount of the peroxides per irradiation dose. In other word, the formation amount of the peroxides of PE is smaller than that of isotactic polypropylene at the same irradiation dose.²⁴ The concentration of the grafts (1.06×10^{-5} mol g⁻¹ (PE)) and PE peroxide (1.56×10^{-5} mol g⁻¹) along to PE chain gives initiation efficiency of PE peroxide. The initiation efficiency can be calculated to be 68% that is close to the calculated value of 60–70% for PP-*graft*-PS specimens.¹⁰

**Figure 7.** Grafting ratio vs. M_n of the PS_{free} (solid) and PS_{graft} (open). Irradiated PE (40 kGy) was used for first grafting. The PE-*graft*-PS (20 wt% 0.3 g), ST (13 mmol), TEMPO (3.84×10^{-2} mmol) and benzoyl peroxide (1.92×10^{-2} mmol) were used for the chain extension polymerization. After chain extension, M_n of the PS_{free} was 1.4×10^4 .

Chain Extension of PS_{graft}

The PE-*graft*-PS samples prepared by the “living” radical graft polymerization should be terminated with TEMPO moieties at the chain ends of the PS_{graft}. The nitroxides terminated PS grafted to PE can be used as a macroinitiator for a chain extension polymerization using the SFRP initiation system. The successful chain extension of ST to PP by SFRP process was confirmed previously.⁹ Here, the chain extension polymerization of ST with the PE-*graft*-PS (grafting ratio = 20 wt%, $M_{n,free} = 3.7 \times 10^4$, $M_w/M_n = 1.16$, $M_{n,graft} = 4.3 \times 10^4$, $M_w/M_n = 1.12$) as the initiator was conducted. After chain extension for 5 h at 398 K, the free PS having the M_n of 1.4×10^4 and $M_w/M_n = 1.10$ was obtained. The grafting ratio increased from 20 wt% to 26.5 wt%. The grafted PS was cleaved from PE-*graft*-PS sample as mentioned previously. The M_n of the PS_{graft} after the extension grew up to be 5.7×10^4 and the molecular weight distribution of the PS_{graft} remained narrow ($M_w/M_n = 1.11$). Figure 7 shows the plot of the grafting ratio against the M_n of PS_{free} (solid) and PS_{graft} (open) chain extension. (The M_n of PS_{free} after the chain extension was the summation of M_n be-

fore and after extension.) The grafting ratio increased linearly with the M_n of PS_{graft} and the sum of the M_n of PS_{free}. These results show that the chain extension of the PS_{graft} was successful and controlled. The PE-graft-PS sample having further high grafting ratio can be expected by SFRP process.

CONCLUSION

The combination of radiation-induced graft and SFRP techniques controlled grafting of ST to high density PE. The PS_{free} and PS_{graft}, which was cleaved from PE main chain, increased linearly with conversion of ST. The polydispersity of the PS_{graft} was narrow as well as that of the PS_{free}. The nitroxide terminated PS grafted to PE allows to further graft polymerize styrene in SFRP initiation system.

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