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"Living" Radical Graft Polymerization of Styrene to Polypropylene with 2,2,6,6-Tetramethylpiperidinyl-1-oxy

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

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Polypropylene (PP) has been used as one of the most useful polymers. Much interest has been directed toward new ways to give functionality for the PP. To develop an excellent material, precise control of the molecular weight of a grafting chain and its microstructure is further needed. Controlled graft polymerizations of styrene (ST) or methyl methacrylate to a silicon wafer and silica surface were reported recently using an atom transfer radical polymerization (ATRP) or a nitroxide stable free radical polymerization (SFRP).[1,2] A synthesis of densely grafted copolymer ((meth)acrylate-*co*-styrene) by ATRP was also reported recently.[3]

In 1993, Georges et al.[4] first reported the controlled radical polymerization of styrene in which polystyrene (PS) with a narrow molecular weight distribution was produced by the SFRP process. The polymerization mechanism involves thermally reversible capping of a propagating chain by a counter stable free radical such as TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy). The SFRP technique has been applied to various block polymerizations.[5−11] The controlled grafting to PP is very useful and of industrial importance. Hawker et al.[12] reported a synthesis of PP-*graft*-PS by a combination of methallocene and "living" free radical polymerization, in which the molecular weight (M_n) and the polydispersity were controlled.

In this work, we will report an application of SFRP technique to a graft polymerization of ST to a commercially available PP. We discuss the influence of TEMPO on the grafting, and a relationship between the M_n of grafted (PS_{graft}) and free (nongrafted) PS (PS_{free}), which are formed simultaneously. As a result, the M_n of the PS_{graft} was controlled.

"Living" Radical Graft Polymerization of Styrene to Polypropylene with TEMPO. In SFRP system, benzoyl peroxide (BPO) as an initiator has been used generally, and TEMPO controls a polymerization. PP peroxides produced by γ-irradiation in air were used as macromolecular initiators of grafting instead of BPO, in this work. It has been reported that γ-irradiation to PP in air produces mainly peroxides,[13] which can initiate a radical polymerization effectively.[14]

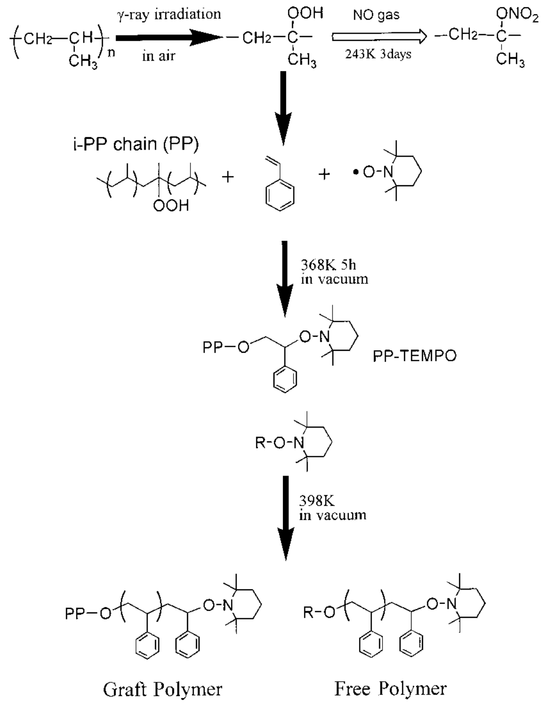

Figure 1. Reaction scheme of the graft polymerization of styrene to PP.

Figure 1 shows a reaction scheme of the grafting. The PP peroxides were used as initiators of the graft polymerization. A 0.20 g sample of the ^{60}Co γ-irradiated PP (the total doses were ca. 7.2, 12, and 35 kGy at dose rates of 0.10, 0.17, and 0.20 kGy/h, respectively) (isotactic-PP, $M_v = 400$K, Mitsubishi Chemical Co., Ltd.), 1.50 mL (12.96 mmol) of styrene (ST) (Nacalai Tesque Co., Ltd.) and 4.05 mg (2.59×10^{-2} mmol) of TEMPO (Aldrich Chemical Co., Ltd.) 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. During polymerization, the PP powder became completely soluble in ST, the solution became transparent and colorless and its viscosity increased substantially. Quenching them to liquid nitrogen temperature terminated the reactions. Carlsson et al.[13] reported the peroxides were identified and quantified by an infrared spectroscopy. As shown in Figure 1, reaction of the peroxides with nitrogen monoxide (NO) results in nitrates. They quantified the amount of nitrates by FT-IR and then succeeded in the quantification of the peroxides. Concentrations of the PP peroxides were estimated by their method in this work. 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 of PP), respectively. The molar ratio of PP−peroxide:ST:TEMPO was 1:5500:11 for a PP sample with a total dose of 7.2 kGy, for example. If the concentration of TEMPO were comparable with that of the peroxides, the former would be too small to control the grafting well. Thus, a large amount of TEMPO compared to that of PP−peroxide must be introduced. In a typical SFRP with BPO and TEMPO, a growing polymer concentration is determined not by a concentration of BPO but by that of nitroxyl radical.[15] The excess of TEMPO molecules to the PP peroxides was consumed by free radicals initiated by autopolymerization[16] of ST. This reaction system resulted in yielding PS_{free}. The PS_{graft} and PS_{free}, thus, were prepared simultaneously. After the reaction, the samples were immersed into THF and filtered in order to extract the PS_{free}. Thus, the PS_{free} and the grafted

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[†] Nagoya Institute of Technology.
[‡] Ichimura Gakuen College.

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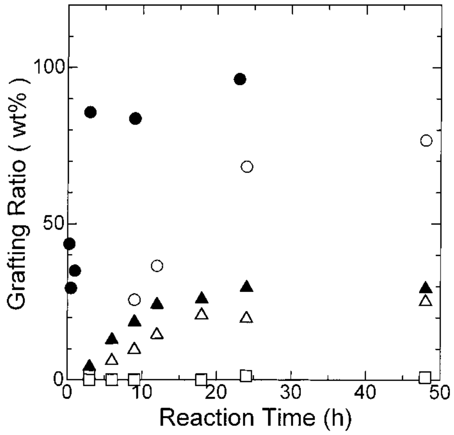

Figure 2. Grafting ratio vs graft polymerization time, showing the grafting to the irradiated PP (35 kGy) in the absence of TEMPO (solid circle), irradiated PP with 35kGy (open circle), 12 kGy (solid triangle), and 7.2 kGy (open triangle), and nonirradiated PP (open square) in the presence of TEMPO.

PS to PP were separated. The PS_{free} was precipitated from THF solution into methanol, and dried in a vacuum at 343 K for 24 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 (wt %) (GR) of the PS_{graft} to the PP (see below) before and after second extraction. The amount of PS_{graft} was calculated from the GR. Percent conversions of ST were calculated from the amount of the extracted PS_{free} plus that of the PS_{graft}.

Characterization of PS_{free} and PS_{graft}. The M_n and polydispersity of the PS_{free} were determined by GPC in THF at 313 K on four polystyrene gel columns (Tosoh TSK gel GMH, G4000H, G2000H, and G1000H) 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. The M_n of the PS_{graft} was defined as follows:

$$M_n \text{ of } PS_{graft} = \text{weight of } PS_{graft} \text{ (g/g (PP))/number of PP peroxides (mol/g of PP)} \quad (1)$$

Weight of the PS_{graft} was estimated from the GR, which was defined as follows:

$$\text{GR (wt \%)} = (W_{graft} - W_{PP,ini})/W_{PP,ini} \times 100 \quad (2)$$

Here, W_{graft} is the weight of the sample after grafting, and $W_{PP,ini}$ is the initial weight of the irradiated PP. The GR was estimated by FT-IR (IMPACT400D, Nicolet Instrument Co.; KBr) method because of a large experimental error involving in measuring a weight increase after grafting. GR's 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.[17] In advance, some mixtures of PS and PP were prepared to make a calibration curve of the GR (weight ratio of the mixture) against the absorbance ratio.

Result and Discussion. Figure 2 shows the relationships between the GR and the reaction time in the presence and absence of TEMPO. It was found that the presence of TEMPO suppressed the grafting rate considerably and controlled the GR of ST. The GR increases with an increase in the irradiation dose. No grafting is obtained for the sample of the non irradiated PP. This fact indicates that the peroxides can initiate the graft polymerization of ST.

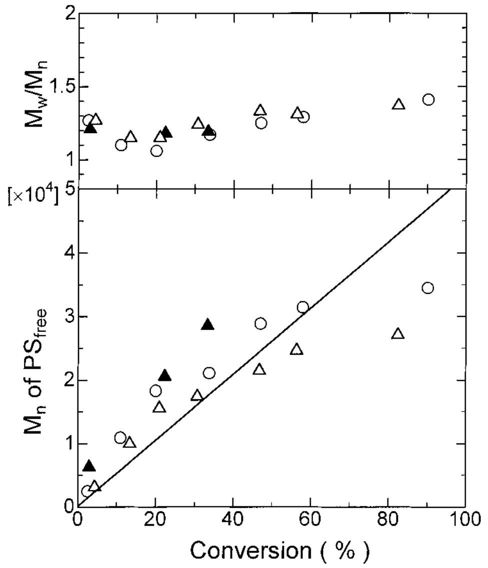

Figure 3. M_n of the PS_{free} vs conversion. Symbols mean the same as those in Figure 2. The expected M_n of the PS_{free} was indicated with the solid line.

It is very hard to directly estimate the M_n and polydispersity of the PS_{graft}. Therefore, the PS_{free} formed was used as an index of the PS_{graft} in this work. The large excess addition of TEMPO to the PP peroxides allowed controlling not only the M_n of the PS_{free} by autopolymerization[16] but also that of the PS_{graft}. Figure 3 shows the M_n and polydispersity of the PS_{free}, determined by GPC. The M_n of the PS_{free} is proportional to the percent conversion of ST in the early stage. In addition, it shows narrow polydispersity at the stage. These results indicate that the M_n and polydispersity of the PS_{free} should be controlled by a "living" free-radical polymerization. However, the "living" polymerization process was somewhat poor when the polymerization came to the final stage. The reaction system in the early stage was homogeneous but in the final stage seemed to be inhomogeneous. As the system becomes inhomogeneous, it may be relatively hard for TEMPO to trap the propagating radicals of PS. The PS propagating radicals may abstract a proton from PP chains, resulting in a dead polymer. However, it is still difficult to prove it.

Comparisons of the M_n of the PS_{free} with that of the PS_{graft} are shown in Figure 4. The M_n of the PS_{graft} is in proportion to the M_n of the PS_{free} for all samples. From this result, the addition of TEMPO controlled the M_n of the PS_{graft} as well as the PS_{free} during the grafting period. In addition, the data points almost lie on one straight line despite the different total doses of the irradiation. This result indicates the propagating rate of the PS_{graft} did not differ from that of the PS_{free} in all cases. The M_n of the PS_{graft} was estimated to be smaller than that of the PS_{free}. The small value is caused by an overestimation of concentration of the peroxide that initiated the grafting. The "number of PP peroxides" in eq 1 should not be that of ones formed by the irradiation but that of ones consumed as the grafting initiator. In

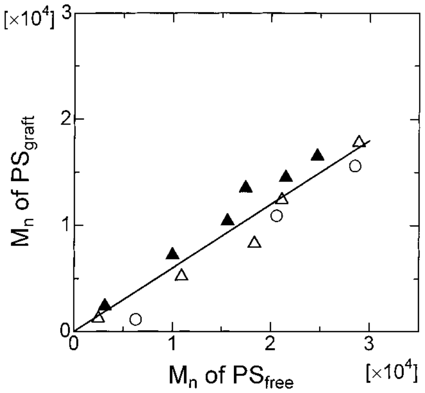

Figure 4. Relationship between M_n of the PS_{free} and that of the PS_{graft}. Symbols mean the same as those in Figure 2.

this work, however, the former values quantified by FT-IR were tentatively substituted into the eq 1 because the later values cannot be estimated. Thus, the M_n of the PS_{graft} was necessarily calculated to be smaller than the real M_n, since the weight of the PS_{graft} was divided by a large numerical value in the eq 1. The slope of 0.6 in Figure 4 shows the 40% of the PP peroxides could not initiate the ST monomer. Some reasons can be considered as follows: The PP powder is insoluble at room temperature but swollen at 368 K in ST. During heat treatment up to/at 368 K, some PP peroxides might vanish without producing the PP−TEMPO (Figure 1). In addition, the PP peroxide concentration included an experimental error of ca. 10%[13] by FT-IR, and the grafting ratio also includes the error in our experiments. Therefore, the value of "40%" may not be absolute. Anyhow, since the linear relation between the M_n of the PS_{graft} and that of the PS_{free} determined by the same procedures in this work was obtained, the ratio of the PP peroxides initiated ST to the total ones estimated by FT-IR was held to be about 0.6. We conclude that the molecular weight of the PS_{graft} is controlled by the "living" free radical polymerization.

In conclusion, we have succeeded in the grafting of styrene to irradiated PP powder using SFPR method. The PP peroxide can be used as a macromolecular initiator for SFRP. The M_n of the grafted PS to the PP was controlled and the PS_{graft} had narrow polydispersity as well as the PS_{free}. We confirmed that SFRP could be applied to the graft polymerization.

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