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New methodology for synthesizing polypropylene-*graft*-polystyrene (PP-*g*-PS) by coupling reaction with brominated polypropylene

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Summary

Polypropylene-*graft*-polystyrene (PP-*g*-PS) was synthesized by the coupling reaction of brominated polypropylene produced by metallocene-catalyzed copolymerization of propylene with 11-bromo-1-undecene and polystyryl lithium salts made by living anionic polymerization, for the first time. These structures were confirmed by ^{1}H NMR analysis. TEM micrographs of PP-*g*-PS copolymers indicated the nanometer level microphase-separation morphology between the polypropylene segment and the polystyrene segment. Obtained PP-*g*-PS copolymers could work as an effective compatibilizer for PP and PS.

Introduction

Recent advances in polyolefin (PO) chemistry have led to the creation of polymer hybrid linking between PO and polar polymer segments, bringing the ordinary PO some improved and unique properties to broaden the applications of PO to highly profitable fields such as compatibilizers, adhesion bonds, and so on [1-5].

While an effective strategy for improving the compatibility of immiscible polymer systems is the use of block or graft copolymers as compatibilizing agents [6, 7], the synthetic challenges in preparing well-defined block or graft polymers of POs has proven formidable. So far, the synthetic route of well-defined polyolefin-*graft*-polystyrene (PP-*g*-PS) has been reported in several papers. Chung has developed an interesting approach to polypropylene (PP) / polystyrene (PS) block and graft polymers by introduction of oxygen to a borane-functionalized PO [8-11]. A styrene-terminated PP has been adopted for atom transfer radical polymerization (ATRP) to prepare PP-*g*-PS after bromination [12]. Additionally, graft copolymer of PO-*g*-PS has been synthesized by the copolymerization of olefins with PS macromonomers by several scientists [13-16].

As part of our interest in developing a new and convenient methodology for the synthesis of well-defined PP-*g*-PS, we were fascinated with the coupling reaction between functional polymers. This paper briefly reports on the synthesis method of

PP-*g*-PS by coupling reaction. At first, we synthesized propylene/bromoundecene copolymer (PP-Br) using En(Ind)$_2$ZrCl$_2$/MAO catalyst system. Then, PP-*g*-PS was synthesized by the coupling reaction between PP-Br and polystyryl lithium salts (PS-Li) as a result of living anionic polymerization.

Experimental parts

Materials

Ethylenebis(indenyl)zirconiumdichloride (En(Ind)$_2$ZrCl$_2$) was purchased from Aldrich Chemical Co., Inc.. Methylalumoxane (MAO) was purchased from Albemarle Co. as toluene solution. Toluene was purified through a molecular sieve and activated almina. Propylene was obtained from Mitsui Chemicals, Inc. and used without further purification. n-Butyllithium was purchased from Wako Pure Chemical Industries, Ltd. as hexane solution (1.54 M). 11-bromoundec-1-ene (Un-Br) was purchased from Aldrich Co. and purified by distillation under reduced pressure. Styrene was purchased from Wako Pure Chemical Industries, Ltd. and purified by the distillation with calcium hydride under reduced pressure.

Analysis

Molecular weights of polymers were recorded on alliance GPC2000 and determined by gel-permeation chromatography (GPC) using o-dichlorobenzene as solvent. The detector was a differential refractive index detector. ^{1}H NMR spectra were recorded on a JEOL JNM GX-270 series in pulse Fourier transform mode using 1,1,2,2-tetrachloroethane-d$_2$ (TCE) as solvent. Bromide atom amount was recorded on Dionex DX-500 using IonPacAS14A as a column by Ion chromatography (IC) method. The ultimate viscosity of polymers was measured in decalin at 135 ºC.

The peaks of melting temperatures of the polymers were measured with a Shimazu DSC-60 differential scanning calorimeter. The samples were heated to 200 ºC at 50 ºC min^{-1}, maintained at 200 ºC for 10 minutes, and cooled to 30 ºC at 10 ºC min^{-1} for recrystallization followed by reheating to 200 ºC at 10 ºC min^{-1}. To estimate the thermal history, the thermogram of each sample was recorded during the second heating run. The instrument was calibrated with the melting points of indium and lead. TEM analysis was carried out with ultrathin (ca. 100 nm) sections of the polymer, which had been pressed into a sheet, were cut on a Reica Ultracut microtome equipped with a diamond knife at a low temperature and then were stained with RuO$_4$. TEM observations were made with a Hitachi H-7000 transmission electron micro-scope at an acceleration voltage of 75 kV.

Copolymerization of propylene with Un-Br (Typical procedure)

In a 500 ml reactor equipped with stirrer, gas inlet tube and thermometer, was placed 250 ml of toluene. The toluene was saturated with propylene at 40 ºC, then 1.2 ml of 11-bromoundec-1-ene (5 mmol), 13.5 ml of MAO in toluene solution (20 mmol as [Al]) and En(Ind)$_2$ZrCl$_2$ (0.02 mmol) were added to the reactor. The polymerization was performed at that temperature under constant propylene monomer gas feed (100 NL/h). After 30 min., the polymerization was stopped by addition of 20 ml of isobutanol to the reactor. The reaction mixture was poured in 1 l. of acidic methanol.

The resulting polymer was collected by filtration and washed with methanol, then dried at reduced pressure (160mmHg) at 80 ºC for 10 hours.

Coupling reaction (Typical procedure)

In a 200 ml Schlenk Flask equipped with magnetic stirrer was placed 3.37 g of styrene (32.3 mmol) and 100 ml of toluene. 2.17 ml of n-butyllithium in hexane solution (1.54 M; 3.34 mmol) was added to the solution. The polymerization was performed at 0 °C for 15 min. and at r.t. for 15 hours with stirring. In a 500 ml glass reactor equipped with mechanical stirrer was placed 1.00 g of the PP-Br (Pol-1, [Br]: 0.34 mmol). The PP-Br was diluted in 200 ml of toluene at 80 °C. The styrene polymerization solution that was obtained with the above procedure was added to the PP-Br toluene suspension. The reaction mixture was stirred at 80 °C for 6 hours. After that, it was poured into 1 l. of methanol. The obtained polymers were purified with boiling THF by Soxhlet extractor for 16 hours, and dried at 80 °C in a vacuum for 10 hours. 1.31 g of purified polymer was obtained.

Polymer blend

The blended polymers, used for transmission electron microscopy (TEM) images, were prepared with 0.42 g of PP-Br (Pol-1) and 0.42 g of PS (M_w = 5,500; M_w / M_n = 1.05) with or without 0.084 g of PP-*g*-PS in solution to obtain molecular-level mixing. The polymers and o-xylene (50 ml) were added to a 100 ml, round-bottom flask equipped with a stirring bar and were stirred at 130 °C until the polymer mixture was homogeneous for 2 hours. The blended polymer was precipitated into methanol, and then dried at 80 °C for 10 hours in a vacuum.

Results and discussion

Synthesis of the PP-g-PS copolymer

The synthesis of PP-*g*-PS involved two steps (figure 1), namely, olefin polymerization and a coupling reaction.

The first step in the preparation of the graft copolymer concerns the synthesis of suitable propylene copolymers containing Un-Br with a metallocene catalyst. A series of copolymerizations were performed under variable monomer feed ratios, in the presence of $En(Ind)_2ZrCl_2$ activated by MAO, to obtain the copolymers with variable composition. The amounts of comonomer contents in resulting polymers were estimated by ^{1}H NMR analysis as shown in figure 2 (a). The multiple peaks of 3.2-3.4 ppm were assigned to methylene ($-CH_2-Br$) adjacent to the bromine atom. The result of copolymerization was summarized in table 1. Resulting polymers contained comonomer, Un-Br, at a range from 1.5 to 10.3 mol %, that were proportional to the amounts of comonomer used in polymerization. And, the values of molecular weight distribution (M_w / M_n) of copolymers were under 2.

The graft copolymers (PP-*g*-PS) were obtained through the coupling reaction of PP-Br and polystyryl lithium salts (PS-Li). Styrene polymerization was performed with n-butyllithium as initiator at r.t. in toluene as a living nature. Without quenching of polymerization solution, it was mixed into the suspension of PP-Br in toluene. After the coupling reaction, the reaction mixture was poured into methanol, collecting all

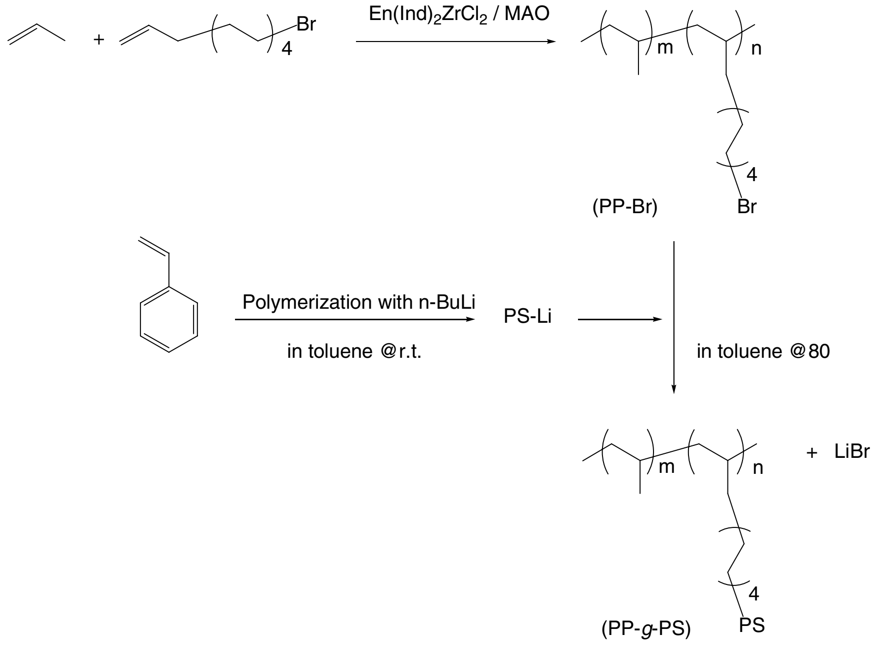


Figure 1. The synthetic pathway for preparing PP-g-PS copolymers

polymers. To remove homo-PS, the obtained polymers were purified by Soxhlet extractor with boiling THF. Table 2 summarizes the results of the coupling reactions. In both cases, the amounts of purified polymers after the Soxhlet extraction increased compared with the PP-Br starting material. The ^{1}H NMR analysis of the resulting polymers (figure 2(b)) indicated that the PS segment was included in the resulting polymer, because new peaks appeared from 6.6 ppm to 7.7 ppm, and that the bromine atom was consumed because the peaks of 3.2-3.4 ppm disappeared, suggesting that PS-Li reacted with the bromine atom. From the ^{1}H NMR analysis, the purified polymers contained 20 and 51 wt% of PS segment, respectively. It was also suggested

Table 1. Results of propylene and Un-Br copolymerization$^{a)}$

Run No.	Un-Br (mmol)	Activity (kg/mol[Zr]/h)	M_w $^{b)}$ (g/mol)	M_w/M_n	Comonomer$^{c)}$ Contents (mol %)	Tm (℃)
Pol-1	5	1851	19600	1.87	1.5	131.7
Pol-2	11	853	14900	1.77	3.9	111.7
Pol-3	21	624	11200	1.84	10.3	87.4
Pol-4	-	4636	30100	1.72	-	133.9

a) Polymerization condition; Metallocene (En(Ind)$_2$ZrCl$_2$, 0.02 mmol), MAO (20 mmol), Hexane (250 mL), 40 ℃, 30min.
b) Determined by GPC (PS standard).
c) Determined by ^{1}H NMR.

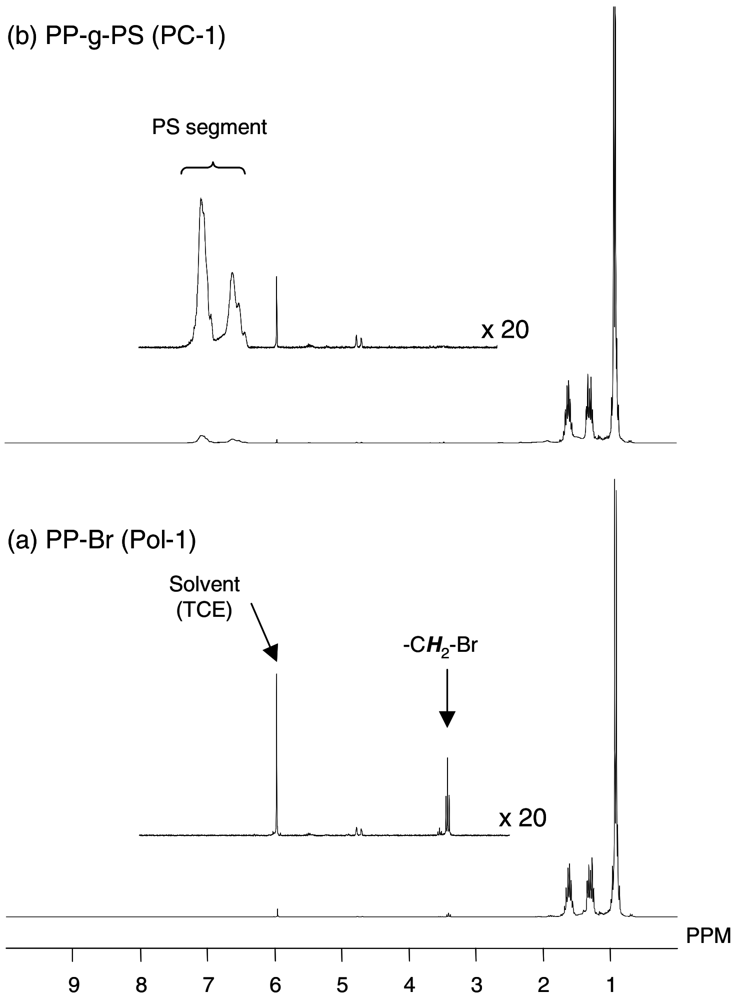


Figure 2. ^{1}H NMR spectra of PP-Br and PP-g-PS

Table 2. Results of coupling reaction$^{a)}$ of PP-Br and PS-Li

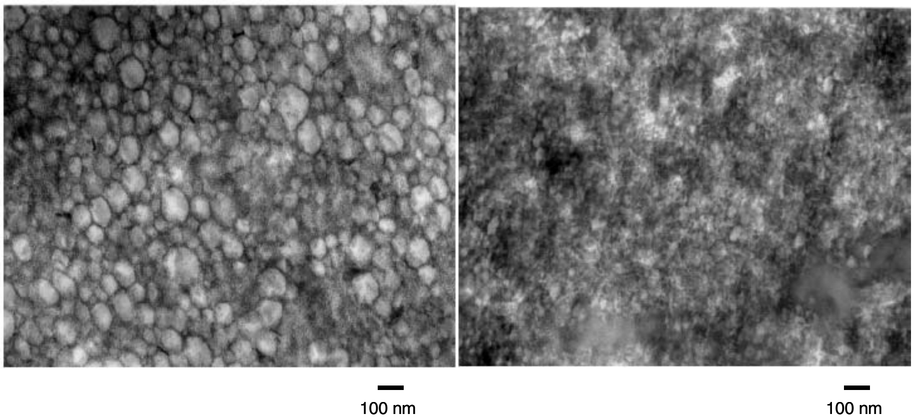
Run No.	Styrene Polymerization $^{b)}$				PP-Br	Yield $^{d)}$	PS contents $^{e)}$	[η]	Tm
	Styrene	n-BuLi	M_w $^{c)}$	M_w/M_n					
	(mmol)	(mmol)			(g)	(g)	(wt%)	(dl/g)	(°C)
PC-1	33	3.4	1100	1.12	1.00	1.31	20	0.24	129.9
PC-2	161	3.4	4900	1.08	1.00	2.39	51	0.28	127.1
Pol-1							-	0.22	131.7

a) Reaction condition; 80 °C, in toluene, 6 hr. b) Polymerization condition; ambient temperature, in toluene, 15 hr. c) Determined by GPC (PS standard). d) After purification by Soxhlet extraction. e) Determined by ^{1}H NMR.

by the measurement of ultimate viscosity that molecular weights of the resulting polymers were increased beyond what the weights were as starting materials [17]. Those results show that PP-*g*-PS was synthesized by a coupling reaction.

Morphology of PP-g-PS copolymer

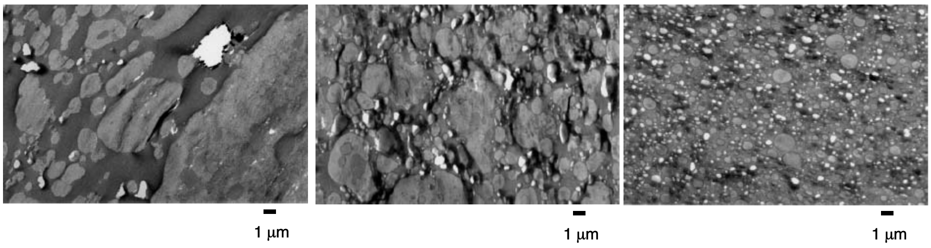
Figure 3 shows TEM micrographs of two PP-*g*-PS copolymers (PC-1 and PC-2). TEM images of the PP-*g*-PS copolymers reveal the microphase-separation morphology at the nanometer level between the PP segment and the PS segment. That would also indicate that PP-*g*-PS was synthesized.



a) PC-1 b) PC-2

Figure 3. TEM images of a PP-g-PS polymer sheet

Obtained block copolymers were expected to work as a compatibilizer for improving the interfacial interactions between blended polymers. To estimate this effectiveness, we blended the PP-*g*-PS copolymer and homo-PP and homo-PS (homo-PP/homo-PS/PP-*g*-PS = 5/5/1 wt ratio) at 130 °C in o-xylene. For comparison, a blended sample without PP-*g*-PS (homo-PP/homo-PS = 5/5 wt ratio) was also prepared. Figure 4 shows TEM images of these blended polymers. The blended polymers containing PP-*g*-PS showed morphology in which the size of the dispersed domains was smaller than that of the blended polymer without PP-*g*-PS. And the PS domain in PC-2 was finely



a) PP/PS blend (5/5 wt ratio) b) PP/PS/PC-1 (5/5/1 wt ratio) c) PP/PS/PC-2 (5/5/1 wt ratio)

Figure 4. TEM images of PP/PS polymer sheet with or without PP-g-PS

dispersed compared with PC-1. It can also be suggested that the size of the domain in the PP/PS blended polymer depended on the PS contents of PP-*g*-PS. These results indicate that such PP-*g*-PS copolymers effectively improve the compatibility between PP and PS.

Conclusion

The new synthetic method of PP-*g*-PS copolymers has herein been described. The PP-*g*-PS was synthesized by the coupling reaction of the PP-Br produced by metallocene-catalyzed copolymerization and PS-Li made by living anionic polymerization. These structures were confirmed by ^{1}H NMR analysis. TEM micrographs of PP-*g*-PS copolymers indicated the nanometer level microphase-separation morphology between the PP segment and the PS segment, thus being evidence of the production of PP-*g*-PS. Obtained PP-*g*-PS copolymers could function as effective compatibilizers of PP and PS.

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17. In this study, we adopted the ultimate viscosity to evaluate molecular weights of PP-*g*-PS copolymer because it’s difficult to measure molecular weights of the copolymer by GPC due to the detector.