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Synthesis and Mechanical Properties of Polypropylene-based Polymer Hybrids via Controlled Radical Polymerization

Hideyuki Kaneko, Shingo Matsuo, Nobuo Kawahara, Junji Saito,*
Tomoaki Matsugi, Norio Kashiwa

Summary: Isotactic polypropylene-based graft copolymers linking poly(methyl methacrylate), poly(*n*-butyl acrylate) and polystyrene were successfully synthesized by a controlled radical polymerization with isotactic polypropylene (iPP) macroinitiator. The hydroxylated iPP, prepared by propylene/10-undecen-1-ol copolymerization with a metallocene/methyl-aluminoxane/triisobutylaluminum catalyst system, was treated with 2-bromoisobutyryl bromide to produce a Br-group containing iPP (PP-*g*-Br). The resulting PP-*g*-Br could initiate controlled radical polymerization of methyl methacrylate, *n*-butyl acrylate and styrene by using a copper catalyst system, leading to a variety of iPP-based graft copolymers with a different content of the corresponding polar segment. These graft copolymers demonstrated unique mechanical properties dependent upon the kind and content of the grafted polar segment.

Keywords: graft copolymers; mechanical properties; poly(propylene); radical polymerization

Introduction

Isotactic polypropylene (iPP) is one of the most widespread commodity plastics due to its outstanding combination of cost performance and excellent physical properties. Its blending with other polymers can be expected to broaden its property range and applications in highly profitable fields. However, in many cases their simple physical blend tends to bring out the poor properties rather than the improved properties because of incompatibility. To overcome this problem, a combination of PP and other polymers by chemical linkage has been attracting a lot of attention as a new polymer hybrid between immiscible segments such as crystalline/amorphous, polar/nonpolar or hydrophilic/hydrophobic segments. Such new polymer hybrid can be used as a compatibilizer for the polymer blends. For example, Chung *et al*. reported that PP-based block or graft copolymers, such as PP-*g*-poly(methyl methacrylate)[1] and PP-*g*-poly(ε-caprolactone),[2] could be prepared by using borane-contained PP in combination with radical or ring-opening anionic polymerization of polar monomers and then used as a compatibilizer for PP-based polymer blends. Recently, metallocene catalysis was used to realize the copolymerization of olefin with 10-undecen-1-ol,[3,4] allyl alcohol[5] or other polar monomers[6–9] to bring the corresponding polyolefins with hydroxyl group or other polar groups. These polar groups could be converted to initiation sites for several polymerization systems, such as controlled radical polymerization and ring-opening anionic polymerization. In our previous papers, by a combination of the polyethylene (PE) macroinitiator derived from the hydroxylated PE and these polymerization systems, we successfully synthesized PE- based block or graft copolymers, such as PE-*b*-poly(methyl methacrylate),[10] PE-*g*-poly (propylene glycol) and PE-*g*-poly (ε-capro-

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Research Center, Mitsui Chemicals, Inc. 580-32 Nagaura, Sodegaura-city, Chiba 299-0265, Japan
Fax: (+81) 438 64 2377;
E-mail: hideyuki.kaneko@mitsui-chem.co.jp

lactone).[11] These copolymers demonstrated nano-order phase separation morphology, due to the chemical linkage between PE and polar segments, to work as a good compatibilizer for the immiscible polymer blends.

On the other hand, these new polymer hybrids based on polyolefins are expected not only to work as a compatibilizer but also to have unique and improved properties. In this article, we focus on PP-based polymer hybrids, which can be produced by controlled radical polymerization with a PP macroinitiator derived from the hydroxylated PP, and evaluated the mechanical properties of such new polymer hybrids themselves. For example, we introduce synthesis and properties of PP-*g*-poly(methyl methacrylate) (PP-*g*-PMMA), PP-*g*-polystyrene (PP-*g*-PS) and PP-*g*-poly(*n*-butyl acrylate) (PP-*g*-PnBA) graft copolymers.

Experimental Part

General Procedures and Materials

All manipulations of air- and water-sensitive materials were performed under dry N_2 atmosphere in a conventional N_2-filled glove box. Copper bromide [CuBr(I)], N,N,-N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), 2-bromoisobutyryl bromide (BiBB), methyl methacrylate (MMA), Styrene (St) and *n*-butyl acrylate (nBA) were purchased from Wako Pure Chemical Industries and used without further purification. Propylene was obtained from Mitsui Chemicals. Methylaluminoxane (MAO) was purchased from Albemarle as 1.2 M toluene solution with the remaining trimethylaluminum and evaporated *in vacuo* before use. Toluene and *n*-hexane used as a solvent were dried over Al_2O_3 and degassed by bubbling with N_2 gas.

Preparation of Hydroxylated PP (PP-*g*-OH)

Toluene (800 ml) was introduced to a N_2-purged 1-l glass reactor equipped with a mechanical stir bar, a temperature probe and a condenser and stirred vigorously. The reactor was kept at 40 °C with an oil bath and then triisobutylaluminum (3.3 mmol) and 10-undecen-1-ol (3.0 mmol) were added. After 10 min, dimethylsilylene-bis(2-methyl-4-phenyl-1-indenyl)zirconium dichloride (0.002 mmol) and 1.31 M toluene solution of MAO (1.0 mmol) were introduced into the reactor and immediately the feeding of propylene gas was started. After adding isobutyl alcohol, the polymerization mixture was poured into acidic methanol. The polymer was collected by filtration, washed with methanol and dried *in vacuo* at 80 °C for 10 h to give PP-*g*-OH (19 g; number-average molecular weight $(M_n) = 54{,}600$, melting temperature $(T_m) = 153\,°C$, 0.14 mol% of hydroxyl group according to ^1H NMR measurements). By repeating this procedure, a sufficient amount of PP-*g*-OH for this study was obtained.

Preparation of PP Macroinitiator (PP-*g*-Br)

PP-*g*-OH (150 g), BiBB (10.9 ml) and *n*-hexane (1500 ml) were introduced into a N_2-purged 2-l glass reactor equipped with a mechanical stir bar and then were stirred vigorously at 60 °C for 3 h. The reaction mixture was cooled to 25 °C and poured into 2 l of acetone. The resulting polymer was collected by filtration, washed with acetone and dried *in vacuo* at 80 °C for 10 h.

Radical Polymerization with PP Macroinitiator

A typical polymerization process is as follows: PP-*g*-Br (100 g) and MMA (800 ml) were placed in a 1-l glass reactor equipped with a mechanical stir bar and then N_2 gas was fed into the reactor at 90 °C. A solution of CuBr(I)/PMDETA in toluene (0.69 mmol as a copper atom) was added to the reactor and the mixture was maintained at 90 °C for 30 min under stirring. The polymerization was stopped by cooling the mixture in an ice bath and then quenched by the addition of methanol. The resulting mixture was filtered and the obtained powdery polymer was washed by methanol and then dried *in vacuo* at 80 °C for 10 h.

Polymer Characterization Methods

^{1}H NMR spectra were recorded on JEOL GSX-270 or GSX-400 spectrometers using *o*-dichlorobenzene-d_4 or 1,1,2,2-tetrachloroethane-d_2 as a solvent at 120 °C. For the measurements of mechanical properties, 40 g of the obtained copolymer and 0.04 g of the antioxidant (Irganox 1010, Ciba-Geigy Corporation) were blended and then kneaded by a labo plastomill at 200 °C. After 5 min of kneading, the specimens were prepared by compression molding at 200 °C for 5 min in a laboratory press. The flexural strength and modulus were measured according to ASTM D 790 and the Izod impact strength was measured at 23 °C according to ASTM D 256.

Results and Discussion

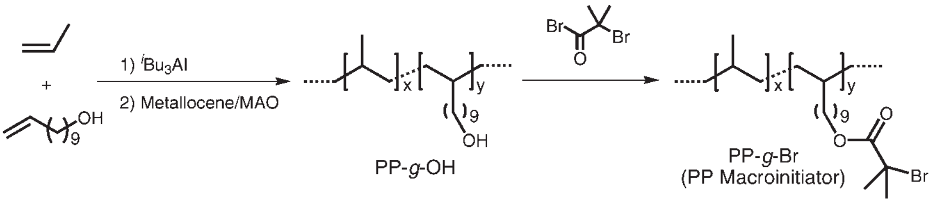
Preparation of PP Macroinitiator

The synthetic route of PP macroinitiator is shown in Scheme 1. In the first step, PP-*g*-OH possessing hydroxyl groups at the side-chain ends was successfully obtained through the copolymerization of propylene with aluminum-capped 10-undecen-1-ol by using a metallocene catalyst system. In the second step, the hydroxyl groups in PP-*g*-OH were reacted with BiBB to produce 2-bromoisobutyrate group containing PP (PP-*g*-Br), which could initiate the controlled radical polymerization.

Figure 1 shows the ^{1}H NMR spectra of PP-*g*-OH and PP-*g*-Br. For PP-*g*-OH (Figure 1(a)), the triplet signals of δ 3.5 ppm are assigned to methylene protons ($-CH_2-OH$). For PP-*g*-Br (Figure 1(b)), other triplet signals of δ 4.1 ppm correspond to methylene protons ($-CH_2-OCO-$) and the single signal of δ 1.8 ppm corresponds to methyl protons ($-OCOC(CH_3)_2Br$). On the other hand, no signals at δ 3.5 ppm were detected and this indicates almost all of the hydroxyl groups in PP-*g*-OH were converted to the 2-bromoisobutyrate groups. From the relative intensities of the signals between PP backbone and 2-bromoisobutyrate groups, the content of 2-bromoisobutyrate group was calculated to be 0.14 mol%. From the number-average molecular weight of the obtained PP-*g*-Br (54,600), the average number of the 2-bromoisobutyrate groups as the initiation site can be estimated to be 1.9 units per chain. Thus-obtained PP-*g*-Br was used as a macroinitiator for the controlled radical polymerization.

Radical Polymerization of Polar Monomers Initiated by PP Macroinitiator

It is well known that transition metal catalyzed radical polymerization results in the controlled radical polymerization of various vinyl monomers, represented by (meth)acrylates and styrenes, to produce precisely controlled polymers.[12,13] In particular, it is a very effective method for the synthesis of block and graft copolymers when using macroinitiators. We applied this method to create the polymer hybrids based on polyolefins. The radical polymerization for three kinds of polar monomers, such as MMA, St and nBA, with the obtained PP-*g*-Br as a PP macroinitiator were carried out using a CuBr(I)/PMDETA catalyst system. The molar ratios of each monomer to the initiation site in the PP macroinitiator were set at 2181, 1272 and 1627, respectively and the molar ratio of CuBr to the initiation site was



Scheme 1.
Synthetic route for preparing PP-*g*-Br.

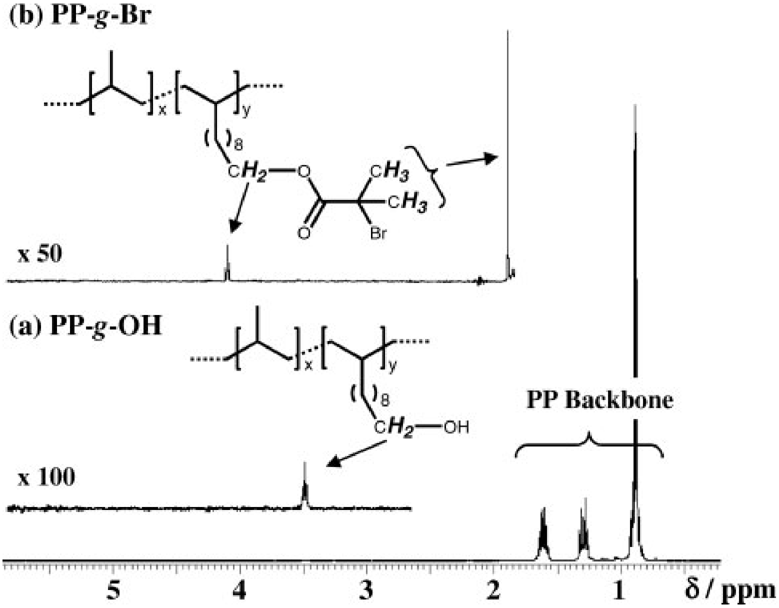


Figure 1.
^{1}H NMR spectra of (a) PP-*g*-OH and (b) PP-*g*-Br (400MHz in *o*-dichlorobenzene-d_4 at 120 °C).

set at 0.2 for MMA and nBA polymerization and 0.5 for St polymerization. Polymerization temperature was controlled in the range of 50–90 °C and polymerization time was set in the range of 15–240 min to give polymer hybrids with different polar monomer contents. Since PP-*g*-Br was not dissolved at these polymerization conditions, the polymerization proceeded at a slurry state. To remove the homopolymer of the polar monomer contained in the obtained polymer, the polymers were purified by the Soxhlet extraction with boiling THF. In each sample, the amount of the extracted homopolymer was only little, and therefore, most of the consumed monomer was obviously grafted onto the PP backbone. This result indicates that the formation of the graft copolymers consisted of PP backbone and polar polymer branches, such as PP-*g*-PMMA, PP-*g*-PS and PP-*g*-PnBA. Table 1 summarizes the

Table 1.
Summary of Radical Polymerization.[a)]

Run	Monomer	Polymerization Temperature (°C)	Polymerization Time (min)	Monomer Conversion (%)[b)]	Polar Monomer Contents (wt%)[c)]
1	MMA	90	30	11.1	46.9
2	MMA	70	40	6.4	34.0
3	MMA	70	15	2.9	18.6
4	MMA	50	15	0.1	0.7
5	St	90	240	17.5	46.6
6	St	90	120	2.6	11.6
7	St	90	60	2.2	9.9
8	nBA	90	60	6.1	32.8
9	nBA	70	30	1.8	12.4
10	nBA	50	30	0.03	0.3

[a)] MMA polymerization: PP-*g*-Br 100 g, MMA 800 ml, $[CuBr]_0/[PMDETA]_0 = 0.858/1.72$ mM. St polymerization: PP-*g*-Br 100 g, St 500 ml, Anisole 500 ml, $[CuBr]_0/[PMDETA]_0 = 1.72/3.43$ mM. nBA polymerization: PP-*g*-Br 100 g, nBA 800 ml, $[CuBr]_0/[PMDETA]_0 = 0.858/1.72$ mM;
[b)] Calculated from polymer yield;
[c)] Determined by ^{1}H NMR.

results by altering the polymerization conditions. The purified copolymers were analyzed by ^{1}H NMR at 120 °C in 1,1,2,2-tetrachloroethane-d_2 as a solvent. Figure 2 shows the ^{1}H NMR spectra of some purified copolymers. From the ratio of the integrated intensities between both signals assigned to propylene and polar monomer units, the content of the polar segments in the graft copolymers could be calculated as shown in Table 1.

Mechanical Properties of Graft Copolymers

The obtained copolymers were kneaded at 200 ° for 5 min by labo plastomill and then the specimens were prepared by compression molding at 200 °C for 5 min. Mechanical properties of these copolymers were characterized by flexural modulus, flexural strength and Izod impact strength measurements. As was expected, the mechanical properties were influenced by the kind and content of the grafted polar segments. Figure 3(a) shows a plot of the flexural modulus *versus* the content of the polar segment. For PP-*g*-PMMA and PP-*g*-PS, the flexural modulus clearly increased in comparison with the base polymer (PP-*g*-OH) and the increase of the flexural modulus depended on the content of the grafted segment. On the other hand, for PP-*g*-PnBA the flexural modulus considerably decreased with the increase of PnBA content because of its softness. Figure 3(b) shows a plot of the flexural strength *versus* the content of the polar segment. As in the case of the flexural modulus, the flexural strength has also been expected to increase by the grafting of PMMA and PS segment and decrease by PnBA segment. However, the flexural strength of PP-*g*-PS copolymers gradually decreased with the increase of PS content. This demonstrates that the balance of the mechanical properties for these new graft copolymers can be controlled by the kind of grafting polar segment. Furthermore, since the flexural strength of the physical blended sample of PP-*g*-OH and PMMA (weight ratio = 70/30) was much lower than that of the obtained PP-*g*-PMMA graft copolymers, it was confirmed that the chemical linkage between both segments significantly contributes to the enhancement of the mechanical properties.

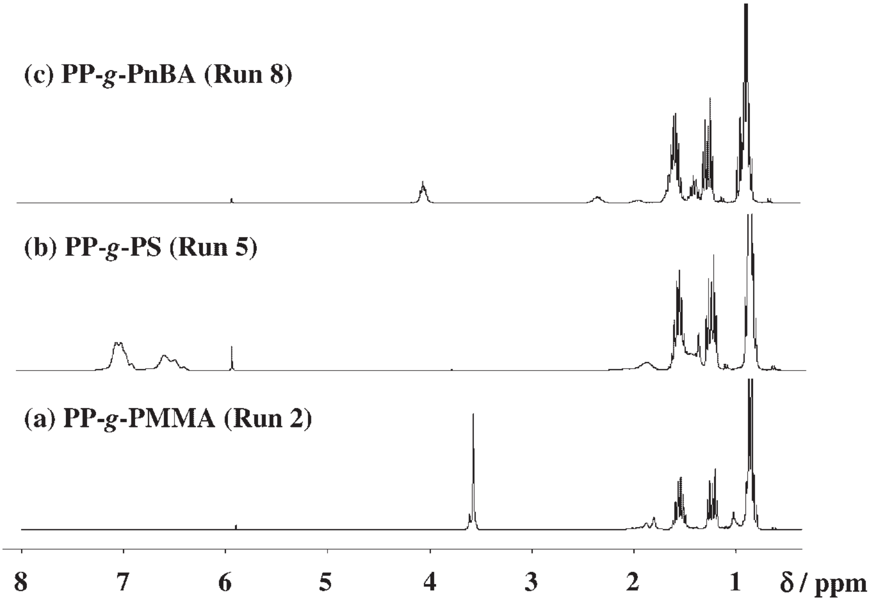


Figure 2.
^{1}H NMR spectra of (a) PP-*g*-PMMA, (b) PP-*g*-PS and (c) PP-*g*-PnBA graft copolymers (270 MHz, in 1,1,2,2-tetrachloroethane-d_2 at 120 °C).

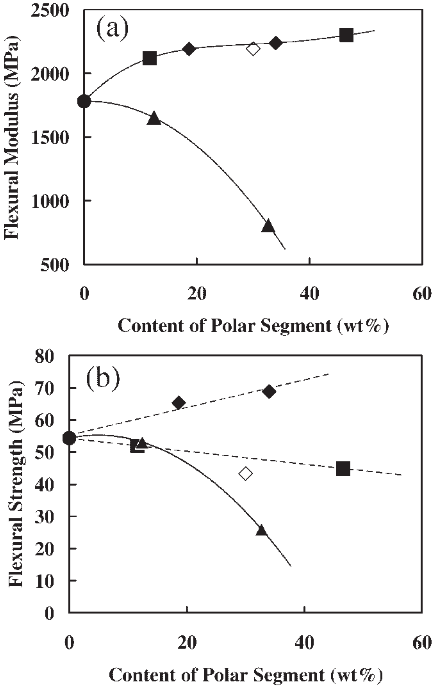


Figure 3.
Plot of (a) flexural modulus and (b) flexural strength *versus* content of polar segment (◆: PP-g-PMMA, ■: PP-*g*-PS, ▲: PP-*g*-PnBA, ●: PP-*g*-OH, ◇: PP-*g*-OH/PMMA (7/3) Blend).

Finally, the result of Izod impact test is shown in Figure 4. The Izod impact strength was remarkably improved by the incorporation of the PnBA segment, indicating the function of the PnBA segment as an impact modifier of PP.

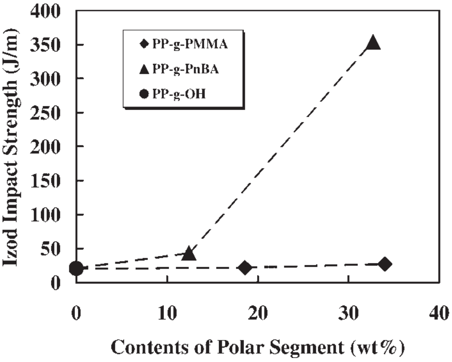


Figure 4.
Plot of Izod impact strength *versus* content of polar segment.

Conclusion

PP macroinitiator was prepared by a metallocene-catalyzed copolymerization of propylene/10-undecen-1-ol and subsequent reaction with 2-bromoisobutyryl bromide. The radical polymerization of MMA, St and nBA with the obtained PP macroinitiator using a CuBr(I)/PMDETA catalyst system resulted in most of the consumed monomer being grafted onto the PP backbone following a Soxhlet extraction test. The content of the polar segments in the obtained graft copolymers were controlled in the range of 11.6–46.6 wt%. The flexural and Izod impact tests revealed that the incorporation of PMMA and PS into the PP backbone effectively enhanced stiffness and concerning PnBA remarkably improved toughness. Thus, the polymer hybrids by chemical linkage between PP and other polymers are useful as a new material possessing unique and improved mechanical properties reflecting the kind and content of the grafted polar segments.

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