New Methodology for Synthesizing Polyolefinic Graft Block Copolymers and their Morphological Features

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Summary: This paper describes a new synthetic route for polyolefinic graft block copolymers by adopting coupling reaction between terminally hydroxylated polyolefins and maleic anhydride grafted polyolefins. Terminally hydroxylated polypropylene (PP-OH) was coupled with maleic anhydride modified polyethylene (PE-g-MAH) and such ethylene-propylene random copolymer (EPR-g-MAH) to give polyolefinic graft block copolymers (PE-g-PP and EPR-g-PP, respectively). The formation of PE-g-PP was confirmed by enhancement on molecular weight and it brought about distinctive decrease in size of dispersed domain in its phase separation morphology. Occurrence of coupling reaction to give EPR-g-PP was indicated by extreme decrease in its solubility to *n*-decane and it led to unique morphology demonstrating lamella microstructure that had never been reported for a comparable polyolefin composite.

Keywords: block copolymers, branched, compatibility, polymer coupling, polyolefins

Introduction

Since the birth of Ziegler-Natta catalysts, polyolefin industry has grown rapidly to the huge worldwide industry producing more than 80,000,000 tons of polymers per year owing to such innovations as discoveries and developments of $MgCl_2$-supported $TiCl_4$ and metallocene catalyst systems. Nowadays, a considerable amount of polyolefins is used for the molded products after blending two or more kinds of polyolefins, because polyolefin blends bring about unique and improved properties. Generally speaking, block copolymers play important roles in compatibilizing the blended polymers. Therefore, polyolefinic block copolymers are expected to compatibilize different kinds of polyolefins that are immiscible combinations in nature. Such effort will be able to create new class of plastic materials from polyolefins that are regarded as commodities so far. The polyolefinic block copolymers are classified into two types that are

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linear and graft types. Until now, two and one methodologies have been reported for synthesizing the former and the latter, respectively.

To synthesize the former, living polymerization of olefins has been intensively studied and many useful catalysts have been discovered.[1-7] These catalysts enabled us to observe the well-defined morphologies of linear block copolymers with transmission electron microscopy (TEM).[8, 9] Alternative method for producing polyolefinic linear block copolymers is use of bis(2-arylindenyl) metallocenes to obtain stereoblock PP[10] and its morphological change during and after tensile extension was observed.[11] To synthesize the latter, copolymerization of macromonomers with olefins has been investigated.[12, 13]

Needless to say, the variety of the segments in the block copolymers is limited in the field of applicability of each method. Then, new methodology for synthesizing polyolefinic block copolymers is desired to diversify the combinations of the segments in polyolefinic block copolymers. Therefore, we investigated a new route to polyolefinic graft block copolymers with polymer coupling reaction as an application of our expertise in synthesizing terminally hydroxylated PP (PP-OH).[14] Suitable partners for PP-OH in coupling reaction would be maleic anhydride modified polyolefins that are conventional resins and expected to show high reactivity to hydroxy group of PP-OH.[15] In this paper, we introduce coupling reaction of PP-OH with maleic anhydride modified polyethylene (PE-g-MAH) and maleic anhydride modified ethylene-propylene random copolymer (EPR-g-MAH).

Experimental

Materials. Pyrolysis PP (py-PP) obtained in the conventional way[16] was used for hydroxylation to synthesize PP-OH. Its weight average molecular weight (Mw) was 8,000 and its molecular weight distribution (Mw/Mn) was 2.4. It was isotactic PP copolymerized with 2 mol% of ethylene. PE-g-MAH and EPR-g-MAH that were obtained in the conventional way[17] were used for coupling reaction with PP-OH. The values of Mw of PE-g-MAH and EPR-g-MAH were 45,000 and 130,000, respectively. The Mw/Mn values of PE-g-MAH and EPR-g-MAH were 2.4 and 2.0, respectively. PE was homopolyethylene and EPR consisted of 81 mol% of ethylene and 19 mol% of propylene. The contents of MAH in PE-g-MAH and EPR-g-MAH were 1.8 wt% and 1.0 wt%, respectively.

Hydroxylation. Into a nitrogen-purged 1 L glass reactor equipped with a mechanical stirrer, 26.6 g of py-PP was added with 34.6 mmol of *i*-Bu_2AlH and 800 mL of *n*-decane. It was heated to 100 °C and that temperature was maintained for 7 h with stirring. Then, dried air was fed into it at a rate of 200 L/h at that temperature for 6 h. The resulting solution was poured into a mixture of 2 L of methanol, 2 L of acetone and small amount of HCl, followed by strring with a magnetic stirrer chip for 2 h. Thus-obtained polymer (PP-OH) was recovered by filtration, washed with 1 L of methanol, and dried at 80 °C for 5 h.

Coupling Reaction. Into a nitrogen-purged 400 mL glass reactor equipped with a mechanical stirrer, 1.25 or 1.0 g of PP-OH was added with 150 mL of *n*-decane, catalyst amount of *p*-toluenesulfonic acid and 1.75 g of PE-g-MAH or 2.8 g of EPR-g-MAH, respectively. It was heated to 80 or 140 °C, respectively, and the temperature was maintained for 8 or 7 h with stirring. Then, it was poured into a mixture of 1.5 L of methanol and 1.5 L of acetone, followed by stirring with a magnetic stirrer chip for 5 min. The recovered polymer by filtration was stirred in 2 L of acetone with a magnetic stirrer chip for 2 h. Thus-obtained polymer was recovered by filtration, washed with 0.5 L of acetone, and vacuum-dried at 80 °C for 10 h.

Polymer Blend. For comparison with polyolefinic graft block copolymers, same procedures as described in Coupling Reaction except for using py-PP instead of PP-OH were carried out to prepare polymer blends.

GPC. Molecular weights of a polyolefinic graft block copolymer and a polymer blend were measured by a Millipore Waters 150C gel permeation chromatograph (GPC) equipped with a refractive index detector, using polyethylene calibration.

TEM. Morphologies of polyolefinic graft block copolymers and polymer blends were observed with TEM as following. Ultra-thin (ca. 100 nm) section of the polymer that had been pressed to give a sheet and dyed with RuO_4 was prepared with a Reica Ultracut microtome equipped with a diamond knife at –100 °C. The specimen was examined with a HITACHI H-810 transmission electron microscopy operated at 100 KV at 10,000 and 150,000 magnifications.

^{13}C NMR. The analysis with ^{13}C NMR was performed in the same manner as our previous paper.[14]

C10 Sol. Solubilities of a polyolefinic graft block copolymer and a polymer blend to *n*-decane at 23 °C (C10 Sol) were measured as following. Into a 1 L flask, 1 g of the polymer sample was

added with 10 mg of 2,6-di-*t*-butyl-4-methylphenol and 500 mL of *n*-decane. The mixture was heated to 150 °C in order to dissolve the polymer sample. The obtained solution was cooled to 23 °C during 8 h and kept at that temperature for 8 h. The resulting slurry was filtered and the liquid phase portion was vacuum-dried until it reached constant weight. The percentage of thus-obtained constant weight in the weight of the initial polymer sample was C10 Sol.

Results and Discussion

Hydroxylation of py-PP

Chain-end structures of py-PP were investigated with ^{13}C NMR and the major group was vinylidene group as shown in Table1, which is accordance with the literature on pyrolysis of PP.[18] It was used for preparing PP-OH through hydroalumination with *i*-Bu_2AlH, oxidation with dried air and methanolysis. The chain-end structures of the resulting polymer were analyzed with ^{13}C NMR and summarized in Table 1 in comparison with those of py-PP. The formation of 45 mol% of hydroxyl chain-end group from the vinylidene group accounting for 81 mol% in py-PP means comparable conversion with that observed in the hydroxylation of high molecular weight PP possessing alkylaluminum at its chain end.[14] Consequently, the obtained polymer possessed hydroxyl chain end in the content of 45 mol% of both ends of the polymer chain, namely, 0.9 hydroxyl group per chain on the average, although it would be a mixture of di-hydroxylated, mono-hydroxylated and non-hydroxylated polymers.

Table 1. The proportions of chain-end groups of pyrolysis and hydroxylated PP.

Sample	Chain-end group[a] / mol%				
	Vd	*n*Pr	*i*Pr	*i*Pr-OH	Others
py-PP	81	17	2	n.d.[b]	n.d.
PP-OH	6	15	34	45	n.d.

[a] Vd: vinylydene; *n*Pr: *n*-propyl; *i*Pr: *i*-propyl; *i*Pr-OH: hydroxy *i*-propyl.
[b] Not detected.

Coupling Reaction between PP-OH and PE-g-MAH

Thus-obtained PP-OH was reacted with PE-g-MAH at 80 °C for 8 h in *n*-decane with a molar ratio of 4 to 1 to synthesize PE-g-PP. This kind of coupling reaction between polyolefins has

never been reported so far to the best of our knowledge, although coupling reaction between a maleic anhydride modified polyolefin and a polar polymer such as polyamide has been known well.[19] For its comparison, py-PP was blended with PE-g-MAH under the same conditions as the coupling reaction expect for the replacement of PP-OH by py-PP. Then, the both were compared with GPC analysis. As shown in Figure 1, a peak in low molecular weight region of (a) was obviously lower than that of (b) and, in its place, (a) gave the higher peak in high molecular weight region. They would clearly show that PP-OH forming the peak in low molecular weight region was bonded to PE-g-MAH by the reaction between –OH and –MAH.

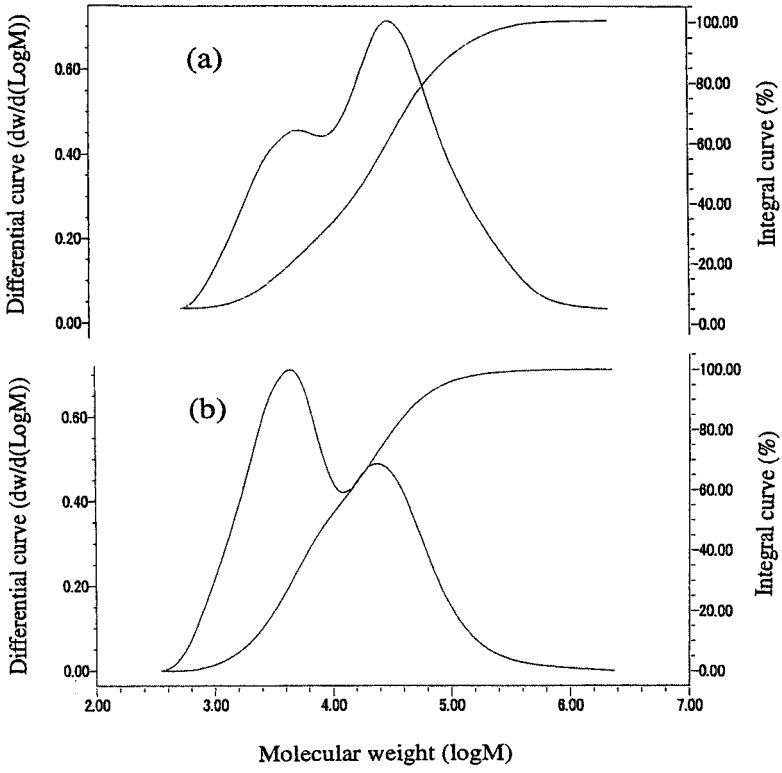

Fig. 1. GPC diagrams of (a) PE-g-PP produced by coupling reaction between PP-OH and PE-g-MAH and (b) polymer blend consisting of py-PP and PE-g-MAH. The molar ratio of PP segment to PE segment is 4 to 1 in any of the both.

Next, the both were compared in observation with TEM. The both showed phase separation morphology where the matrix was PE segment and the dispersed phase was PP segment as in Figure 2. Evidently, the size of the dispersed phase in PE-g-PP was much smaller than that in the polymer blend. Although the peak in low molecular weight region of PE-g-PP in Figure 1 means presence of PP-OH unreacted with PE-g-MAH, there were no coarse dispersed domains as shown in Figure 2 (a). It indicates that the formed PE-g-PP acted as a compatibilizer between unreacted PP-OH and PE segment.

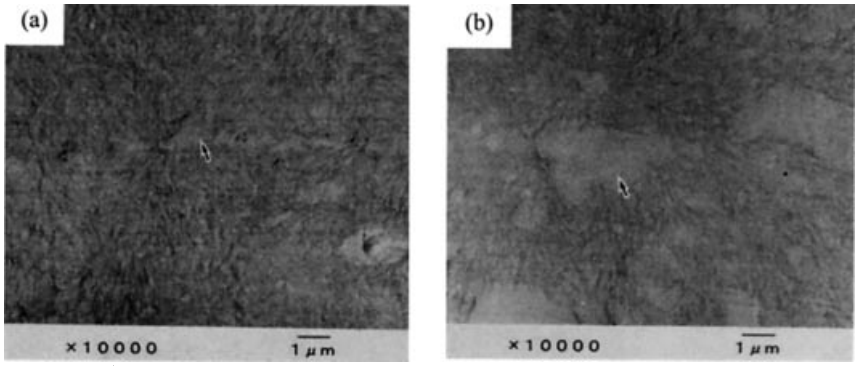

Fig. 2. TEM micrographs at 10,000 magnification from (a) PE-g-PP produced by coupling reaction between PP-OH and PE-g-MAH and (b) polymer blend consisting of py-PP and PE-g-MAH. The molar ratio of PP segment to PE segment is 4 to 1 in any of the both.

Coupling Reaction between PP-OH and EPR-g-MAH

Alternatively, studies on combinations of crystalline polyolefins and amorphous polyolefins are of importance to create new class of plastic materials. As an example, PP-OH was reacted with EPR-g-MAH at 140 °C for 7 h in *n*-decane with a molar ratio of 6 to 1 to synthesize EPR-g-PP. For its comparison, py-PP was blended with EPR-g-MAH under the same conditions as the coupling reaction expect for the replacement of PP-OH by py-PP. In the coupling reaction, its non-viscous initial solution changed to jelly-like product through highly viscous solution, although that in blending the polymers kept the state of non-viscous solution. It strongly suggests the proceeding of the aimed coupling reaction, although GPC analysis was not available for such jelly-like product due to its insolubility to solvents.

Each product was poured into a mixture of methanol and acetone, then the polymer recovered by filtration was washed with acetone followed by vacuum dry to be compared in C10 Sol. The

C10 Sol. of EPR-g-PP was 8.8 wt%, while that of the polymer blend was 75.3 wt% corresponding nearly to the weight proportion of EPR-g-MAH in it. It would indicate that PP segment bonded to EPR prevented the EPR segment from dissolving in *n*-decane.

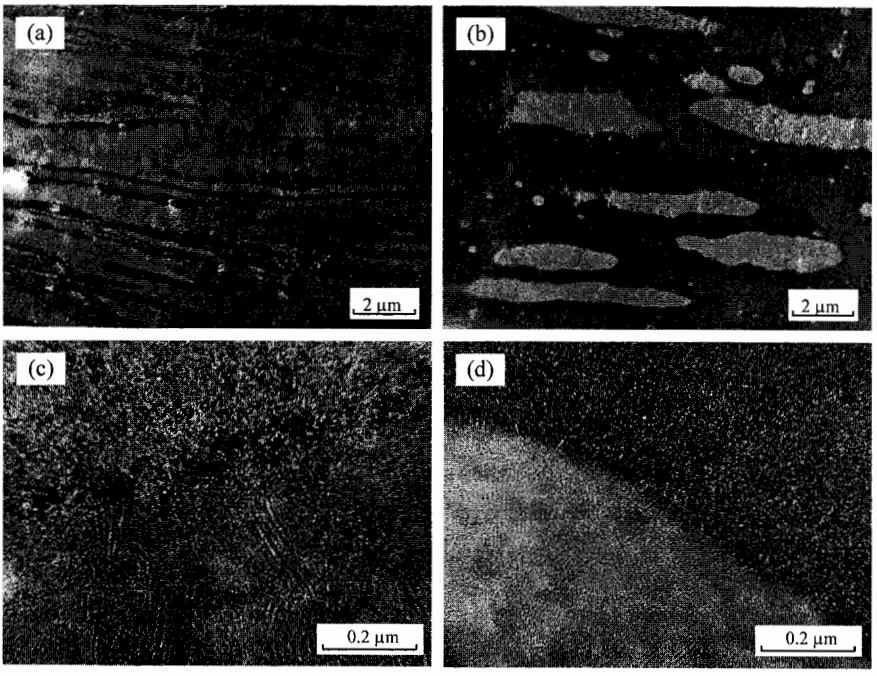

Fig. 3. TEM micrographs at 10,000 magnification from (a) EPR-g-PP produced by coupling reaction between PP-OH and EPR-g-MAH and (b) polymer blend consisting of py-PP and EPR-g-MAH and at 150,000 magnification of (c) the EPR-g-PP and (d) the polymer blend. The molar ratio of PP segment to EPR segment is 6 to 1 in any of the both samples.

Figure 3 shows morphologies observed with TEM for press sheets from the respective polymers. Phase separation morphology was observed in the polymer blend, where the matrix was EPR segment and the dispersed phase was PP segment (Figure 3 (b)). It was common morphology for polyolefins as done in Figure 2 and the dispersed phase was found to be considerably large and non-uniform. On the contrary, EPR-g-PP demonstrated unique lamella microstructure as

shown in Figure 3 (a). Furthermore, its phase boundary was not distinct at high magnification as seen in Figure 3 (c), although the phase boundary was clear in the polymer blend even at high magnification (Figure 3 (d)).

Namely, the lamellar domains looked black or white at low magnification were turned out to include the other component on a nano-order scale by the observation at high magnification. Eventually it was discovered that PP could be compatibilized with EPR completely to give the novel polymer phase morphology by this coupling reaction.

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