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Communications to the Editor

Synthesis of Poly(propylene-*ran*-1,3-butadiene) and Its Metathesis Degradation with Ethylene

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Introduction. Polypropylene (PP) is used worldwide because of its excellent mechanical properties with low cost and supreme recyclability. There is a great demand for PP to be compatibilized with other materials, such as metals, fillers, and other polymers that contain functional groups. There are three main polymerization methods to introduce functional groups in polymer chains. Those are the use of living polymerization systems,[1,2] utilization of chain transfer reactions,[3−7] and copolymerization with functional monomers.[8−12] The living polymerization and chain transfer reaction are effective methods for functionalization of one polymer chain end, whereas copolymerization with functional monomers can introduce functional groups as side chains. Although there are not a few examples for the synthesis of PP with functional groups at one chain end, which can be converted to AB type block copolymer, the examples of PP with functional groups at both chain ends are very limited. The polymer with functional groups at both polymer chain ends can be used as a precursor of ABA type triblock copolymers.

For examples of bifunctional PP, syndiotactic PP with aldehyde groups at both polymer chain ends was obtained using living polymerization with the V-based bifunctional initiator prepared from an α,ω-unconjugated diene followed by a CO quenching technique.[13] α,ω-Divinyl isotactic PP with vinyl side chains was synthesized by the polymerization with $TiCl_3$ using bis(ω-alkenyl)zinc as alkylation and chain transfer reagent followed by the coupling of Zn−alkyl bonds with allyl bromide.[3d,e] PP with vinyl groups only at both chain ends has, however, not been synthesized with this method. Besides these polymerization methods, thermal degradation of PP makes telechelic oligomers having two terminal vinylidene bonds,[14] although the thermal degradation method is limited to the synthesis of polymers with low molecular weights. One of the authors previously reported that the polyethylene terminated with vinyl groups at both chain ends was synthesized from partially hydrogenated *cis*-1,4-polybutadiene by ethenolysis.[15] In this paper, we report random copolymerization of propylene and 1,3-butadiene using an isospecific zirconocene catalyst and synthesis of α,ω-divinyl isotactic PP by ethenolysis of the polymer obtained.

Results and Discussion. a. Copolymerization of Propylene with 1,3-Butadiene. Copolymerization of propylene with 1,3-butadiene was conducted under use of an isospecific zirconocene catalyst, dimethylsilylbis(1-indenyl)zirconium dichloride (Ind-1) activated with methylaluminoxane (MAO). The copolymerization results are shown in Table 1 (runs 1−6). Catalyst concentration and polymerization time were varied to obtain enough polymers to be analyzed with keeping the monomer conversion below 20% of monomers in the feed. Although the catalytic activity and the number-average molecular weight (M_n) declined according to the increase of 1,3-butadiene content in the feed (runs 1−3), they increased proportionally to an increase of propylene concentration (runs 2, 4, and 5). Since 1,4-BD located at the growing polymer chain ends should inhibit next monomer insertion, the increase of butadiene concentration lowered polymerization activities and the molecular weights of copolymers. The ^{1}H NMR spectrum of the polymer obtained with Ind-1 (run 10) is shown

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Table 1. Results of Propylene−1,3-Butadiene Copolymerization with Ind-1−MAO[a]

run no.	cat. (μmol)	time (h)	Pr[b] (mol/L)	Bd[c] (mol/L)	yield (g)	M_n[d] (kg/mol)	M_w/M_n[d]	Bd contents in copolymer[e]		av amount of each Bd unit per polymer chain[f]		T_m[g] (°C)
								1,4-BD	1,2-BD	1,4-BD	1,2-BD	
1	3	1	0.60	0.09	0.17	6.0	2.0	1.52	0.08	2.2	0.12	132
2	5	3	0.60	0.23	0.10	4.1	1.7	2.72	0.20	2.7	0.20	120
3	6	5	0.60	0.46	0.17	2.9	1.5	5.38	0.38	3.8	0.27	97
4	1	2	1.49	0.23	0.24	11.9	2.1	1.25	0.19	3.5	0.55	134
5	1	2	2.38	0.23	0.57	17.1	2.1	0.79	0.15	3.2	0.60	137
6	10	2	0.60	0.23	0.16	4.4	1.9	2.99	0.23	3.1	0.24	128
7[h]	10	3	0.60	0.23	0.25	6.9	2.2	2.91	0.26	4.8	0.43	121
8[h]	0.5	1	1.80	0.09	0.09	31.8	1.9	0.36	0.07	2.8	0.53	143
9[h,i]	2	14	1.80	0.09	0.61	62.1	1.9	0.31	0.10	4.6	1.43	148
10[h,i]	3	14	7.10	0.46	2.36	69.4	1.9	0.57	0.22	9.4	3.67	146
11[h,i]	5	24	1.80	0.09	2.33	49.0	2.1	0.23	0.06	2.7	0.60	150
12[h,i]	3	14	5.95	0.46	1.12	66.1	2.0	0.47	0.20	7.5	3.08	147

[a] Polymerization conditions: 100 mL autoclave; toluene 40 mL; polymerization temperature 40 °C; Al/Zr (mol/mol), 10000 (runs 1−5), 2000 (runs 6−12). [b] Propylene concentration. [c] Butadiene concentration. [d] Determined by GPC. [e] Mole fractions (mol %) of each unit calculated by ^{1}H NMR. [f] Average amounts of each unit per polymer chain (mol/mol) calculated from the M_n values and the mole fractions. [g] Measured by DSC. [h] MMAO was used for aluminoxane. [i] Polymerization temperature was 0 °C.

Table 2. Metathesis Degradation of Poly(propylene-*ran*-1,3-butadiene) with Ethylene[a]

run no.	M_n[b] (kg of PP/mol)	M_w/M_n	C=C content[c]			av amount of each unit per polymer chain (mol/mol)[d]			T_m[e] (°C)	ΔH_f[e] (J/g)
			1,4-BD	1,2-BD	new vinyl bond	1,4-BD	1,2-BD	new vinyl bond		
run 11	49	2.1	0.23	0.06	0	2.7	0.6	0	150	102
product of run 11	23.7	1.9	0.03	0.05	0.38	0.2	0.3	2.1	151	139
run 12	66	2.0	0.47	0.2	0	7.5	3.1	0	147	88
product of run 12	12.1	2.7	0.09	0.18	0.63	0.3	0.5	1.8	148	123

[a] Metathesis reaction conditions: WCl_6 0.3 mmol, $SnMe_4$ 0.6 mmol, propyl acetate 3 mmol, sample 300 mg, ethylene 0.41 mol, chlorobenzene 20 mL, 140 °C, 48 h. [b] Determined by GPC. [c] Mole fractions of each unit in the polymer (mol %) calculated by ^{1}H NMR. [d] Average amounts of each unit per polymer chain (mol/mol) calculated from the M_n values and the mole fractions. [e] Heat of fusion measured by DSC.

in Figure 1a. The resonance at 5.4 ppm can be attributed to 1,4-inserted butadiene units (1,4-BD) and those at 5 and 5.7 ppm to 1,2-inserted butadiene units (1,2-BD). The mole fractions of each structure were calculated from the relative intensities of these resonances to those of propylene units in the ^{1}H NMR spectra and are shown in Table 1. The presence of these olefin units was also confirmed by the ^{13}C NMR spectrum (Figure 1b). The resonances at 128 and 132 ppm were assigned to 1,4-BD and those at 113 and 145 ppm to 1,2-BD.

The copolymers generally had high 1,4-BD selectivity: Up to 95% of butadiene units in the copolymer reached the selectivity toward the insertion as 1,4-BD in run 1. The mole fractions of butadiene units, i.e., 1,4-BD and 1,2-BD, of copolymers increased with the decrease in propylene concentration or the increase in butadiene concentration. The average amounts of 1,4-BD per polymer chain, which can be estimated from the M_n value and 1,4-BD mole fraction of the copolymer, were independent of propylene concentration in the feed (runs 2, 4, and 5) and therefore determined by butadiene concentration. As a result, the average length of propylene units between butadiene units in copolymer became longer according to propylene concentration.

The melting temperatures (T_m) of copolymers decreased with a decrease of mole ratio of propylene to butadiene in the feed (runs 1−5) because of the incorporation of butadiene in the copolymer. The T_m value was also influenced by the polymerization temperature because the change in isotacticity of propylene sequences.

The effects of alkyl substituent of aluminoxane and polymerization temperature were examined to increase molecular weights of copolymers for metathesis degradation. The molecular weight of the copolymer doubled by using modified aluminoxane (MMAO), which was synthesized from trimethylaluminum (TMA) and triisobutylaluminum, instead of aluminoxane (MAO) which was prepared from only TMA (runs 6 and 7) or by lowering polymerization temperature from 40 to 0 °C (runs 8 and 9). The 1,4-BD selectivity was not changed by using MMAO in place of MAO but decreased to 80−90% by lowering the polymerization temperature. The copolymer that contained about 9 units of 1,4-BD per chain on average with 70 000 in M_n was obtained under an adequate polymerization conditions (run 10).

b. Metathesis Degradation of Poly(propylene-*ran*-1,3-butadiene) with Ethylene. Since the isotactic PP which selectively had 1,4-BD in main chain was obtained, the ethenolysis of some copolymers was conducted with $WCl_6/SnMe_4$/propyl acetate. The results are summarized in Table 2. The M_n value of the copolymer was decreased by the ethenolysis, i.e., metathesis degradation with ethylene. The ^{1}H NMR spectra of the copolymer before and after the degradation are shown in Figure 2. The intensity of 1,4-BD at 5.4 ppm decreased after the degradation: the selectivities of ethenolysis calculated from the change in the intensity of 1,4-BD were 89% in run 11 and 81% in run 12. On the contrary, new signals which can be assigned to terminal vinyl groups appeared at about 5.1 and 5.8 ppm. The mole fraction of 1,2-BD roughly unchanged before and after the degradation. The amount of new vinyl group per one polymer chain which was estimated from the M_n value and the mole fraction of new vinyl bond in the copolymer was almost two. The results indicated that the ethenolysis of 1,4-BD successfully

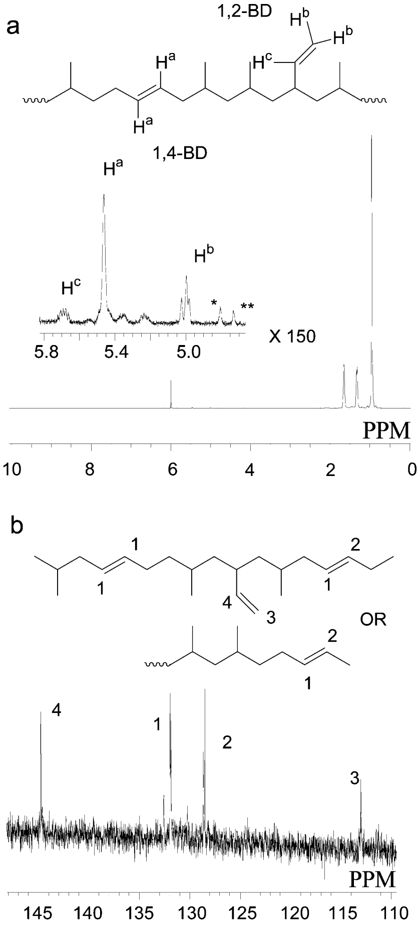

Figure 1. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of poly(propylene-*ran*-1,3-butadiene) obtained with Ind-1 (run 10): *, vinylidene + unknown; **, vinylidene.

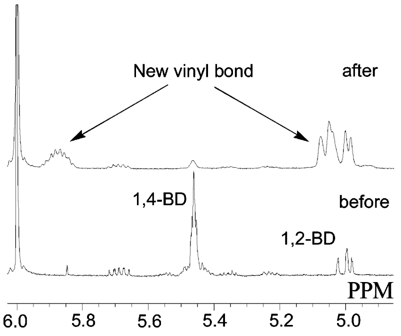

Figure 2. ^{1}H NMR spectra of poly(propylene-*ran*-1,3-butadiene) before and after metathesis degradation with ethylene (run 11 and its product).

proceeded to give isotactic PP with vinyl bonds at both polymer chain ends. The ethenolysis raised the melting temperature of the isotactic polymers accompanied by the increase of the heat of fusion. The same phenomena were also observed in the ethenolysis of partially hydrogenated 1,4-polybutadiene reported previously.[15] These phenomena should be due to the improved packing of shorter polymer chains in the crystalline phase.

Conclusions. Poly(propylene-*ran*-1,3-butadiene) that contained selectively inserted 1,4-butadiene units was successfully synthesized by Ind-1 activated with MAOs. The average amounts of 1,4-BD per polymer chain and thus the average length of propylene units between 1,4-BDs of the copolymer could be controlled by the butadiene concentration in the feed. The copolymers with high molecular weight were converted to α,ω-divinyl isotactic PP by ethenolysis.

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Supporting Information Available: Details of synthesis and characterization of copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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