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Synthesis of terminally functionalized polyolefines

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Summary

Propylene-ethylene copolymer (PER), atactic polypropylene (PP) and atactic poly- 4-methyl-1-pentene (P4MP1) were prepared with a Cp_2ZrCl_2-methylaluminoxane catalyst system. These polymers containing terminal vinylidene groups were made to react with halogen, sulfuric acid, 9-borabicyclo [3,3,1] nonane (9-BBN) or percarboxylic acid, leading to terminally halogenated, hydrogen-sulfated, hydroxy-(OH)- or epoxy- functionalized polyolefines.

Introduction

Polyolefines are the most important polymers from commercial standpoints, but the lack of functional groups has limited many of their potential applications. In order to solve such issues, copolymerizations with olefines and polar monomers, and graft or block copolymers were investigated [1]. Metallocene-catalyzed polyolefines have well-controlled molecular structure such as narrow molecular weight distribution and narrow comonomer distribution. If metallocene catalyzed polyolefines are modified with polar monomers, they would show unique properties for additives, for lubricant oils, for paints, and for compatibilizers for polymer blends. They carry terminal double bonds [2], [3] which have been used for preparation of terminally aluminum-functionalized polyolefines [4], borane-containing polyethylene [5], and block copolymers [6], [7]. In this paper, metallocene catalyzed propylene-ethylene copolymer (PER), polypropylene (PP) and poly-4-methyl-1-pentene (P4MP1) having terminal double bonds were prepared and used for syntheses of various functionalized polyolefines by applying well-established organic reactions [8] in the syntheses.

Experimental

Materials

Cp_2ZrCl_2, Br_2, ICl, CCl_4, H_2SO_4, *m*-chloroperbenzoic acid, performic acid, H_2O_2,

Na_2SO_3, $NaHCO_3$, K_2CO_3, NaOH, tetrahydrofuran (THF), 1,4-dioxane, acetic acid were purchased from Wako Chemicals, and used without further purification.
9-Borabicyclo [3,3,1]nonane (9-BBN) was purchased from Aldrich and used without further purification. Methylaluminoxane (MAO) was prepared according to the previous paper [9]. Hexane and 4-methyl-1-pentene were used after nitrogen bubbling for two hours. Ethylene, propylene (Mitsui Chemicals) were used without further purification.

Preparation of PP, PER and P4MP1 PER

In a 4 litre glass continuous polymerization reactor equipped with a stirrer, propylene - ethylene copolymer (PER) was synthesized under atmospheric pressure at 40 ºC for 4 hr, using toluene as a solvent. The 4 l/hr of toluene, 100 l/hr of ethylene, 500 l/hr of propylene, 0.016 mmol/hr of Cp_2ZrCl_2 and 20 mmol/hr (based on Al atom) of MAO were continuously fed into the reactor under 0.5 hr of the residence time, and polymerization was terminated by the addition of a small amount of methanol. The polymer solution was washed several times with HCl aq solution and water. The 416 g of polymer was separated as a viscous liquid by evaporating of toluene. The resulting polymer had a number-average molecular weight (M_n) of 700, iodine value of 35.3, and ethylene content by NMR of 45 mole %.

PP

Into a 8 litre glass batchwise polymerization reactor equipped with a stirrer, toluene (5 litres) was placed and the system was fed with propylene at 500 l/hr. The 25 mmol (based on Al atom) of MAO and 0.1mmol of $Cp_2Zr\ Cl_2$ were added at 30 ºC in this order. Polymerization was carried out under atmospheric pressure at 30 ºC for 4 hr and terminated by the addition of methanol. The 224g of the viscous liquid polymer was recovered with the same way as PER. The resulting polymer had iodine value of 38.3.

P4MP1

Into the same reactor as PP synthesis, 4-methyl-1-pentene (5 litres) was placed and heated to 50 ºC. Subsequently, 25 mmol (based on Al atom) of MAO and 0.1 mmol of Cp_2ZrCl_2 were added at 50 ºC in this order. Polymerization was carried out under atmospheric pressure at 50 ºC for 3 hr and terminated by the addition of methanol. The 450g of the viscous liquid polymer was recovered with the same way as PER. The resulting polymer had iodine value of 28.5.

Reaction with halogen

Using a 0.2 litre glass flask, equipped with a stirrer, the 10.5 g of PER was reacted with 2.5 g of ICl in 100 ml of acetic acid at 20 ºC for 1 hr. The resulting pale yellowish polymer had iodine value of 0.9. The other experiment with using PP and Br_2 was performed in a similar way as above by substituting PP and Br_2 for PER and ICl, respectively.

Reaction with sulfuric acid

Using the same flask as the reaction with halogen, the reaction of 35.0 g of PER was carried out with 10.1 g of 96 % sulfuric acid without any solvent at 40 ºC for 6 hr. The resulting polymer had iodine value of 1.7.

Hydroboration with 9-BBN and oxidation with H_2O_2

Into a 0.4 litre glass flask equipped with a stirrer, 42 ml of 0.5M THF solution of 9-BBN was placed and cooled to 10 ºC. Subsequently, 107 ml of THF solution containing 5.0 g of PER were added dropwise into the flask over 5 min at 10 ºC and the mixture was stirred at 23 ºC for 5 hr, and cooled to 0 ºC. After that, 21 ml of 3N NaOH aq solution and 7.1 g of 35wt% H_2O_2 aq solution was added into the flask, and the temperature of the system was raised from 0 ºC to 22 ºC. Next, the mixture was heated at 30 ºC for 2 hr and then 50 ml of saturated K_2CO_3 aq solution was added. The crude polymer was recovered by extraction with hexane and the polymer solution was further washed with water. The polymer was obtained by removal of hexane and vacuum drying after the addition of toluene in order to remove water. The resulting polymer had iodine value of zero, which means that 0.14 mol of hydroxy group per 100 g of polymer was introduced to it.

Reaction with percarboxylic acid

Into a 0.2 litre glass flask equipped with a stirrer, 81 ml of toluene and 8.1 g of P4MP1 were placed. Subsequently, 54 ml of 0.2 M toluene solution of *m*-chloroperbenzoic acid was added dropwise at 25 ºC over 3 hr and further the mixture was stirred for 1 hr at 25 ºC. After that, 2.7 g of Na_2SO_3 was added to decompose excess *m*-chloroperbenzoic acid and then the polymer solution was washed several times with $NaHCO_3$ aq solution and water. The polymer was recovered by evaporation of toluene, followed by vacuum drying to constant weight. The resulting polymer had iodine value of 3.3, which means that 0.10 mol of epoxy group per 100 g polymer was introduced to it. In the case of performic acid, the reaction was carried out in the same conditions as above for preparing epoxy-functionalized polyolefines.

Characterization of polymers

The amounts of comonomer unit ratio in the copolymers were analyzed with ^{13}C-NMR [3], and the IR absorbance spectra were measured with a Perkin Elmer FTIR model 1640 IR spectrophotometer (KBr cell). Iodine values were measured as described in paper [10]. Number-average molecular weight was calculated from iodine values based on the estimation [3] that a double bond exists in each terminal end of the polymer chain.

Results and discussion

The characterizations of metallocene-catalyzed PER, PP and P4MP1 synthesized in this report are shown in Table 1. Terminal vinylidene groups were detected by infrared spectroscopy as shown in Figure 1, suggesting that chain transfer reactions with the catalyst system proceed mainly via 1,2-insertion and ß-hydrogen elimination [2], [3].

Table 1: Iodine values and Molecular weights of PER, PP and P4MP1

	PER	PP	P4MP1
Iodine value (*)	35.3	38.3	28.5
M_n	700	650	900

*; gram-I_2/100 g-polymer

Halogenated Polyolefines

PER of M_n=700 and iodine value of 35.3 gram-I_2/100 g-polymer was allowed to react with iodine chloride. IR spectra of the reaction product (PER-ICl) are shown in Figure 2. Absorbance at 890 cm^{-1} for vinylidene group disappeared and the absorbance at 560-570 cm^{-1} for carbon-halogen bonds was detected after the reaction. Iodine value was reduced from 35.3 to 0.9, thus 97% of the double bond reacted with the halogen. PP of M_n=650 and iodine value of 38.3 was made to react with bromine. In this case, the reaction product (PP-Br), also, showed no vinylidene group and the iodine value became nearly zero, which indicated that almost all double bonds in PP reacted with Br_2.

PER-ICl was forced to react with calcium carbonate in order to convert the subject PER to a OH-functionalized one (Run 3 in Table 2). Absorbance for the OH group was hardly detected and the iodine value was slightly increased from 0.9 to 3.2, indicating that reproducing of a double bond had occurred by elimination of halogen. It was concluded that the PER-ICl and the PP-Br were stable and difficult to be converted to the OH-functionalized one by hydrolysis as is well known in organic chemistry.

Hydrogen-sulfated Polyolefines

PER was made to react with sulfuric acid. As shown in Table 2 (Run 4), the iodine value decreased from 35.3 to 1.7 after the reaction, indicating that 95 % of the double bonds reacted with sulfuric acid. Hydrogen-sulfated PER (PER-HSO_4) was tried to react with a 16 weight % of H_2SO_4 aq solution in order to obtain hydroxylated polyolefines. The formation of hydroxylated PER was not observed in this experiment. Hydrogen sulfate group disappeared and vinylidene group was reproduced. The results suggested that it was difficult to convert hydrogen-sulfated PER to PER-OH.

Hydroxylated Polyolefines

In order to obtain terminally hydroxylated PER, hydroboration with 9-BBN and oxidation with H_2O_2 were performed. The vinylidene group disappeared and OH-group was detected on infrared spectra. The iodine value decreased from 35.3 to 0 after the reaction, indicating that all double bonds were made to react with 9-BBN.

Epoxy-functionalized polyolefines

Next, an investigation on synthesis of epoxy-functionalized polyolefine was performed by applying a reaction between polyolefines having a terminal vinylidene group and *m*-chloroperbenzoic acid. Terminal double bonds in PER, PP or P4MP1 were made to react with the percarboxylic acid, and epoxy groups were introduced into them. Absorbance at 890 cm^{-1} for the vinylidene group disappeared and absorbance at 3050-2990 cm^{-1}, 1250 cm^{-1}, 950-810 cm^{-1}, and 840-750 cm^{-1} for epoxy groups was detected as shown in Figure 3. The 95-97% of double bonds in PER or PP was made to react with the percarboxylic acid. In case of P4MP1, 90 % of them reacted with it (Table 3). It is suggested that the reactivity of vinylidene groups in P4MP1 is lower than those of PER and PP due to higher bulkiness of isobutyl groups in 4MP1. In order to obtain terminally-hyroxylated polyolefines, the epoxy-functionalized PER (PER-epoxy) was forced to react in the presence of sulfuric acid (Run 10). The epoxy groups were mainly converted to a hydroxy group, but small amounts of double bonds were reproduced (iodine values : 1.7 →11.1).

Table 2: Results of reactions of polyolefines with terminal vinylidene groups with halogens, sulfuric acid, or 9BBN/H_2O_2, and further hydrolysis (*1, *2) of the reaction products

Run	Polymers	Reactants	Iodine value Before	Iodine value After	Conversion (%)	Hydroxy group
1	PER	ICl	35.3	0.9	97	-
2	PP	Br_2	38.3	0	100	-
3(*1)	PER-ICl	-	0.9	3.2	-	Slightly detected
4	PER	H_2SO_4	35.3	1.7	96	-
5(*2)	PER-HSO_4	-	1.7	13.0	-	Not detected
6 (*3)	PER	9-BBN/H_2O_2	35.3	0	100	Detected

Hydrolysis conditions; *1; Solvent:1,4-dioxane, H_2O/polymer molar ratio:1000, polymer/$CaCO_3$ molar ratio:0.5, the reaction was carried out under reflux, *2; Hydrolysis was performed in hexane solvent. 16 weight % of H_2SO_4 aq solution was used. Reaction temperature was 100 °C. After reaction, neutralization with sodium hydroxide and washing with water were carried out.

*3; PER was made to react with 9-BBN, followed by oxidation with H_2O_2.

Table 3: Results of reactions of PER, PP and 4MP1 with *m*-chloroperbenzoic acid

Run	Polymers	Results Iodine value Before	Results Iodine value After	Results Conversion (%)	Results Epoxy group (by IR)
7	PER	35.3	1.7	95	Yes
8	PP	38.3	1.1	97	Yes
9	P4MP1	28.5	3.3	88	Yes
10(*1)	PER-epoxy	1.7	11.1	-	No (*2)

*1; Hydrolysis of epoxy group was performed in hexane in the presence of sulfuric acid at 60 °C. *2; Absorbance of hydroxy groups and C-O bonds of alcohol was detected by IR

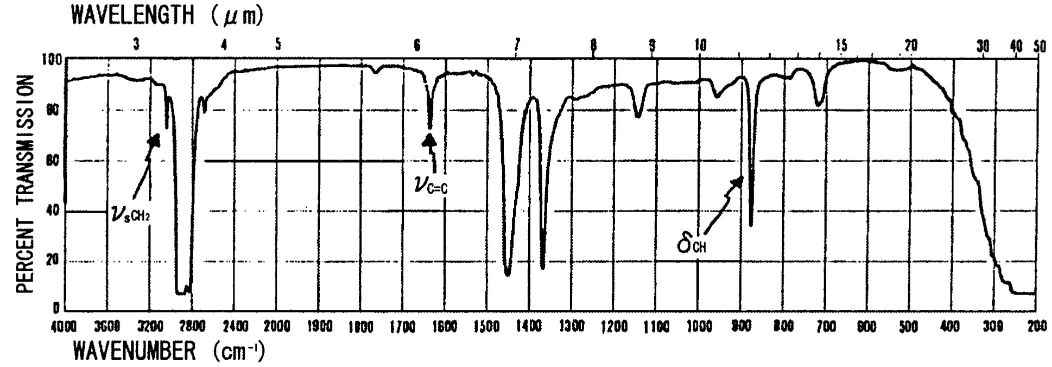

Figure 1. IR spectra of PER

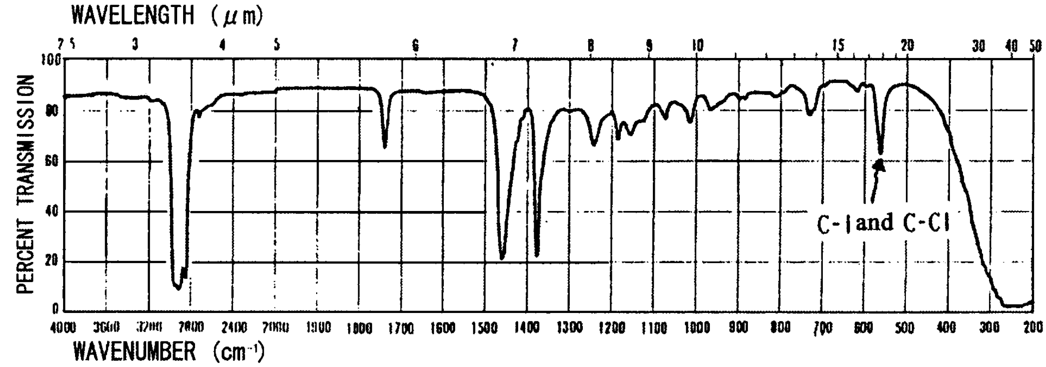

Figure 2. IR spectra of PER-Icl

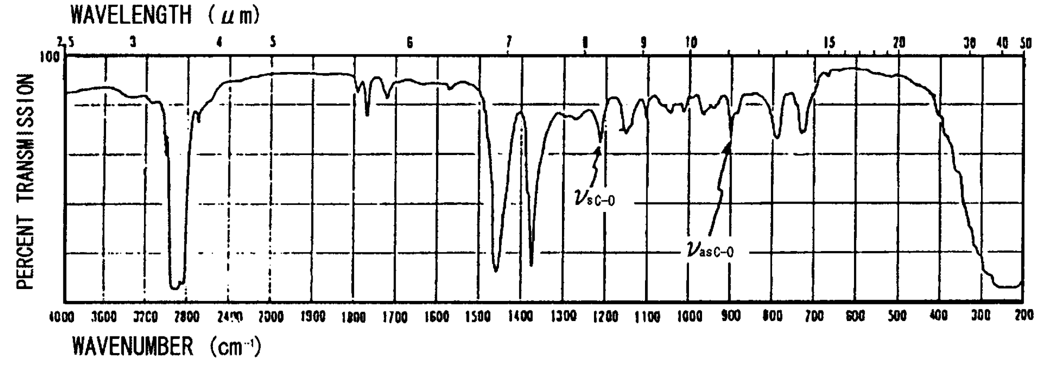

Figure 3. IR spectra of PER-epoxy

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