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Synthesis and characterization of metallocene-catalyzed propylene–ethylene copolymer with end-capped functionality

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Abstract

Metallocene-catalyzed propylene–ethylene copolymer (PER) having a terminal vinylidene group, reacted with maleic anhydride without free radical conditions to prepare terminally MAH-functionalized PER. Through the analysis of the obtained polymer by ¹³C NMR spectroscopy, it was shown that a large part of a terminal vinylidene group isomerizes to a more stable internal double bond in this reaction and that the PER–MAH is formed via the reaction of MAH with isomerized PER and original PER. © 2002 Published by Elsevier Science Ltd.

Keywords: Functional polyolefin; PER–MAH; Metallocene-catalyzed polyolefin

1. Introduction

Maleic anhydride modified polyolefins (PO-MAH) are well known as useful materials from an industrial viewpoint, due to some excellent properties such as compatibility, adhesion and paintability. They are used in many applications, e.g. glass fiber reinforced PP, anticorrosive coatings for metal pipes, multi-layer films and sheets, and polymer blends [1].

Usually, PO-MAH was prepared by chemical modification of preformed polyolefins under free radical conditions [2,3]. The grafting reaction is, however, accompanied by many potentially undesirable side reactions, such as a β -scission, chain transfer and coupling [3]. Heinen et al. reported that the grafting to PER occurred at the sites of the methine and methylene under the free radical grafts [3]. Thus, the sites of attachment and the structures of the grafts were difficult to control Fig. 1.

On the other hand, Chung and Lu reported that terminally MAH-functionalized polypropylene was prepared by a new synthetic route via borane-terminated polypropylene [4].

Metallocene-catalyzed polymers have well-defined molecular structure, that is, a narrow molecular weight distribution, a narrow comonomer distribution, etc. Furthermore, it is known that they have a terminal vinylidene group [5,6]. The reaction of the double bonds with functional monomers such as anhydrides, esters, amines, halogens, alcohols, etc. was reported [4,7,8] and it was pointed out that part of vinylidene groups isomerize to a more stable internal double bond in the reaction at elevated temperatures. However, no detailed analysis of microstructures of the reaction products with functional monomers has been reported, so far.

In this paper, we will report a synthesis and detailed microstructures of a functional olefinic polymer synthesized through the reaction between preformed PER with Cp₂ZrCl₂/MAO and MAH.

2. Experimental

2.1. Materials

Cp₂ZrCl₂, maleic anhydride, and toluene were purchased from Wako Chemicals, and used without further

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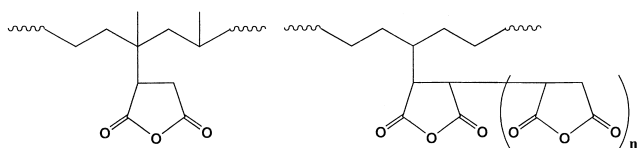


Fig. 1. Grafts structures of PER–MAH [3].

purification. Methylaluminoxane (MAO) was prepared according to the previous paper [9]. Hexane was used after nitrogen bubbling for two hours. Ethylene, propylene (Mitsui Chemicals) was used without further purification.

2.2. Preparation of PER

In a 4 l glass continuous polymerization reactor equipped with a stirrer, propylene–ethylene copolymer (PER) was synthesized under atmospheric pressure at 40 °C for 4 h, using toluene as a solvent. Four l/h of toluene, 100 l/h of ethylene, 500 l/h of propylene, 0.016 mmol/h of Cp_2ZrCl_2 and 24 mmol/h as Al atom of MAO were continuously fed into the reactor under 0.5 h of the residence time. 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. Polymer was separated as a viscous liquid by evaporation of toluene. The resulting polymer had M_n of 600, and ethylene content of 47 mol% by ^{13}C NMR.

2.3. Reaction with maleic anhydride

Into a 0.1 l glass flask equipped with a stirrer, 15.0 g of PER and 4.9 g of maleic anhydride were placed and bubbled with nitrogen at room temperature for one night. Subsequently, the system was heated to 200 °C and reacted for 24 h. The resulting polymer was extracted with hexane and recovered as transparent pale brown viscous liquid by vacuum drying at 180 °C for 2 h after evaporation of hexane.

2.4. Polymer fractionation

Polymer of 1 g was dissolved in hexane and poured into a

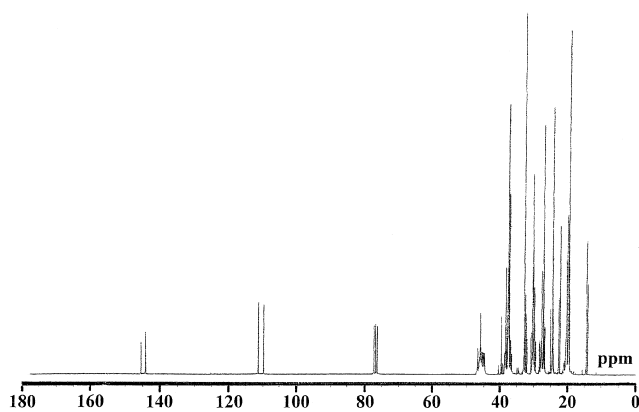


Fig. 2. ^{13}C NMR spectrum of original PER.

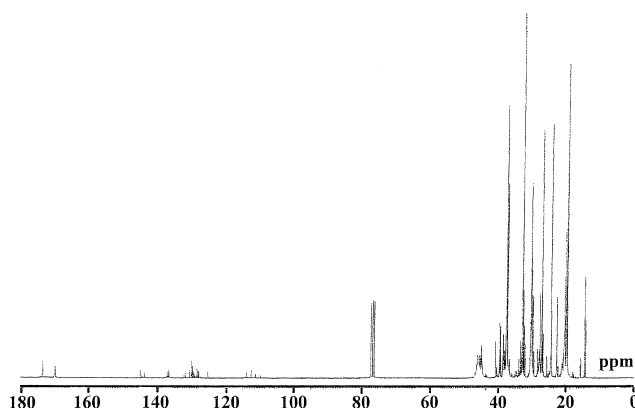


Fig. 3. ^{13}C NMR spectrum of PER–MAH.

glass column packed with silica gel. The first fraction was eluted by 300 ml of hexane, followed by 100 ml, two times, and collected in 500 ml flask. The second fraction was eluted by chloroform in the same manner as the first fraction. The first and second fractions weighed 0.22 and 0.75 g, respectively, after evaporation of the solvent and drying in vacuum. The polymers of the fractions were analyzed by NMR analysis.

2.5. ^{13}C NMR analysis

The polymer solution was prepared by dissolving 250 mg of the polymer sample in 0.6 ml of deuteriochloroform. ^{13}C NMR spectra were recorded on a JEOL GX-270 spectrometer operating at 67.8 MHz under proton noise decoupling in Fourier-transform mode. Instrument conditions were as follows: pulse angle 45°; pulse repetition 4.03 s; spectral width 13,624 Hz; temperature 55 °C; data points 64,000.

3. Results and discussion

The ^{13}C NMR spectrum of the PER is shown in Fig. 2. From the NMR spectrum, it is determined that α -terminal and ω -terminal groups are *n*-propyl and vinylidene, respectively, [6] indicating that the chain transfer reaction is induced by propylene monomer when the propagating chain end is a propylene unit. From the ratio of carbon peak intensities of terminal groups to all the ^{13}C peaks, the average molecular weight is estimated to be ca. 600.

PER reacted with MAH without free radical conditions. The ^{13}C NMR spectrum of the reaction product (PER–MAH) is presented in Fig. 3. The new peaks are observed in the chemical shift range between 169 and 174 ppm, showing that MAH exists as a form of succinic anhydride.

Moreover, the peaks assigned to olefinic carbons were remarkably changed by MAH introduction, while the peaks of the saturated carbon skeleton were only slightly changed. From this result, it is evident that the vinylidene group is responsible for the reaction with MAH. In order to study the

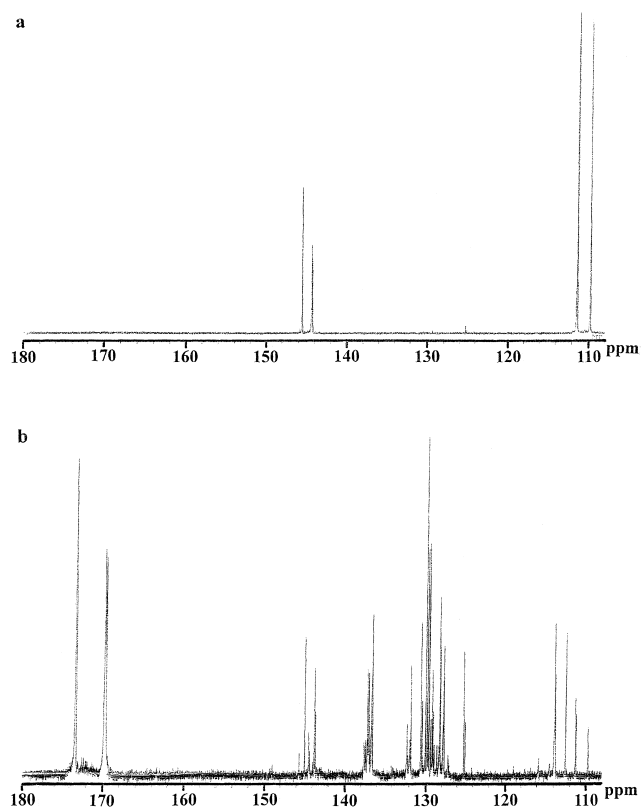
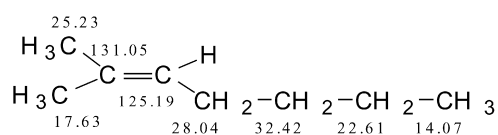


Fig. 4. Expanded ^{13}C NMR spectrum between 108 and 180 ppm of the original PER (a) and PER-MAH (b).

MAH addition in detail, the expanded spectra between 108 and 180 ppm of the original PER and PER-MAH are shown in Fig. 4.

As the ^{13}C NMR spectrum of the olefinic region of PER-MAH was too complicated to analyze, the fractionated polymers of PER-MAH separated by column chromatographic method were also measured by ^{13}C NMR. The expanded spectra between 108 and 180 ppm of the fractions are presented in Fig. 5. Although the peaks assigned to C=O of succinic anhydride unit were not observed in the first fraction (Fig. 5a), new peaks appeared in the olefinic carbon region. The newly observed peaks at 125.0, 125.2, 131.8 and 132.3 ppm were determined to be CH and those at 129.0–129.5 and 130.5–130.7 ppm quaternary carbon by the ^{13}C NMR measured in DEPT mode. The olefinic CH peaks at 125.0 and 125.2 ppm indicate the terminal structure of $(\text{CH}_3)_2\text{C}=\text{CHCH}_2-$ by reference to a model compound of 2-methyl-2-heptene [10].

^{13}C chemical shifts of 2-methyl-2-heptene



trans-CH₃ and *cis*-CH₃ were also observed at 25.7–25.8 and 17.5–18.0 ppm, respectively, in Fig. 5a. The quaternary carbon peaks were observed at 130.5–130.7 ppm.

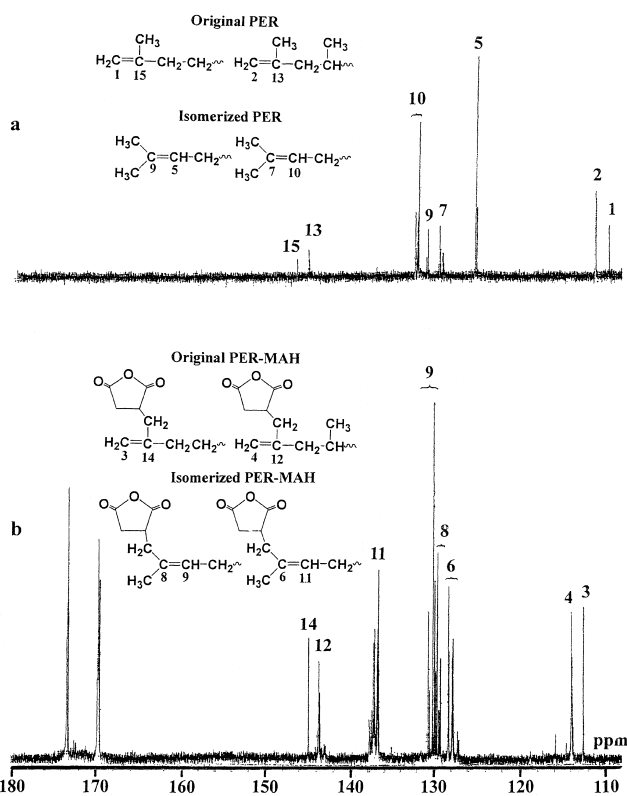
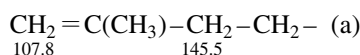
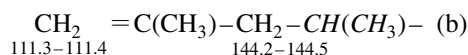


Fig. 5. Expanded ^{13}C NMR spectra between 108 and 180 ppm of the first (a) and the second (b) fractions of PER-MAH.

Since the original PER has two types of vinylidene structures shown below

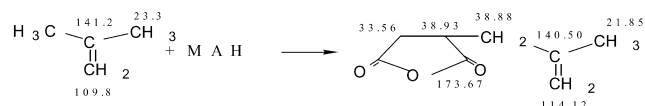


and



it is obvious that newly formed terminal groups formed by isomerization have two corresponding groups, that is, $(\text{CH}_3)_2\text{C}=\text{CHCH}_2-$ (c) and $(\text{CH}_3)_2\text{C}=\text{CHCH}(\text{CH}_3)-$ (d). The olefinic CH carbon of (d), which undergoes a downfield shift due to the additional β -methyl carbon, resonates at 131.8–132.3 ppm. On the other hand, quaternary carbon of (d), which has induced an upfield shift by the additional γ -methyl carbon, is observed at 128.6–129.5 ppm, respectively.

On the other hand, the peaks assigned to C=O of succinic anhydride unit were clearly observed at 169.7–169.9 and 173.5 ppm in the second fraction (Fig. 5b). The terminal groups of (a)–(d) reacted with MAH to form adducts. The olefinic carbon peaks of MAH adducts were assigned on the chemical shifts of model compounds shown below [11,12]

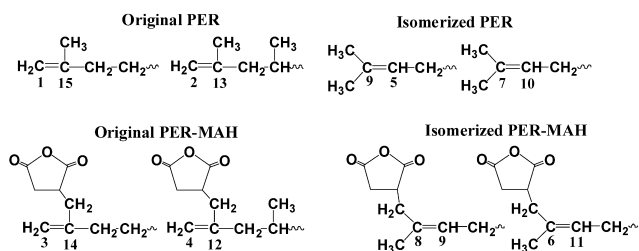


The addition of MAH induces the lower field shift (ca.

Table 1
Chemical shifts of PER–MAH

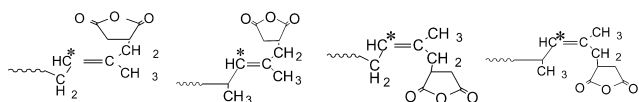
Number	δ (ppm)	Carbon species	Comments	For determination
1	109.7	CH ₂ =	Original PER	Use
2	111.4	CH ₂ =	Original PER	Use
3	112.5	CH ₂ =	Original PER–MAH	Use
4	113.8–113.9	CH ₂ =	Original PER–MAH	Use
5	125.0–125.2	CH=	Isomerized PER	Use
6	127.1–128.3	C(quaternary carbon)	Isomerized PER–MAH	
7	128.6–129.1	C(quaternary carbon)	Isomerized PER	
8	129.2–129.8	C(quaternary carbon)	Isomerized PER–MAH	
9	129.8–130.6	CH=C, C(quaternary carbon)	Isomerized PER–MAH, isomerized PER	Use
10	131.8–132.3	CH=	Isomerized PER	Use
11	136.6–137.7	CH=	Isomerized PER–MAH	Use
12	143.7–143.8	C(quaternary carbon)	Original PER–MAH	
13	144.3–144.5	C(quaternary carbon)	Original PER	
14	145.0	C(quaternary carbon)	Original PER–MAH	
15	145.7	C(quaternary carbon)	Original PER	

Numbering of atoms is as follows:



4 ppm) for vinylidene CH₂ and the upper field shift (ca. 0.7 ppm) for quaternary carbon. Newly detected CH₂ at 112.5 and 113.9 ppm and quaternary carbon at 143.7, 143.8 and 145.0 ppm are attributable to MAH addition to the original vinylidene group from the shift differences.

The addition of MAH induces the similar chemical shift change to the olefin carbon of tri-substituted structure of (CH₃)C=CH-. From the induced chemical shift change and DEPT data, the peaks at 136.6–137.8 and at 129.8–130.1 ppm were assigned to the carbons with the asterisk marks, respectively, shown below,



The quaternary carbons of the above structures were likewise assigned by the chemical shift empirical rules.

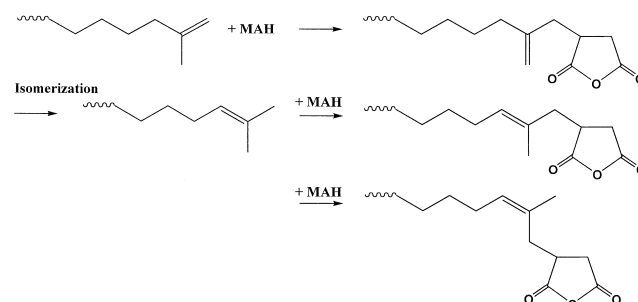
The *cis*-CH₃ group of the above structures was observed at 15.5–15.8 ppm and *trans*-CH₃ at 22.5–22.8 ppm, (where 22.7 ppm were assigned to methylene adjacent to methyl of allyl terminal) with the equal intensities, which means that both *cis* and *trans*-CH₃ have the same reactivity to MAH.

The peak assignments concerning the olefin carbons are listed in Table 1, which shows the existence of the following four main polymer structures, that is, PER–MAH, isomerized PER–MAH, original PER, and isomerized PER with

the ratio of 21:60:6:13 on the basis of the areas of the relating peaks. As ca. 80% of terminal group reacted with MAH, PER–MAH has M_n of 680 ($600 + 98 \times 0.8$), giving that this obtained polymer has 12 wt% of succinic anhydride content. Terminally MAH-functionalized PER was produced via the reaction of MAH with PER. The presence of the structures of isomerized PER suggests that reaction between PER and MAH causes isomerization of vinylidene double bond and a formation of a double bond (CH₃)₂=CH- as shown Scheme 1.

4. Conclusion

Metallocene-catalyzed PER, which is a potentially useful polymer from the scientific and industrial viewpoint, was



Scheme 1. Reaction of MAH with PER.

made to react with MAH for introducing functionality. The obtained reaction product (PER–MAH) was fully investigated by ^{13}C NMR spectroscopy to elucidate the detailed structure. From NMR analysis, it is clarified that a large part of the vinylidene end groups isomerize to form the thermodynamically more stable internal double bond. Both of olefinic end groups reacted with MAH to form terminally MAH-functionalized PER. The reaction products were analyzed to contain PER–MAH, isomerized PER–MAH, original PER and isomerized PER in the ratio of 21:60:6:13 at this experiment.

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