

Communication

# Synthesis of Brominated Polyethylene by Copolymerization of Ethylene with $\omega$ -bromoalkene Catalyzed by a Metallocene and Methylaluminoxane System

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**Abstract:** The metallocene-catalyzed copolymerization of ethylene and 11-bromo-1-undecene was carried out to synthesize brominated polyethylene (PE). A modified methylaluminoxane (MMAO) solution was used as a cocatalyst and *rac*-Et(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub> as a catalyst. The copolymerization showed a high activity and afforded the copolymer with a 11-bromo-1-undecene incorporation ranging from 1.0 to 4.3 mol%. When using a dried methylaluminoxane (dMAO) as a cocatalyst, the incorporation ratio of 11-bromo-1-undecene increased remarkably to 25.2 mol%. It was demonstrated that the type of MAO used as a cocatalyst affects the composition of the ethylene/11-bromo-1-undecene copolymer without changing the structure of the catalytic complex.

**Keywords:** metallocene; methylaluminoxane; copolymerization;  $\omega$ -bromoalkene; brominated PE

## 1. Introduction

Polyolefins, such as polyethylene (PE) and polypropylene (PP), account for more than half of the industrial polymers used worldwide. In recent years, specialized applications require polyolefins with various functionalities. However, since polyolefins consist only of carbon and hydrogen, they lack functional groups, and the diversification of their structure is limited. For this reason, several investigations have been conducted into the introduction of functional groups into the polyolefin structure. In general, three methods can be used for the functionalization of polyolefins. The first consists of the direct introduction of a functional group into the polyolefin by using a radical. The second is functionalizing a polyolefin with a reactive site inside the polymer [1–7]. The third is the copolymerization of an olefin and a monomer with a functional group [8–10]. The functionalization of polyolefins using radicals is performed under severe conditions, which may affect the decomposition and crosslinking of the polymer, changing the properties of the original polymer. Therefore, it seems that copolymerization is a more efficient and simple method. Some studies on olefin copolymers have used monomers with an active functional group that can be substituted, such as halogenated alkyl moieties. From such halogen-containing polymers, the synthesis of a polyolefin functionalized by the polymer reaction of various reagents is expected. For example, the synthesis of homo-poly(11-chloro-1-undecene), a modified polymer, was carried out using highly reactive side-chain chlorine with a base, such as potassium carboxylate or potassium hydroxide [6]. The copolymerization of halogenated olefins and non-functionalized olefins has also been reported; *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> and (pyridine-amido)hafnium are used as catalysts, and halogen-containing isotactic polypropylene is obtained [6,7].

It was reported that the polymerization characteristics change based on the comonomer used for the copolymerization and the length of the methylene chain between the olefin and the halogen [6,7]. Comparing the copolymerization of 11-bromo-1-undecene and propylene with that of 4-bromo-1-butene and propylene, 4-bromo-1-butene could not be introduced into the synthesized polymer under the same conditions in which 4-bromo-1-butene was added, and only homo-polypropylene was formed. It is known that in the copolymerization with a halogenated olefin, the chain length of the monomer is an important parameter. In addition, for the copolymerization using 11-chloro-1-undecene and 11-iodo-1-undecene as monomers, the amount of comonomer in the polymer and the activity changed when increasing the monomer amount [6,7]. Comparing the activity when using 11-halogenated undecenes with different halogen atoms in a copolymerization system using *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>/methylaluminoxane (MAO), the activity increases as follows: chloro < bromo < iodo. However, when the amount of the alkenes introduced in the copolymer was compared, there was almost no difference. As mentioned above, halogenated olefins are known to exhibit interesting polymerization properties. In many cases, changing the ligand structure of the complex in the catalyst system can change the polymerization activity and the microstructure of the polymer [11–14].

MAO, which is widely used as cocatalyst, also has a great influence on the polymerization and is still a subject of investigation [15–19]. In particular, free-AlR<sub>3</sub> causes coordination to the metal center, which leads to a decrease in the polymerization activity and molecular weight due to transmetalation [20–26]. Thus, it is important to verify the effect of the catalyst system in copolymerization. However, there are few reports in which the composition of the copolymer changes without changing the structure of the complex used.

In this work, we examined the copolymerization of ethylene and an 11-bromo-1-undecene (C'11-Br) using *rac*-Et(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub> (Figure 1) as a complex catalyst. Brominated polyethylene would be a potential graft polymer with a polar segment provided by copolymerization initiated using the controlled radical polymerization of polar monomers and polyethylene-based materials modified by S<sub>N</sub>2, Friedel-Crafts and cross-coupling reactions. The activity and polymerization characteristics for the copolymerization of ethylene with 11-bromo-1-undecene were compared by using two kinds of MAO as cocatalyst: a toluene solution of modified MAO (MMAO) containing trialkylaluminum (AlR<sub>3</sub>), and dried MAO (dMAO) with no trialkylaluminum (AlMe<sub>3</sub>).

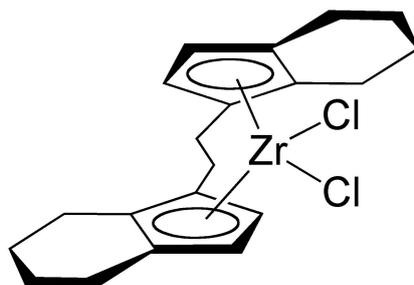


Figure 1. The structure of *rac*-Et(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub>.

## 2. Results and Discussion

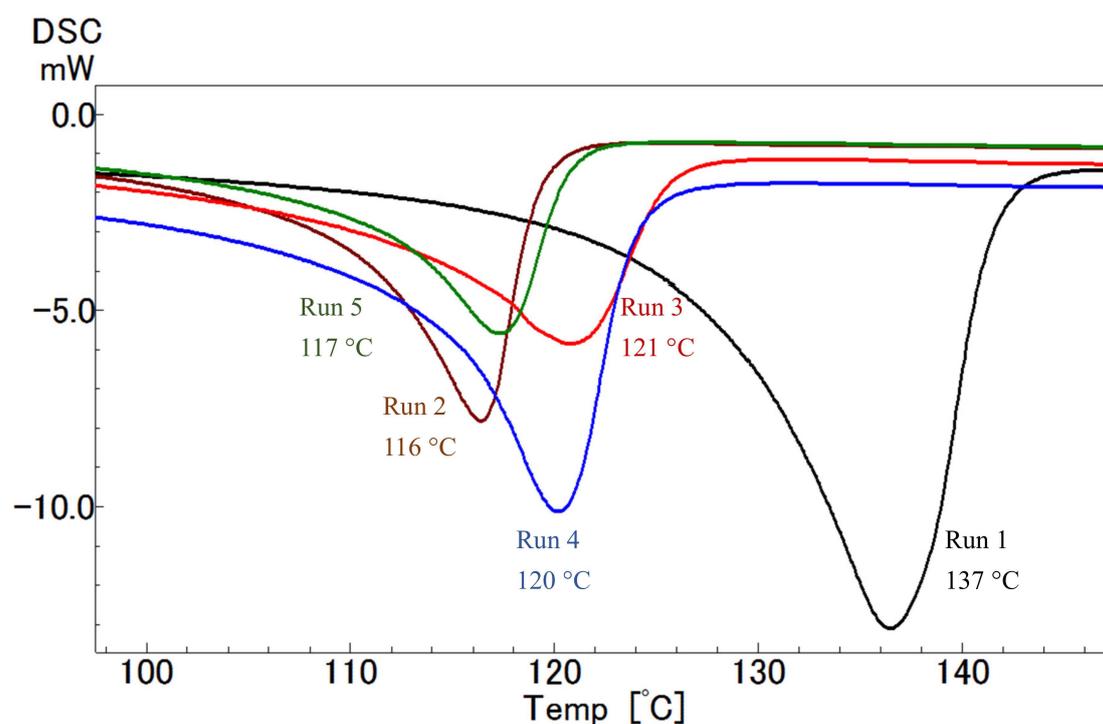
Table 1 shows the results of the copolymerization of ethylene and C'11-Br. First, ethylene homopolymerization proceeded in a *rac*-Et(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub>/MMAO system in ethylene at 0.1 MPa to give a white powder polymer (run 1). A linear methylene chain was observed in the <sup>1</sup>H NMR spectrum, and a high melting point (137 °C) derived from a crystalline phase was recorded during DSC, confirming that the product corresponds to a high density polyethylene. Next, the ethylene and C'11-Br copolymerization with the catalytic system was examined. The reaction proceeded under similar conditions to the homopolymerization (run 1), and a white solid was obtained (run 2). The polymer had a melting point (T<sub>m</sub>) at 116 °C (Figure 2). Compared to the polyethylene obtained by homopolymerization (run 1, 137 °C), the melting point was significantly lowered, suggesting that

C'11-Br was introduced into the copolymer. In addition, the activity in run 2 (copolymerization) was significantly reduced compared to run 1. Although a decrease in the polymerization activity is generally observed in the copolymerization of ethylene and other olefins, it is considered that C'11-Br, which is a  $\omega$ -halogenated- $\alpha$ -olefin, could cause a remarkable decrease in the polymerization activity.

**Table 1.** Copolymerization of ethylene with 11-bromo-1-undecene (C'11-Br).

Run	C'11-Br (mmol)	Cocatalyst	Ethylene	Activity ( $10^4$ g/mol h)	Incorp of C'11-Br <sup>b</sup> (mol%)	T <sub>m</sub> <sup>c</sup> (°C)	Degree of Crystallinity <sup>c</sup> (%)
1	-	MMAO	1 atm	27.0	-	137	45
2	4.6	MMAO	1 atm	2.9	2.9	116	23
3	4.6	MMAO	3.5 L	108.7	1.0	121	27
4	9.2	MMAO	3.5 L	25.2	3.3	120	25
5	13.8	MMAO	3.5 L	20.4	4.3	117	22
6	4.4	dMAO	3.5 L	30.9	25.2	T <sub>g</sub> = -69	-

a: Polymerization conditions. CH<sub>2</sub>Cl<sub>2</sub> = 100 mL, Zr = 2.3  $\mu$ mol, Al = 5.3 mmol, at 25 °C, reaction time = 1 h.  
 b: Determined by <sup>1</sup>H NMR. c: Determined by differential scanning calorimetry (DSC). Degree of crystallinity from  $\Delta H_m/\Delta H_{m0}$ ;  $\Delta H_{m0}$ ; the heat of fusion for 100% crystalline PE is 293 J/g.



**Figure 2.** The DSC melting curves of the polymers (runs 1–5).

The <sup>1</sup>H NMR spectrum of the polymer obtained in run 2 shows a signal at around 3.51 ppm (Figure 3). The signal of methylene ( $-\text{CH}_2-\text{Br}$ ) adjacent to bromine in the C'11-Br monomer is observed at 3.4 ppm, and the peak at 3.5 ppm has also been reported in the copolymerization using C'11-Br [7]. This signal was considered to correspond to  $-\text{CH}_2-\text{Br}$ , thus confirming that the copolymerization proceeded. These results show that the copolymer has a linear polyethylene structure with a  $-\text{CH}_2\text{Br}$  side-chain group. In addition, the signals at 6.13 ppm and 5.29 ppm have integral values of 0.48 and 0.85 H, respectively; i.e., the intensity of the 5.29 ppm signal is about twice that at 6.13 ppm, which is derived from the terminal olefin proton.

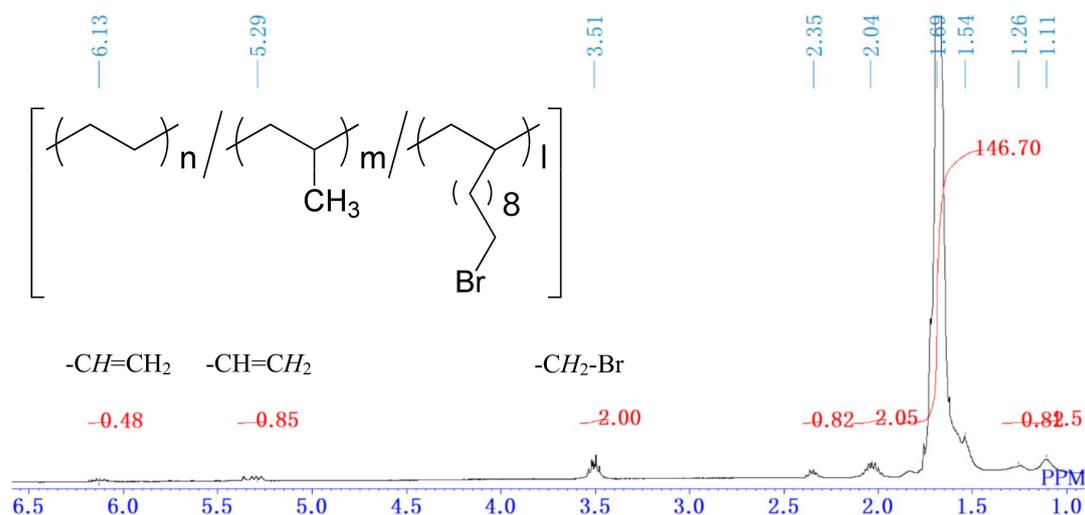
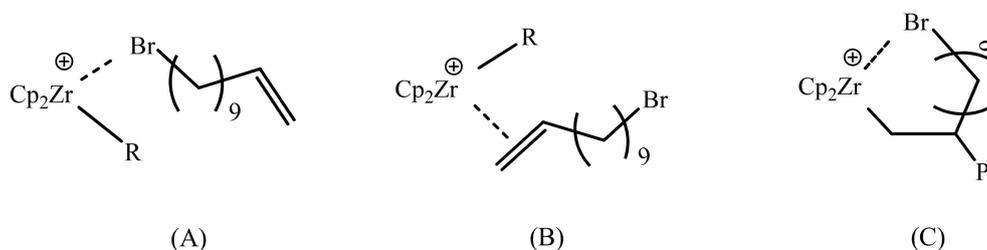


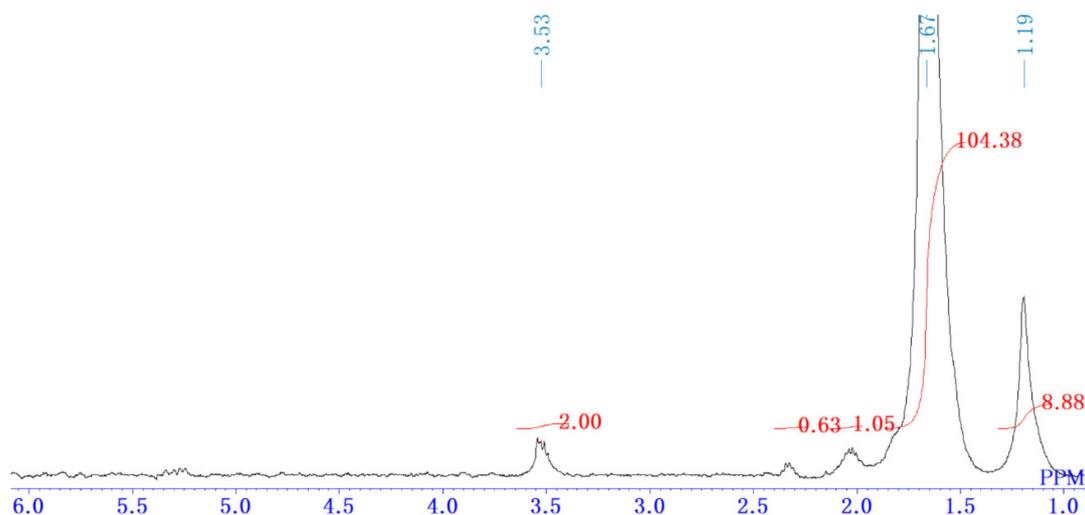
Figure 3. The NMR spectrum of brominated polyethylene (run 2),  $C_6D_6/ODCB$ , at  $100\text{ }^\circ\text{C}$ .

This olefin proton was not observed in the homopolymerization of ethylene, suggesting that the addition of  $C'11\text{-Br}$  to the polymerization system leads to a decrease in the molecular weight of the polymer when compared to run 1. In other words, during copolymerization,  $\beta$ -hydrogen elimination occurred, and olefin protons can be observed. Previous studies have predicted that  $\omega$ -halogenated- $\alpha$ -olefins coordinate to the zirconium cation [6,7]. Furthermore, in this system, the addition of a  $C'11\text{-Br}$  monomer may inhibit the polymerization, where the coordination to the metal center of the  $C'11\text{-Br}$  monomer by bromine (A) or olefin (B), and the  $C'11\text{-Br}$  part in the end units of a grown polymer chain inserted to a Zr catalyst (C), is expected (Scheme 1) [7]. Such coordination in the active species would inhibit the insertion of the next monomer and promote the termination of  $\beta$ -hydrogen elimination.



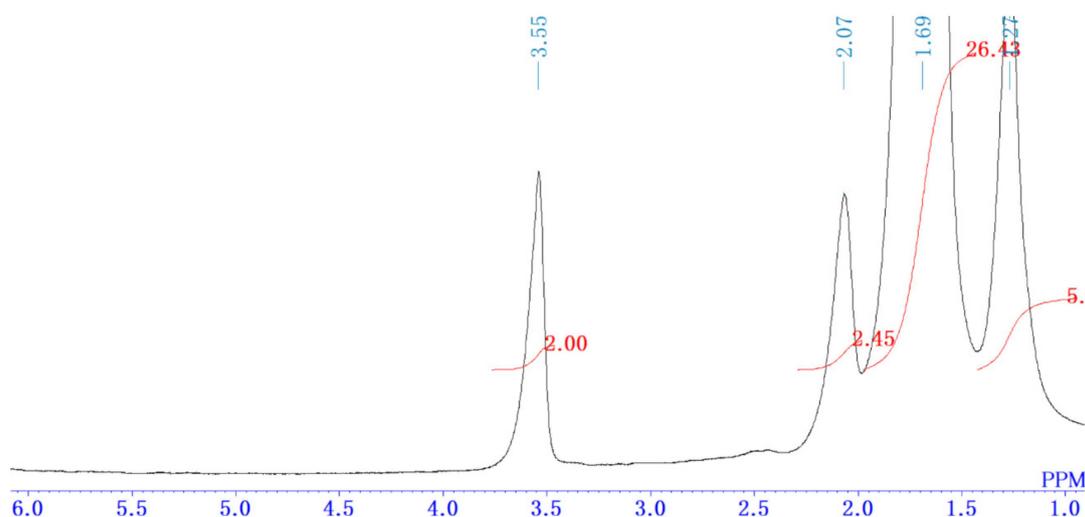
Scheme 1.  $C'11\text{-Br}$  monomer coordination to the metal center by (A) bromine or (B) olefin, and (C)  $C'11\text{-Br}$  in the polymer chain inserted into the Zr catalyst.

When polymerization was carried out in a pressurized system using 3.5 L of ethylene in a 500 mL autoclave (run 3), the amount of  $C'11\text{-Br}$  decreased and the activity increased compared to run 2, which was a normal pressure system. Thus, it is considered that the polymerization of ethylene was promoted by the increase of the ethylene concentration; also, the ratio of ethylene in the copolymer increased. Similarly, by increasing the amount of  $C'11\text{-Br}$  to 9.2 and 13.8 mmol under high-pressure conditions and with 3.5 L of ethylene, the proportion of  $C'11\text{-Br}$  in the copolymer increased, and the activity and melting point decreased. The  $^1\text{H}$  NMR spectrum of the polymer obtained in run 5 is shown in Figure 4. In the propylene/ $C'11\text{-Br}$  copolymerization using *rac*-Et(Ind) $_2$ ZrCl $_2$ /MAO, it was reported that, as the amount of  $C'11\text{-Br}$  increased its incorporation into the polymer increased, the activity decreased and the melting point was no longer observed [7].



**Figure 4.** The  $^1\text{H}$ -NMR spectrum of brominated polyethylene (run5) in  $\text{C}_6\text{D}_6/\text{ODCB}$  at  $100\text{ }^\circ\text{C}$ .

Next, to evaluate the effect of a cocatalyst in the copolymerization, we used a dMAO, which is a trialkylaluminum-free cocatalyst. In this case, although the activity was lower than that of the system using MMAO as a cocatalyst under the same conditions, the incorporation of C'11-Br increased dramatically (25.2 mol%, run 6, Figure 5). The  $^1\text{H}$  NMR signal that was observed was broad. Accordingly, it was considered that the sample used for the NMR measurement was completely dried after reprecipitation, and thus the broad signal resulted from crosslinking and gelation. As described later, the polymer obtained when using dMAO had the highest incorporation of C'11-Br; thus, the influence of gelation is remarkable in the  $^1\text{H}$  NMR spectrum. Moreover, a melting point was not observed in the DSC of the copolymer. This is likely because the number of polyethylene segments in the copolymer decreases and their corresponding crystalline section also decreases. Meanwhile, the glass transition temperature ( $T_g$ ) was at  $-69\text{ }^\circ\text{C}$ . In previous reports, where ethylene and 1-hexene, a long-chain  $\alpha$ -olefin, are copolymerized using Group 4 CGC-catalysts, the copolymer with 15.8% of 1-hexene has a melting point of  $T_m = 52\text{ }^\circ\text{C}$ , but no melting point is reported for systems with 22.3% and 27.3% of 1-hexene [27–29]. Similarly, for the copolymer from run 6, using dMAO, where the amount of incorporated C'11-Br was 25.2%, the melting point was not observed.



**Figure 5.** The  $^1\text{H}$  NMR spectrum of brominated polyethylene (run6) in  $\text{C}_6\text{D}_6/\text{ODCB}$  at  $100\text{ }^\circ\text{C}$ .

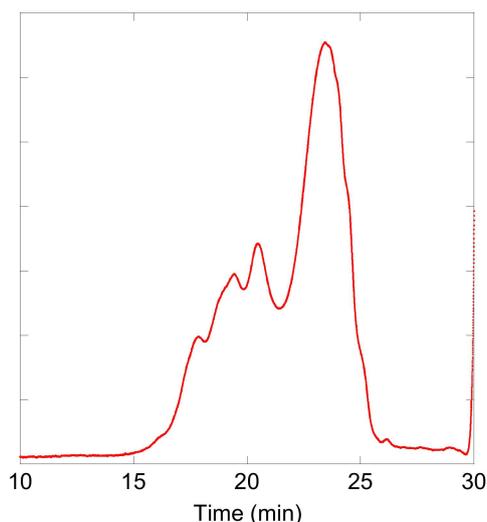
When using dMAO as the cocatalyst, the amount of C'11-Br introduced into the copolymer significantly increased. Comparing aluminoxanes, when MAO, ethylaluminoxane and

isobutylaluminumoxane are used as cocatalysts in ethylene polymerization, with  $\text{Cp}_2\text{ZrCl}_2$  as the catalyst, MAO is the most active [30]. In our system, focusing on the isobutyl and methyl groups to compare MMAO and dMAO as cocatalysts, it is likely that the rate of transmetalation and extraction of the alkyl group may change when releasing the polymerization active species. C'11-Br is easily inserted in the presence of the expected  $\text{rac-Et}(\text{H}_4\text{Ind})_2\text{Zr}^i\text{Bu}$  cation or in the presence of the hydride zirconium cation that is generated when the isobutyl group of this cation species is eliminated as isobutene. However, only the first monomer in the polymerization is easily inserted when the zirconium cations are involved, and it is thus unlikely that this is the cause of the remarkable increase in the amount of introduced C'11-Br. Instead, the amount of C'11-Br in the copolymer may be related to free  $\text{AlR}_3$ , which is another difference between dMAO and MMAO. The latter contains 19.4 mol% ( $\text{AlMe}_3$ : 10.6 mol%,  $\text{Al}^i\text{Bu}_3$ : 8.8 mol%) of free  $\text{AlR}_3$  in total, but dMAO has no free  $\text{AlMe}_3$ . Recent studies reported that in the Zirconocene/MAO system, two species are observed, an ion pair of  $[\text{Cp}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]$  cation with some Me-MAO counteranions, and a species containing a  $\text{Cp}_2\text{ZrMe}$  cation in contact with a  $\text{CH}_3$  group of a stable Me-MAO anion [16–18]. In that case, the cocatalyst is expected to take the state of the  $\text{Cp}_2\text{Zr}(\mu\text{-R})_2\text{AlR}_2$  cation ( $\text{R} = \text{Me}$ , polymer chain). For C'11-Br, which is bulkier than ethylene, the steric hindrance of the cationic center in the active species is a relevant factor. Therefore, in the dMAO system, it is considered that the steric hindrance around the active species is relatively smaller, C'11-Br is easily coordinated and inserted, and the incorporation amount increases. In addition, some coordination of C'11-Br is expected, and when the Zr cation coordinated by C'11-Br is stable, the next insertion is unlikely to occur, and the activity decreases. Hence, the activity is lower than that of the system using MMAO as a cocatalyst under the same conditions. Usually, the role of MAO is to generate active species from a complex precursor, and in the middle of polymerization this effect is not very relevant. It is known that some living polymerizations are successful depending on the type of counter anion. However, in this study it was demonstrated that the type of MAO affects the composition of the copolymer, which is relevant for the synthesis of new functional polymers.

The copolymers (runs 2–5) obtained using MMAO as the cocatalyst were insoluble in THF, but the products obtained using dMAO (run 6) were soluble. However, they precipitated when left to stand at room temperature in the air for a few days. For the copolymer of run 6, SEC showed a multimodal chromatogram with a number average molecular weight of 2.4 kg/mol as the main peak and a polydispersity ( $M_w/M_n$ ) of 4.6 (Figure 6). This multimodal chromatogram probably arises because the unit derived from C'11-Br in the copolymer is decomposed and causes crosslinking, resulting in a unit with a high molecular weight. The thermal stability of the copolymer was investigated by IR and by Soxhlet extraction; the results are described in the following sections. In addition, the  $^1\text{H}$  NMR spectrum of the copolymer of run 6 shows no signal from an olefin proton. In the system using MMAO as a cocatalyst, the olefin proton was observed, and it is possible that  $\beta$ -hydrogen elimination easily occurs when free  $\text{AlR}_3$  is present. Therefore, it was concluded that  $\beta$ -hydrogen elimination was suppressed by the lack of free  $\text{AlR}_3$  in the polymerization system.

### 2.1. Soxhlet Extraction of E/C'11-Br Copolymer

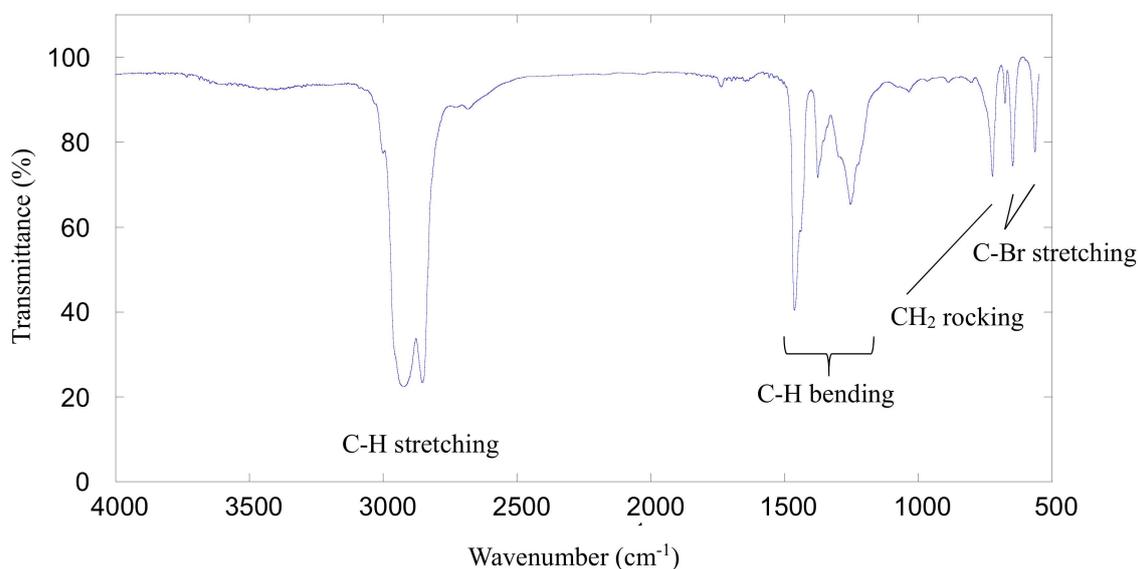
To evaluate the thermal stability of the obtained polymer, the degree of crosslinking was investigated using the copolymer obtained when dMAO was used as a cocatalyst (run 6; C'11-Br: 25.2 mol%). The sample was decanted after the reprecipitation of the polymer and was used without drying. The degree of crosslinking was investigated using two samples. The first sample was obtained by heating the obtained polymer, and the second sample was a non-heat-treated polymer. For the former, the polymer was heated at 100 °C for 12 h, and a Soxhlet extraction was performed for 10 h using 150 mL of  $\text{CH}_2\text{Cl}_2$ . After extraction, 60 wt% of the sample was dissolved in  $\text{CH}_2\text{Cl}_2$ , and the insoluble component was 40 wt%. A Soxhlet extraction was similarly performed for the non-heated sample. In this case, the insoluble component was 12 wt%. Based on these results, it can be inferred that crosslinking occurred during the heat treatment, when the polymer was insolubilized due to gelation.



**Figure 6.** The SEC chromatograms of brominated polyethylene (run 6).

## 2.2. IR Spectrum of E/C'11-Br Copolymer

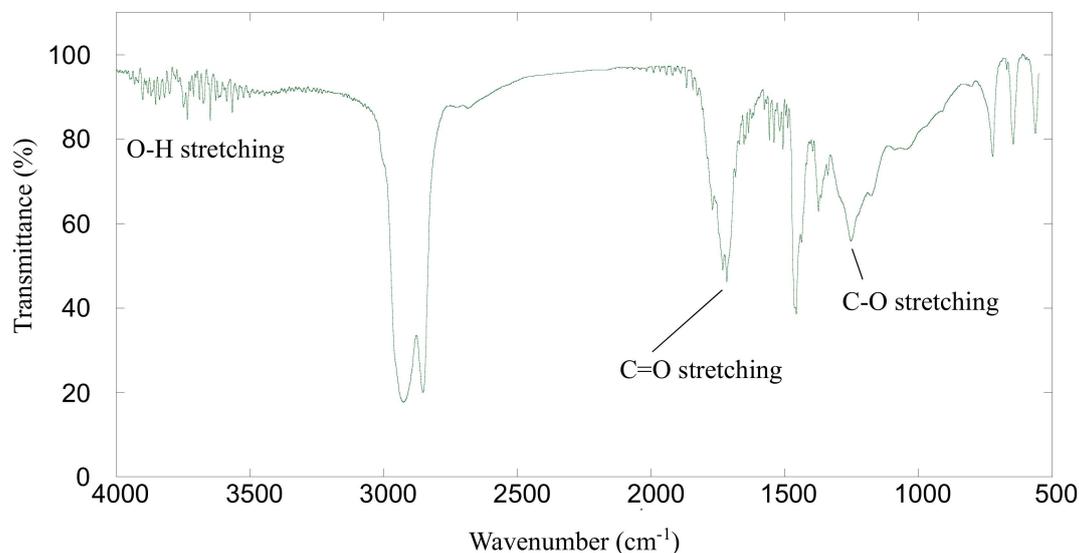
The copolymer containing C'11-Br units becomes insoluble during the drying for the instrumental analysis. Therefore, it was suspected that gelation occurs due to aging or heating. IR was performed to confirm whether the structure of the copolymer changes when heated. The sample used was the ethylene/C'11-Br copolymer from run 6 (C'11-Br: 25.2 mol%), and it was used without drying after reprecipitation. For the measurement, a thin film was prepared by dripping the sample dissolved in THF onto a single crystal silicon wafer and then drying. Then, the measurement was repeated after drying at 150 °C for 10 h in air. The spectra before and after heating are shown in Figures 7–9.



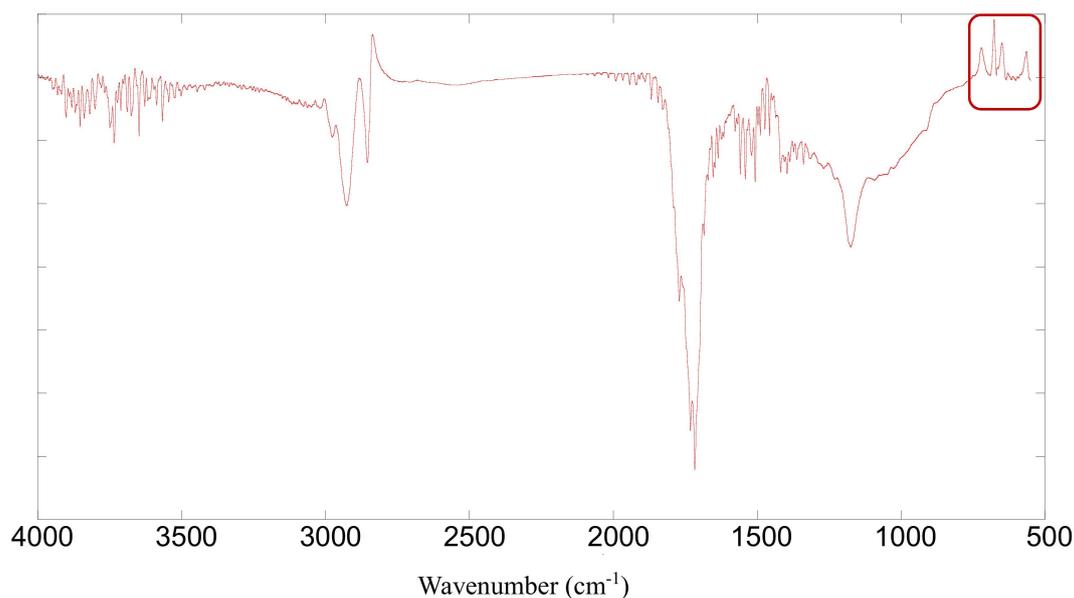
**Figure 7.** The IR spectrum of brominated polyethylene (run 6) before heating.

The spectrum of the heated sample indeed changed. Before heating, there are absorption bands that can be assigned to C–Br stretching at 647 and 564  $\text{cm}^{-1}$ , in addition to the C–H stretching at around 2900  $\text{cm}^{-1}$ , C–H bending at 1458, 1374, and 1253  $\text{cm}^{-1}$ , and  $\text{CH}_2$  rocking at 722  $\text{cm}^{-1}$ , derived from polyethylene (Figure 7) [31]. The IR spectrum after heating shows strong absorption bands at 1716 and 1175  $\text{cm}^{-1}$ , assigned to C=O and C–O stretching, and a weak absorption considered to be O–H stretching (Figure 8). Furthermore, the differential spectrum (Figure 9) shows that the absorption band corresponding to C–Br stretching and that of  $\text{CH}_2$  rocking decrease after heating. This suggests

that bromine elimination and oxidation by oxygen in the air have occurred. The attenuation at  $720\text{ cm}^{-1}$  further suggests a decrease in crystallinity, which is believed to be due to the crosslinking of the polymer chains, in addition to the oxidation described above [32].



**Figure 8.** The IR spectrum of brominated polyethylene (run 6) after 10 h at  $150\text{ }^{\circ}\text{C}$ .



**Figure 9.** The differential IR spectrum obtained from Figures 7 and 8.

### 3. Experimental Section

#### 3.1. General Methods

Air- and/or moisture-sensitive compounds were manipulated using either standard Schlenk-line techniques or inside a glovebox under an inert atmosphere (argon or nitrogen). 11-Bromo-1-undecene (C'11-Br) and all solvents were purchased from FUJIFILM Wako Pure Chemical Corp (Osaka, Japan) and were dried over a molecular sieve before use. Ethylene was purified by passing through deoxygenated and dehydrated columns from GL Sciences Inc (Tokyo, Japan). *rac*-Et( $\text{H}_4\text{Ind}$ ) $_2\text{ZrCl}_2$  was donated by KOEI CHEMICAL Co. Ltd (Tokyo, Japan). MMAO (MMAO-3A, toluene solution) and solid-MAO

slurry were donated by Tosoh Finechem Corp (Yamaguchi, Japan), and dried MAO (dMAO) was prepared by the filtration of the solid-MAO slurry in toluene.

### 3.2. Ethylene Homopolymerization and Ethylene/C'11-Br Copolymerization (Atmospheric Pressure Polymerization System)

CH<sub>2</sub>Cl<sub>2</sub> (95 mL) and a MMAO solution were introduced in an Ar-filled 200 mL two-necked flask. After that, the flask was filled with ethylene (200 mL/min for 1 h). In the copolymerization system, C'11-Br was added, and the mixture was stirred for 5 min. Thereafter, polymerization was initiated by introducing 5 mL of *rac*-Et(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>. The reaction was carried out at 25 °C for 1 h at 0.1 MPa and then quenched using a small amount of methanol. The mixture was purified by reprecipitation by adding the solution to *ca.* 500 mL of methanol/12 N hydrochloric acid (490 mL/10 mL). The solid was filtered, washed with methanol and vacuum dried at 50 °C until a constant weight was obtained.

### 3.3. Ethylene/C'11-Br Copolymerization (High-pressure Polymerization System)

After replacing the inside of the container of a 500 mL autoclave with argon, 100 mL of CH<sub>2</sub>Cl<sub>2</sub>, MMAO solution or dMAO, C'11-Br, and *rac*-Et(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub> were added. Then, the autoclave was cooled using liquid nitrogen to freeze the solution. Using a gas flow meter, 3.5 L of ethylene were introduced, and simultaneously liquefied, into the autoclave. The reaction vessel was sealed and heated at 25 °C in a water bath. The polymerization reaction started when the solution melted and the rotational noise of the stirrer tip could be heard. The temperature was maintained at 25 °C for 1 h. After the polymerization, the remaining monomer gas was released from the inside of the reaction vessel using the autoclave's valve. A small amount of methanol was added to quench the reaction. Reprecipitation was performed to purify the mixture by adding the solution to *ca.* 500 mL of methanol/12 N hydrochloric acid (490 mL/10 mL). The obtained polymer was filtered, washed with methanol and vacuum dried at 50 °C until a constant weight was achieved.

### 3.4. Characterization of the Polymer

A size-exclusion chromatogram (SEC) was obtained at 40 °C using a TOSOH HLC-8220 instrument equipped with three polystyrene gel columns [TOSOH TSKgel G2000HXL+G3000HXL+G4000HXL (7.8 mm × 30 cm)] and UV (254 nm) and refractive index detectors. THF was used as the carrier solvent at a flow rate of 1 mL/min. The molecular weight was based on the polystyrene standard calibration (580, 840, 2630, 5200, 9500, 18,100, 37,900, 96,400 g/mol). The glass transition temperature (T<sub>g</sub>) and melting point (T<sub>m</sub>) of the polymers were measured using a Shimadzu DSC-60Plus differential scanning calorimeter (DSC) under nitrogen flow. Any thermal history difference of the polymers was eliminated by first heating to 150 °C at 20 °C min<sup>-1</sup>, cooling to -130 °C at 20 °C min<sup>-1</sup>, then heating again to 150 °C at 10 °C min<sup>-1</sup>, and recording the second scan results. FT-IR spectra of the polymers were obtained by cast film FTIR on silicon wafers using a JASCO FT-IR4200 instrument. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the obtained polymers were recorded in CDCl<sub>3</sub> at RT or in C<sub>6</sub>D<sub>6</sub>/*o*-dichlorobenzene at 100 °C using a JEOL JNM-AL-400 spectrometer. The solvent peak was used as the reference.

$$\text{C'11-Br (mol\%)} = (12\text{I}_{3.4-3.6\text{ppm}})/(6\text{I}_{1.4-2.5\text{ppm}} + 2\text{I}_{1.0-1.4\text{ppm}} - 45\text{I}_{3.4-3.6\text{ppm}})$$

## 4. Conclusions

In the copolymerization of ethylene and 11-bromo-1-undecene (C'11-Br) using a *rac*-Et(H<sub>4</sub>Ind)<sub>2</sub>ZrCl<sub>2</sub>/MMAO catalytic system, the amount of C'11-Br incorporated into the copolymer (1.0 to 4.3 mol%) increased according to the amount of C'11-Br monomer added into the polymerization system. In addition, when using dMAO instead of an MMAO solution as a cocatalyst, the incorporation of C'11-Br increased dramatically (25.2 mol%). Thus, it was demonstrated that the kind of cocatalyst used in coordination polymerization affects the composition of the copolymer without changing the structure of the complex.

Since the ethylene/C<sup>11</sup>-Br copolymer was insolubilized when left standing for a few days, it was suspected that a reaction occurred. The thermal stability of the copolymer was analyzed by Soxhlet extraction and IR measurements. It was found that gelation easily occurs in the brominated polyethylene due to crosslinking and oxidation that result from the cleavage of the C-Br bond

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