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# Study on unsaturated structures of polyhexene, poly(4-methylpentene) and poly(3-methylpentene) prepared with metallocene catalysts

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## Abstract

Hex-1-ene (hexene), 4-methylpent-1-ene (4-MP-1) and 3-methylpent-1-ene (3-MP-1), homopolymerizations were conducted by using metallocenes, En(Ind)$_2$ZrCl$_2$ and *i*Pr(Cp)(Flu)ZrCl$_2$, with methylaluminoxane. $^1$H NMR analyses of the resulting polymers were carried out to identify the unsaturated structures of these polymers. In polyhexene and poly(4-MP-1), the detected main unsaturated structure was di-substituted vinylene. On the other hand, in poly(3-MP-1), vinylidene and tri-substituted vinylene structures were mainly observed for the first time.

*Keywords:* Polymer chemistry; Metallocene catalyst; Unsaturated structures in polyolefins

## 1. Introduction

Since the discovery of the metallocene catalyst system, the field of olefin polymerization has accelerated from just being considered technology to being seen as cutting-edge science due to the homogeneous active sites of the metallocene catalysts. It is generally known that metallocene-catalyzed polyolefins possess several unsaturated structures [1–11]. For example, vinyl, butenyl, isobutenyl and internal unsaturated structures have been reported as unsaturated structures in metallocene-catalyzed polypropylene. These unsaturated structures in the polymer chain can be utilized for the addition of a polar or other functional groups [12–17].

One of the other characteristics of metallocene catalysts is that they have good comonomer incorporation for polymerization with narrow molecular weight distribution polymers [5,9,18]. Furthermore, they can polymerize the branched bulky olefins compared with other catalysts. For instance, polyhexene and poly(3-MP-1) have already been synthesized by metallocene catalysts, and their stereochemistry [19–24] has been the subject of study. However, only a few studies have reported on the unsaturated structures of these polymers [25,26] although they are important industrially.

This paper briefly reports on the study of the unsaturated structures in polyhexene families, namely, polyhexene, poly(4-MP-1) and poly(3-MP-1), produced with metallocenes, En(Ind)$_2$ZrCl$_2$ and *i*Pr(Cp)(Flu)ZrCl$_2$, by $^1$H NMR analysis.

## 2. Experimental section

### 2.1. Materials

*i*Pr(Cp)(Flu)ZrCl$_2$ was prepared according to the literature [27]. En(Ind)$_2$ZrCl$_2$ was purchased from Sigma–Aldrich Co., and used as received. MAO was purchased as toluene solution (10 wt%) from Albemarle Co. and used without purification. Toluene purchased from Wako Pure Chemical Industries, Ltd. was dried over sodium metal and distilled. Hex-1-ene purchased from Wako Pure Chemical Industries,

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Ltd. was dried over molecular sieves (4 Å). 4-Methylpent-1-ene and 3-methylpent-ene monomers (Mitsui Chemicals) were dried over molecular sieves (4 Å) before use. Organometallic compounds were treated under a nitrogen atmosphere.

### 2.2. Polymerization

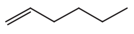
All polymerization experiments were carried out in 500 ml glass flasks equipped with mechanical stirrers, thermocouple and monomer inlet tubes. Monomer (250 ml) was added to the reactor. After heating the monomer to 45 °C, MAO in toluene (5 mmol [Al]) was added to the reactor, and then, the polymerization was started by the addition of 5 ml of toluene solution in dissolved metallocene (0.005 mmol) in the reactor. The temperature was maintained during the polymerization. After that, 5 ml of isobutanol was added to the reactor in order to terminate the polymerization. The reaction mixture was poured into 1 L of methanol. Polymers (H-3, -4, -5) were corrected by filtration and washed with 500 ml of methanol, then dried under reduced pressure at 80 °C for 10 h. Polymers (H-1, -2, -6) were separated from methanol by decantation and washed with methanol several times, then dried under reduced pressure at 80 °C for 10 h.

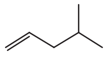
### 2.3. Analysis of polymer

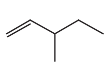
Molecular weights and molecular weight distributions were determined by gel-permeation chromatography (GPC) using *o*-dichlorobenzene as solvent. $^1$H NMR spectra were recorded on a JEOL JNM GSX-400 series in pulse Fourier transform mode. Instrument conditions were as follows: pulse angle, 45°; pulse repetition, 5.0 s; spectral width, 8000 Hz; temperature, 120 °C; data points, 32,768. Polymer solutions used for NMR were prepared by dissolving 50 mg of polymer sample in 0.5 ml of 1,2-dichlorobenzene-$d_4$ (ODCB) as solvents.

## 3. Results and discussion

We selected three kinds of olefin monomers that were isomers of hexene, namely, hex-1-ene (hexene) as linear monomer, 4-methylpent-1-ene (4-MP-1) and 3-methylpent-1-ene (3-MP-1) as branched ones. And we prepared polyhexene, poly(4-MP-1) and poly(3-MP-1), in monomer liquid pools at the same temperature with metallocenes, En(Ind)$_2$ZrCl$_2$ and *i*Pr(Cp)(Flu)ZrCl$_2$, chosen as typical representatives. It is known that these metallocenes could produce isotactic and syndiotactic polymers, respectively.


**Hexene**


**4-MP-1**


**3-MP-1**

Unsaturated structures of the resulting polymers were identified by $^1$H NMR with ODCB as a solvent to restrain the isomerization during the measurement [28]. Expanded $^1$H NMR spectra of the resulting polymers are shown in Fig. 1.

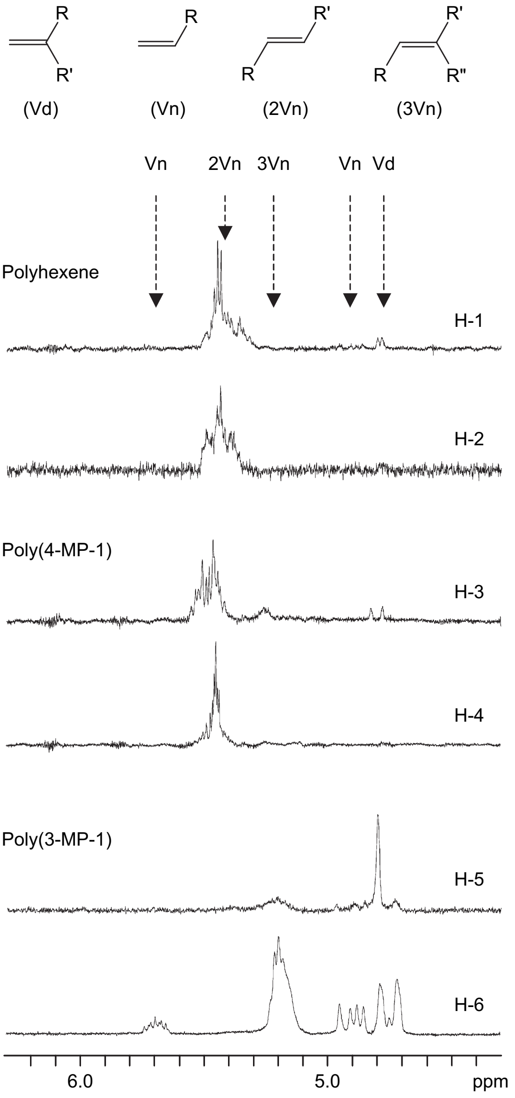


Fig. 1. Expanded $^1$H NMR of the olefinic region of the resulting polymers.

On the basis of the previous papers describing the assignment of $^1$H NMR spectra [1–5], several types of unsaturated structures could be observed in the resulting polymers: vinylidene, $CH_2{=}CRR'$ (Vd, between 4.7 and 4.8 ppm); vinyl, $CH_2{=}CHR$ (Vn, 4.9 and 5.7 ppm); tri-substituted vinylene, $RCH{=}CR'R''$ (3Vn, 5.2 ppm); and di-substituted vinylene, $RCH{=}CHR'$ (2Vn, between 5.3 and 5.5 ppm). The results of polymerization and the data of identified unsaturated structures are summarized in Table 1.

In polyhexene, which were H-1 and -2, di-substituted vinylene structure (2Vn) was identified as the main unsaturated structure, and a small amount of vinylidene one (Vd) was also observed. In the case of poly(4-MP-1), H-3 and -4, di-substituted vinylene structure (2Vn) was identified as the main unsaturated one, and a small amount of vinylidene one (Vd) was formed in both polymers. Furthermore, tri-substituted vinylene structure (3Vn) was observed in both polymers. In poly(3-MP-1), H-5 and -6, a tri-substituted vinylene structure (3Vn) was formed. Vinylidene one (Vd)

Table 1
Results of polymerization[a] with metallocene catalysts

| Run (#) | Monomer | Metallocene | Activity (g/mmol[Zr]/h) | $M_w$[b] (g/mol) | $M_w/M_n$ | Unsaturated groups in polymer[c] (unit mol%), in brackets, percentage of units in unsaturated structures | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 2Vn (RCH=CHR′) | Vd ($CH_2$=CRR′) | 3Vn (RCH=CR′R″) | Vn ($CH_2$=CHR) |
| H-1 | Hexene | En(Ind)$_2$ZrCl$_2$ | 32,448 | 29,500 | 1.94 | 0.54 (95) | 0.03 (5) | – | – |
| H-2 | Hexene | *i*Pr(Cp)(Flu)ZrCl$_2$ | 35,808 | 48,400 | 1.80 | 0.45 (97) | 0.01 (3) | – | – |
| H-3 | 4-MP-1 | En(Ind)$_2$ZrCl$_2$ | 4004 | 25,000 | 1.81 | 0.60 (79) | 0.04 (5) | 0.12 (16) | – |
| H-4 | 4-MP-1 | *i*Pr(Cp)(Flu)ZrCl$_2$ | 697 | 34,000 | 1.85 | 0.64 (80) | 0.02 (2) | 0.14 (18) | – |
| H-5 | 3-MP-1 | En(Ind)$_2$ZrCl$_2$ | 955 | 41,000 | 2.51 | – | 0.19 (46) | 0.19 (46) | 0.03 (8) |
| H-6 | 3-MP-1 | *i*Pr(Cp)(Flu)ZrCl$_2$ | 37 | 3150 | 2.14 | – | 0.61 (16) | 2.72 (74) | 0.38 (10) |

[a] Polymerization conditions: [Zr], 0.005 mmol; MAO, 5.0 mmol in 250 ml of monomer liquid pool. Polymerization time; 15 min (H-1, -2, -3, -4) and 60 min (H-5, -6).
[b] GPC data (PS standard).
[c] Estimated by $^1$H NMR.

was identified at some level. Moreover, vinyl structure (Vn) was formed in both polymers.

Unsaturated structures in polyolefin, in general, would be formed by termination reaction of a polymerization. Based on previous papers [1–8,28], schemes of possible formation reactions of unsaturated structures might be as indicated in Fig. 2. Accordingly, the following could be suggested: (a) the termination reaction of polymerization of hexene mainly occurred at the 2,1-inserted active chain-end by the elimination of a β-hydrogen of the growing polymer chain to a monomer or to the metal center of the catalyst as shown in Scheme (4). (b) In 4-MP-1 polymerization, the reactions at the 1,2-inserted active chain-end as shown in Schemes (1) and (2) occurred at some level besides at the 2,1-inserted active chain-end shown in Scheme (1). (c) In the case of 3-MP-1 polymerization, the termination reaction occurred at the 1,2-inserted active chain-end by the elimination of a β-hydrogen or a β-alkyl group as shown in Schemes (1)–(3).

In this study, remarkable differences were not observed in metallocenes, En(Ind)$_2$ZrCl$_2$ and *i*Pr(Cp)(Flu)ZrCl$_2$. Therefore, the differences in unsaturated structures among the resulting polymers could be attributed to an interaction between the branched methyl groups of the monomers and metallocene catalysts more than an influence of metallocene structures. In further investigations of detailed unsaturated structures of polymers, we should consider the isomerization by chain working [27] and the internal unsaturated ones by an allylic activation [26].

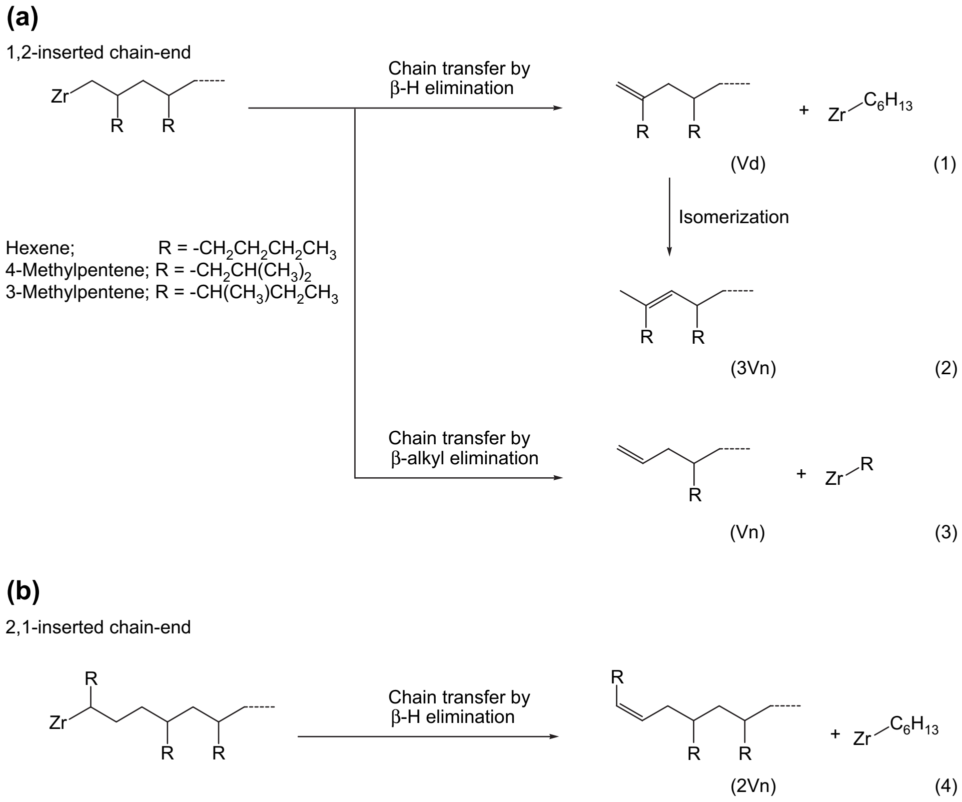


Fig. 2. Schemes of the possible formation reactions of unsaturated structures at the polymer chain-end.

## 4. Conclusion

Hexene, 4-MP-1 and 3-MP-1, homopolymerizations were conducted with metallocenes, En(Ind)$_2$ZrCl$_2$ and *i*Pr(Cp)(Flu)-ZrCl$_2$. $^1$H NMR analyses of the resulting polymers were carried out to identify the unsaturated structures of these polymers. In polyhexene and poly(4-MP-1), the di-substituted vinylene structure (2Vn) was mainly observed. On the other hand, in poly(3-MP-1), the tri-substituted vinylene (3Vn), vinylidene (Vd) and vinyl (Vn) structures were identified for the first time.

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