Higher α-Olefin Polymerizations Catalyzed by rac-Me$_2$Si(1-C$_5$H$_2$-2-CH$_3$-4-tBu)$_2$Zr(NMe$_2$)$_2$/Al(iBu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$]

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ABSTRACT: Polymerizations of higher α-olefins, 1-pentene, 1-hexene, 1-octene, and 1-decene were carried out at 30 °C in toluene by using highly isospecific rac-Me$_2$Si(1-C$_5$H$_2$-2-CH$_3$-4-tBu)$_2$Zr(NMe$_2$)$_2$ (rac-1) compound in the presence of Al(iBu)$_3$/[CPh$_3$][B(C$_6$F$_5$)$_4$] as a cocatalyst formulation. Both the bulkiness of monomer and the lateral size of polymer influenced the activity of polymerization. The larger lateral of polymer chain opens the π-ligand of active site wide and favors the insertion of monomer, while the large size of monomer inserts itself into polymer chain more difficultly due to the steric hindrance. Highly isotactic poly(α-olefin)s of high molecular weight (MW) were produced. The MW decreased from polypropylene to poly(1-hexene), and then increased from poly(1-hexene) to poly(1-decene). The isotacticity (as [mm] triad) of the polymer decreased with the increased lateral size in the order: poly(1-pentene) > poly(1-hexene) > poly(1-octene) > poly(1-decene). The similar dependence of the lateral size on the melting point of polymer was recorded by differential scanning calorimetry (DSC). $^1$H NMR analysis showed that vinylidene group resulting from β-H elimination and saturated methyl groups resulting from chain transfer to cocatalyst are the main end groups of polymer chain. The vinylidene and internal double bonds are also identified by Raman spectroscopy. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 1687–1697, 2000

Keywords: isospecific ansa-metallocene diamide; poly(1-pentene); poly(1-hexene); poly(1-octene); poly(1-decene); molecular weight; microstructure

INTRODUCTION

Due especially to the low commercial interest with the higher α-olefin polymers, studies on the polymerization and polymer characterization of higher poly(α-olefin) (PO) have not been carried out actively. Products derived from the longer, straight chain, α-olefins can be used in principle as base materials for lubricating oil formulation (low molecular weight) or as pour point depressants and chain transfer to cocatalyst. Chiral ansa-metallocene catalysts have also been studied for the homogeneous polymerization of higher α-olefins (C$_4$–C$_{18}$) in order to get high molecular weight polymer with high polymerization rate. The ansa-metallocene catalysts are single-site catalysts that show high activity coupled with

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high stereospecificity and narrow molecular weight distributions. The isospecific rac-(EBT-HI)ZrCl₂ [EBTHI = ethylene-1,2-bis(1-tetrahydrodrienedenyl)]/methylalumoxane (MAO) catalyst polymerizes 1-butene with high activity to an isotactic and waxy-crystalline material.5(d) From the same catalytic system a lower molecular weight (MW) oligomer was obtained whose end group structure was analyzed in terms the reaction mechanism of initiation and propagation with various transfer reactions.6 Crystalline, syndiotactic poly(1-pentene) was obtained with good polymerization activity using the syndiospecific Me₂C(Cp)(Flu)ZrCl₂/MAO catalyst.7 Polymerization of 1-hexene by using the same catalyst in polar solvent enhanced activity and reduced drastically the amount of MAO to obtain maximum activity.8 The isospecific rac-(EBI)ZrCl₂ [EBI = ethylene-1,2-bis(1-indenyl)]/MAO catalyst polymerizes 1-hexene to yield highly isotactic poly(1-hexene) in various solvents but with low MW even at low polymerization temperature (Tₚ).9,10 Poly(1-hexene) with high MW was obtained by the application of pressure over 100 Mpa with achiral Cp-mediated zirconocene and hafnocene/MAO catalysts.11 Stereospecific polymerization of 1-hexene under high pressures (up to 1,000 Mpa) using various isospecific and syndiospecific metallocone/MAO catalysts yielded highly stereospecific and high MW poly(1-hexene).12 Jordan et al. have recently developed an efficient synthesis method of ansa-metallocene ch₃Cp₂Zr(NR₂)₂ (ch₃Cp₂Zr = chiral ansa-zirconocene framework) via an amine elimination route.13 As a result, the reaction of Me₂Si(1-C₅H₂-2-CH₃-4- t-Bu)₂ZrCl₂, was prepared by Mintzinger et al. by the reaction of Me₂Si(1-C₅H₂-2-CH₃-4-t-Bu)₂Zr(NMe₂)₂ in 90% NMR yield (rac/meso = 2.5/1) and pure rac-Me₂Si(1-C₅H₂-2-CH₃-4-t-Bu)₂Zr(NMe₂)₂ (rac-1) in 52% isolated yield.13(c) Corresponding dichloride compound, rac-Me₂Si(1-C₅H₂-2-CH₃-4-t-Bu)₂ZrCl₂, was prepared by Mintzinger et al. by the reaction of Me₂Si(1-C₅H₂-2-CH₃-4-t-Bu)₂K₂ and ZrCl₄(THF) only in 9% isolated yield.14 In situ alkylation of ch₃Cp₂Zr(NR₂)₂ complexes with AlR₃ followed by ionization by complexes with ammonium salts (e.g., [HNMe₆Ph][B(C₆F₅)₄]) or by alkyl abstraction reagents [e.g., CPh₃, B(C₆F₅)₃] has been proved to be an efficient procedure to activate ch₃Cp₂Zr(NR₂)₂ for olefin polymerizations.15 Diamide compound rac-1 afforded highly isospecific (almost 100% of meso pentad) propylene in the presence of methylalumoxane (MAO) or AlR₃/[CPh₃][B(C₆F₅)₄] as a coactivator.16

In this work, the polymerizations of various α-olefins (1-pentene, 1-hexene, 1-octene, and 1-decene) were carried out with the highly isospecific rac-1 catalyst, which shows very high isospecificity in propylene polymerization, in the presence of MAO free cocatalyst formulation Al(iBu)₃/[CPh₃][B(C₆F₅)₄], in order to investigate polymerization behavior and the microstructure of resulting POs. We also discuss our studies on the chain transfer reactions that control molecular weight in the polymerization of α-olefins. ¹H, ¹³C NMR, and Raman spectroscopies were used for the analysis of end groups formed by chain transfer reactions.

EXPERIMENTAL

Materials

All materials were handled with Schlenk or glove box techniques under argon atmosphere. Toluene was distilled from sodium prior to use. Monomers (1-pentene, 1-hexene, 1-octene, and 1-decene) from Aldrich Chemical Co. were purified by distilling from sodium and stored under molecular sieve. Al(iBu)₃ (15 wt % solutions in toluene) was obtained from Aldrich and used without purification. The catalyst rac-1⁵⁺ and anionic [CPh₃][B(C₆F₅)₄]¹¹ compounds were synthesized according to literature procedures.

Polymerization

Polymerizations were carried out in a 250-mL glass reactor. A Teflon magnetic stirring bar was used for agitation. First, 80 mL of toluene, 80 mmol of monomer (1 M), 1.0 mmol of Al(iBu)₃, and 3.1 μmol of rac-1 were introduced into the reactor sequentially in the glove box. [CPh₃][B(C₆F₅)₄] (3.1 μmol) dissolved in toluene was injected into the reactor and then the polymerizations started at 30 °C for 24 h. The polymerization was stopped by introducing 100 mL of ethanol containing 5 wt % of HCl and dried to constant weight under vacuum.

Measurements

The ¹³C and ¹H NMR spectra of polymer were recorded at 80 °C on a Varian Unity Plus 300 spectrometer using tetramethylsilane as an internal standard. Samples for NMR spectra were prepared by dissolving 50 mg of polymer in 0.5 mL of
benzene-$d_6$/1,2,4-trichlorobenzene-$d_3$ (1/5 v/v). Raman spectra were collected on a Bruker IFS55 FTIR spectrometer with the Raman module (FRA 106), CaF$_2$ beamsplitter, and Ge detector. The excitation source was a diode pumped Nd:YAG laser operated at 1064 nm. The laser power was 200 mW. The sample was placed in a round capillary tube, and 256 scans were taken at a resolution of 2 cm$^{-1}$ in a 180 ° scattering arrangement. Thermal analysis of polymer was carried out by using a differential scanning calorimeter (DSC, Dupont Model-900) at 20 °C/min heating rate. The results of the second scan were reported to eliminate differences in sample history. The molecular weight (MW) and its distribution (MWD) of polymer were examined by gel permeation chromatography (GPC) on a Waters 150C equipped with five columns with pore sizes of 5 $\times$ 10$^2$, 10$^3$, 10$^4$, and 10$^6$. 1,2,4-Trichlorobenzene was employed as a solvent and column oven was maintained at 80 °C. The universal calibration was used to calculate MW and MWD. The details of this procedure have described elsewhere.$^{17}$

### RESULTS AND DISCUSSION

#### Polymerization Activity and Properties of Poly($\alpha$-olefin)s

Polymerizations were carried out by using 38.75 $\mu$M of rac-1 in the presence of [Al(iBu)$_3$] and [CPh$_3$][B(C$_6$F$_5$)$_4$] at 30 °C. Table I summarizes the results of polymerization. For the comparison we added the result of propylene polymerization carried out at the same conditions except a monomer concentration.$^{16(b)}$ All polymerizations record very high yield. In the previous reports we showed that $^6$Cp$_2$Zr(NR)$_2$$_2$ compounds are stoichiometrically alkylated by AlR$_3$, and then form cationic alkylzirconium species by adding anionic compounds [CPh$_3$][B(C$_6$F$_5$)$_4$] and [HNR$_3$][B(C$_6$F$_5$)$_4$].$^{15,16}$ In the $^{15}$rac-1/Al(iBu)$_3$/[CPh$_3$][B(C$_6$F$_5$)$_4$] system, the cationic zirconium species are thus in situ generated according to Scheme 1. In this method Al(iBu)$_3$ functions also to scavenge impurities contained in the polymerization medium.

Even though polypropylene is a very fine powder, poly(1-pentene) is waxy and the others are oily. As can be seen in Table I, the conversion of monomer to polymer firstly increases with the increased size of monomer, in the order of 1-pentene < 1-hexene < 1-octene, then decreases when the size of monomer increases more to 1-decene. These results propose that two factors, lateral size of polymer chain and monomer size, affect the polymerization rate pro and con, respectively. On the pro effect, longer lateral polymer chain opens the $\pi$-ligands wider than a shorter one and makes the insertion of monomer easier. Similar results have been reported for the copolymerization of ethylene with higher $\alpha$-olefins of different size, that is, a longer $\alpha$-olefin opens the $\pi$-ligands wider than a shorter $\alpha$-olefin and makes the insertion of longer $\alpha$-olefin comonomer easier.$^{18}$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymer Yield (g)</th>
<th>Conversion (%)</th>
<th>$\bar{M}_w$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
<th>$T_C$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_f$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polypropylene</td>
<td>–</td>
<td>–</td>
<td>15,600</td>
<td>1.98</td>
<td>—</td>
<td>—</td>
<td>156.6</td>
<td>50.0</td>
</tr>
<tr>
<td>poly(1-pentene)</td>
<td>4.3</td>
<td>76</td>
<td>9,820</td>
<td>2.56</td>
<td>52.8</td>
<td>—</td>
<td>67.0</td>
<td>5.4</td>
</tr>
<tr>
<td>poly(1-hexene)</td>
<td>5.8</td>
<td>86</td>
<td>7,680</td>
<td>3.54</td>
<td>42.9</td>
<td>38.9</td>
<td>51.6</td>
<td>0.5</td>
</tr>
<tr>
<td>poly(1-octene)</td>
<td>8.7</td>
<td>97</td>
<td>12,032</td>
<td>4.12</td>
<td>43.5</td>
<td>39.1</td>
<td>50.5</td>
<td>0.3</td>
</tr>
<tr>
<td>poly(1-decene)</td>
<td>10.2</td>
<td>91</td>
<td>14,369</td>
<td>4.23</td>
<td>12.9</td>
<td>4.7</td>
<td>24.8</td>
<td>19.3</td>
</tr>
</tbody>
</table>

![Scheme 1](image-url)
the con effect, the usual case is that a larger size of monomer inserts itself into the polymer chain more difficultly than a smaller one because of steric hindrance. If the pro effect dominates the polymerization the conversion of monomer to polymer will increase, but the conversion will decrease if the con effect dominates. In the case of 1-decene, the large steric obstacle makes the insertion of 1-decene into the polymer chain difficult, hence decreasing the conversion.

The thermal property of PO is investigated by means of DSC. Figure 1 is the DSC curves of the POs. During heating the polymer at 20 °C/min, exotherms caused by crystallization are observed for all polymers, followed by endotherms caused by melting. Poly(1-hexene), poly(1-octene), and poly(1-decene) present two endothermic peaks separated by an exotherm. One of the endothermic peaks is extremely weak for poly(1-hexene) and poly(1-octene). Poly(1-pentene) shows only one endothermic peak at 67 °C. Attempts were made to crystallize the POs by cooling them from 90 °C to −20 °C over 2 h. However, their crystallization rates were very slow, so that only poly(1-pentene) shows exothermic peak during cooling from the melt.

The presence of two endothermic peaks during heating has been a subject of some controversy. Their origin may be ascribed to the presence of several crystalline forms, to the melting of the main chain or side chain aggregates or to chains with different stereoregularity. Some authors concluded that side chain crystallization occurs at poly(1-tetradecene), poly(1-tridecene), and poly(1-decene). According to the pattern of DSC curves of the present four POs (Fig. 1), it may be concluded that side chain crystallization occurs even for much smaller poly(1-hexene), even if side and main chain melting peaks almost merge for lower members of the series such as poly(1-hexene) and poly(1-octene). Table I summarizes the crystallization temperature (Tc) and melting point (Tm) as well as heats of fusion (∆Hf) during melting. The Tm value of polymer decreases with the increased lateral size of polymer. The Tm values display a close relationship with the stereospecificity of polymer (vide infra). The small ∆Hf values of poly(1-hexene) and poly(1-octene) suggest the crystallizing limitation for long lateral POs. This may be one of the reasons why poly(1-hexene) and poly(1-octene) were reported mostly without melting point.

The rac-1/Al(iBu)3/[CPh3][B(C6F5)4] system affords the polymers with MW as shown in Figure 2 and Table I. Figure 2 is the molecular weight distribution (MWD) curves of various POs recorded by GPC. The GPC curve of polypropylene obtained at the similar polymerization conditions
was included for the comparison. The MWD value increases monotonously with increasing of lateral size of polymer, mainly due to the increase of the amount of low MW fraction. The MW value decreases first with increasing of lateral size from polypropylene to poly(1-hexene). Further increase of monomer size from 1-hexene to 1-octene and 1-decene results in increase of MW of resulting polymers. The increase of MW from poly(1-hexene) to poly(1-decene) seems to be partly related with the increase of conversion of monomer (vide ante).

**Stereospecificity of Poly(α-olefin)s**

Carbon-13 nuclear magnetic resonance (\(^{13}\)C NMR) spectroscopy offers great promise as a tool for molecular structure analysis. Figure 3 shows the \(^{13}\)C NMR spectra of poly(1-pentene), poly(1-hexene), poly(1-octene), and poly(1-decene), respectively. The assignments of the chemical shifts for POs are made according to the results reported by Randall.\(^{21}\)

The very sharp, intensive resonances are assigned to various carbons shown above and the chemical shifts are summarized in Table II. The calculated chemical shifts of POs by Lindeman and Adams method\(^{22}\) are also listed for the comparison. A very good agreement with the experimental values is observed. The chemical shifts of \(br\) and \(a\) carbons of main chain and the end carbon of branch are similar for all polymers. The chemical shifts of \(C_1\) in the branch carbon show fairly different values each other because of the differences in the branch length and the effect caused by neighbor-carbon.

Besides intensive resonances, there are some sharp but very weak signals. The degree of stereoregularity of these polymers can be estimated from the signals due to the \(C_1\) carbon, with the different sequences appearing around \(C_1\). The degree of stereoregularity could not be evaluated from the fraction of \(\text{[mmmm]}\) pentad because of the resolution limit. Asakura and Doi\(^{22}\) investigated the \(^{13}\)C NMR spectrum of isotactic poly(1-butene), along with the tentative assignment and chain dynamics. The spread of the chemical shift of each chemical group due to stereosequence is much smaller in the poly(1-butene) spectrum than that of polypropylene.\(^6,20\) In particular, the spread of the methylene carbon chemical shift of polypropylene exceeds 2 ppm, but only 0.2 ppm in the case of poly(1-butene). This difference between the polypropylene and poly(1-butene) spectra is resulted from differences in the conformational characteristics including the side chain conformations between them.\(^24\) This is the case for higher \(\alpha\)-olefin polymers. Nevertheless, the \(\text{[mm]}\) triad was easily differentiated. For example, the signal of \(C_1\) at 38.01 ppm in Figure 3 denotes \(\text{[mm]}\) triad. The weaker peaks at 37.58 and 37.49 ppm denote \(\text{[mr]}\) and \(\text{[rr]}\) triads, respectively. Table III summarizes the chemical shifts and intensity of \(\text{[mm]}\), \(\text{[mr]}\), and \(\text{[rr]}\) triads of various POs. The \(\text{[mm]}\) value decreases with the increased monomer size. Our previous studies have shown that polypropylene produced by the same catalyst system at the similar reaction conditions is characterized by almost 100% of \(\text{[mmmm]}\) pentad value.\(^{16(b)}\) It can thus be concluded that the isotacticity decreases in the order: polypropylene > poly(1-pentene) > poly(1-hexene) > poly(1-octene) > poly(1-decene). This is because the long branches hinder the rearrangement of the unit in the polymer chain after the monomer inserting it into the catalytic species.

**End-Group Analysis**

All POs synthesized in this study were also analyzed by using \(^1\)H NMR in order to get the informations on the end groups and internal double bonds. The \(^1\)H NMR spectra of all polymers are very similar each other. Figure 4 shows the spectrum of poly(1-hexene) as a representative of PO. There are three different types of proton signals in poly(1-hexene): —CH\(_3\) between 0.8 and 1.0 ppm, —CH\(_2\)— between 1.0 and 1.7 ppm, and the proton bonded to tertiary carbon (CH) between 1.8 and 2.1 ppm. Investigating carefully the region of higher chemical shifts can collect the informations on the end groups and internal bonds. Figure 4 also shows an expended scale of the region of higher chemical shift and indicates the suitable assignments. The double-bond region
Figure 3. $^{13}$C NMR spectra of poly(1-pentene) ($C_5$), poly(1-hexene) ($C_6$), poly(1-octene) ($C_8$), and poly(1-decene) ($C_{10}$).
contains proton signals for trisubstituted, vinyl, and vinylidene double bonds corresponding to 5.4–5.2, 5.2–5.0, and 4.8–4.6 ppm, respectively.\textsuperscript{25} The double bonds are resulting from various chain terminations. Much less is available in the literature on mechanisms for the formation of unsaturated end groups for higher $\alpha$-olefin polymerizations. $\beta$-Hydride transfer is exclusive reaction for the polymerization of 1-butene by Cp$_2$ZrCl$_2$ at 0 °C.\textsuperscript{25} Chain transfer to aluminum becomes important for polymerization by Cp$^*$ZrCl$_2$ (Cp$^*$ = C$_5$Me$_5$).\textsuperscript{25} Chain transfer to aluminum is the exclusive reaction for rac-(EBI)-TiMe$_3$/MAO catalyst at −45 °C.\textsuperscript{26} $\beta$-Hydride transfer, but exclusively after reverse addition of monomer, is the only transfer reaction for polymerization by rac-(EBI)ZrCl$_2$/MAO catalyst at 30 °C.\textsuperscript{27} There are very few other reports of transfer reactions in $\alpha$-olefin polymerizations except for the report of chain transfer to aluminum as exclusive reaction in 1,5-hexadiene cycopolymerization by Cp$_2$ZrCl$_2$ at −25 °C.\textsuperscript{28} As a result, both saturated and unsaturated end groups can be introduced into the polymer chain by various chain-transfer reactions ($\beta$-hydride transfers with and without rearrangement, transfer to aluminum, etc.).

Table II. Chemical Shifts for the $^{13}$C NMR Spectra of Higher Poly($\alpha$-olefin)s

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Poly(1-pentene)</th>
<th>Poly(1-hexene)</th>
<th>Poly(1-octene)</th>
<th>Poly(1-decene)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exptl. (ppm)</td>
<td>Calc.\textsuperscript{a} (ppm)</td>
<td>Exptl. (ppm)</td>
<td>Calc.\textsuperscript{a} (ppm)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>41.22</td>
<td>39.48</td>
<td>40.66</td>
<td>39.48</td>
</tr>
<tr>
<td>br</td>
<td>33.26</td>
<td>32.91</td>
<td>32.81</td>
<td>32.91</td>
</tr>
<tr>
<td>C$_1$</td>
<td>38.01</td>
<td>36.91</td>
<td>34.96</td>
<td>34.22</td>
</tr>
<tr>
<td>C$_2$</td>
<td>19.98</td>
<td>20.20</td>
<td>29.02</td>
<td>29.96</td>
</tr>
<tr>
<td>C$_3$</td>
<td>14.78</td>
<td>14.35</td>
<td>23.56</td>
<td>22.90</td>
</tr>
<tr>
<td>C$_4$</td>
<td>14.41</td>
<td>13.86</td>
<td>32.33</td>
<td>32.40</td>
</tr>
<tr>
<td>C$_5$</td>
<td>23.00</td>
<td>22.65</td>
<td>29.77</td>
<td>29.71</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculated according to ref. 22.
transfer to vinylidene end groups, β-alkyl transfer, etc.):29,30

Generally, in the absence of hydrogen as a chain transfer reagent, growing polymer chain can be terminated by β-H elimination (1) and chain transfer to monomer (2), resulting in vinylidene end group (P_n denotes polymer chain). The trisubstituted double bond comes from the rearrangement of polymer chain, which is then terminated by β-H transfer (3). The vinyl double bond comes from β-alkyl elimination (4). For the polymerization of α-olefins catalyzed by metallocene/MAO, chain transfer to cocatalyst (5), which results in saturated end groups, is also one of the most popular chain terminations. The relative amount of various types of double bonds is summarized in Table IV. The increase of the amount of vinyl double bond from poly(1-pentene) to poly(1-decene) indicates that the longer lateral of polymer chain favors β-alkyl elimination. In addition, the rearrangement reaction (3), which results in trisubstituted (internal) double bonds, occurs more frequently for the longer lateral of polymer chain. However, the major end group of all polymers is vinylidene (Table IV), demonstrating that β-H elimination is a main termination process, if we neglect chain transfer to monomer (2) considering the bulkiness of the monomers.

1H NMR of spectrum of poly(1-hexene) in Figure 4 indicates that there are two different types of vinylidene groups. The major vinylidene signal is a pair of doublets at 4.70 and 4.67 ppm. The splitting of each signal into a doublet is barely visible. The similar doublets of vinylidene signals were also observed for both poly(1-octene) (at 4.73 and 4.71 ppm) and poly(1-decene) (at 4.73 and 4.72 ppm). Poly(1-pentene) showed only singlet of vinylidene at 4.70 ppm, indicating only one kind of vinylidene group. The minor vinylidene signal, only partially resolved from the major vinylidene

![](https://example.com/image1.png)

**Figure 4.** 1H NMR spectrum of poly(1-hexene).
signal, is observed at slightly lower resonance (4.64 ppm) for poly(1-hexene). Two minor vinylidene resonances, 4.69 and 4.72 ppm for poly(1-octene), and 4.70 and 4.72 ppm for poly(1-decene), resolved from the major vinylidene signal, were apparently observed. The major vinylidene signal is assigned to end group 3, while the minor vinylidene signals are assigned to 4 and 5 based on mechanistic considerations (vide infra). The end groups 4 and 5 differ from 3 in having reverse placement of the penultimate and pen-penultimate unit, respectively. The relative amount of major (3) and minor (4 and 5) vinylidenes is calculated and summarized in Table IV.

![Chemical Structures](image)

**Table IV. Analysis of Unsaturated Bond and End-Groups by \(^1\)H NMR**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Relative Amount of Unsaturated Bonds (%)</th>
<th>Vinylidene Signal ((%)-H) (ppm)</th>
<th>(%)-B (ppm)</th>
<th>(%)-E (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(1-pentene)</td>
<td>85.7</td>
<td>12.2</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>poly(1-hexene)</td>
<td>79.3</td>
<td>12.8</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>poly(1-octene)</td>
<td>77.4</td>
<td>12.4</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>poly(1-decene)</td>
<td>76.7</td>
<td>12.2</td>
<td>5.1</td>
<td></td>
</tr>
</tbody>
</table>

**Chain Terminations**

Investigating the results of analysis on double bonds and end groups, it can be assumed that all POs here consisted of two major end groups, saturated end group of structure 1 in eq 5 and vinylidene end group, and that the other end groups containing double bonds are negligible. The polymer chain can thus be simplified two structures of 6 and 7.
amount of $\beta$-H elimination and chain transfer to cocatalyst are calculated. The results in Table IV propose that the polymerization of 1-pentene favors chain termination to aluminum cocatalyst. In the polymerization of a larger monomer such as 1-hexene, 1-octene, and 1-decene, chain termination by $\beta$-H elimination resulting in vinylidene end group competes with chain transfer to cocatalyst.

Raman Spectroscopy

FT Raman spectroscopy can be utilized for the structural analysis of polymers. Figure 5 shows Raman spectra of various POs. The strong peaks from 2700 cm$^{-1}$ to 3100 cm$^{-1}$ are due to the vibration of saturated bonds. The resonance peak at 2962 and 2872 cm$^{-1}$ is assigned to the asymmetric and symmetric vibration of saturated end group $\text{CH}_3$, respectively. The peak at 2850 cm$^{-1}$ is the symmetric vibration of $\text{CH}_2$. The intensities of $\text{CH}_2$ signals (2962 and 2872 cm$^{-1}$) decrease and that of $\text{CH}_3$ signal (2850 cm$^{-1}$) increases with the increased monomer size, because the polymer of larger lateral has more $\text{CH}_2$ than that of smaller lateral. The peak at 2890 cm$^{-1}$ is the vibration of C–H of branch carbon.

If we investigate the lower wave number range carefully, we can get information on the end groups of the polymers. The signals between 1000 cm$^{-1}$ and 1200 cm$^{-1}$ are in-plane bending vibrations of C–H bond and those between 800 and 900 cm$^{-1}$ are out-of-plane bending vibrations of C–H. There are two kinds of C–C stretching vibrations, a relatively strong vibration at 1460 cm$^{-1}$ corresponding to vinylidene end groups and a very weak one at 1300 cm$^{-1}$ corresponding to internal double bonds. The result is in good agreement with that of $^1$H NMR in that the vinylidene groups are the main double bond of the present POs (Table IV).

CONCLUSION

Polymerizations of higher $\alpha$-olefins, 1-pentene, 1-hexene, 1-octene, and 1-decene, were initiated efficiently by rac-Me$_2$Si(1-C$_5$H$_2$-2-CH$_3$-4-tBu)$_2$Zr(NMe$_2$)$_2$[i-Bu]/[CPh$_3$][B(C$_6$F$_5$)$_4$] catalyst to yield high MW polymers. The activity of polymerization is influenced by both polymer chain lateral and monomer size, so that the molar conversion of monomer to polymer was in the order: 1-pentene $<$ 1-hexene $<$ 1-decene $<$ 1-octene. The MW decreased in the order: polypropylene $>$ poly(1-pentene) $>$ poly(1-hexene), and then increased in the order: poly(1-hexene) $<$ poly(1-octene) $<$ poly(1-decene). MWD increases with increasing of the lateral size of PO due to the increase of low MW fractions.

The [mm] triad of polymers decreased with the increased lateral size in the order: polypropylene (almost 100%) $>$ 1-pentene (95.8%) $>$ 1-hexene (92.8%) $>$ 1-octene (92.0%) $>$ 1-decene (85.7%). The similar dependence of the lateral size on the melting point of PO was recorded by DSC thermograms. Two melting points were found for the poly(1-hexene), poly(1-octene), and poly(1-decene) due to the side chain crystallization.

There were various kinds of end groups—vinylidene, trisubstituted (internal) double bonds, vinyl, and saturated end group—in polymer chain. Vinylidene is a major double bond in the chain end and its amount decreases as the monomer size increases, while the amount of internal double bond and vinyl group increase as the monomer size increases. $^1$H NMR spectra showed that chain transfer to cocatalyst resulting in saturated end groups and $\beta$-H elimination resulting in vinylidene end groups are the main chain terminations. The internal double bond and vinylidene end groups can also be observed by using Raman spectral analysis.

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REFERENCES AND NOTES