Ethylene/Propylene Copolymerization Using Cp2ZrCl2/MAO Catalyst: Effects of Copolymerization Conditions on Viscosity Average Molecular Weight

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ABSTRACT

Copolymerization of ethylene with propylene is carried out semi-continuously in toluene at atmospheric pressure and with various propylene/ethylene molar ratios. The polymerization temperature and cocatalyst/catalyst molar ratio were also varied in a wide range. Cp2ZrCl2/MAO System was used as catalyst. The viscosity average molecular weights of copolymers obtained were determined by measuring the intrinsic viscosity $[\eta]$ and application of the Mark-Houwink equation. The values of molecular weights were found to be dependent on operating conditions except on polymerization time in the range 5-30 min. Increasing the polymerization temperature, propylene/ethylene and cocatalyst/catalyst molar ratios caused a continuous decrease in molecular weight. An important reason for this effect was shown to be accelerated chain transfer reactions.

INTRODUCTION

An important point of interest in developing homogeneous metalloocene or as sometimes called “Kaminsky-Sinn catalysts” has been an academic motivation of introducing more simplified systems for mechanistic investigation of olefin homo- and copolymerization. In this respect, these soluble catalysts have shed light on the proposed catalyst cycles by modelling some of the fundamental elementary steps such as olefin insertion or alkyl migration[1]. Kinetic consideration of
olefin polymerization systems composed of these cata-
lysts and application of various techniques have also
led to determination of the nature of propagating
species[2]. For these fascinating capabilities, the metal-
locene/methylaluminoxane systems are expected to
play a decisive role in the future of olefin industry as
they can produce new kinds of polyolefins with reason-
ably narrow molecular weight distribution for the exis-
tence of their single active centres and high activity as
a result of higher concentration of active sites produced
per unit catalyst[3-4].

However, a disappointing aspect in which homoge-
neneous olefin polymerization by metallocene-based cat-
alysts differs from heterogeneous Ziegler-Natta cataly-
sis is that here low degrees of polymerization are
achieved when propylene monomer is present. While
ethylene is polymerized by MAO activated Cp2ZrCl2
to give polymers with high molecular weights in the
range of 100,000 to 1,000,000, the propylene copoly-
merization at room temperature produces polymers of
rather low degrees of polymerization having molecular
weights in the range of 200-1000 [5-6]. Such short
polymer chains may not have any important industrial
usefulness.

In the first part of this series, we studied the catalyt-
ic behaviour of the Cp2ZrCl2/MAO system in copoly-
merization of ethylene with propylene for the semi-
continuous procedure and examined the effects of
process conditions on kinetics of the copolymerization
[7]. In this part, we report the influence of some vari-
able on average molecular weight of products
obtained from the same copolymerization.

EXPERIMENTAL

Chemicals
The sources of polymerization materials, methods of
purification and procedures for the preparation of dilute
methylaluminoxane have been given previously [7].
Toluene was obtained from Aldrich and was refluxed
and freshly distilled under argon from an Mg/K alloy.
All polymerizations were carried out in toluene.

Polymerization Technique
A 250 mL capacity jacketed glass-reactor fitted with an
efficient water-cold condenser was used to perform the
polymerizations. The reactor was of the open-ended
flanged type to facilitate the addition of catalyst, cocat-
alyst, and pure solvent through individual inlets. In this
flow method, the monomers were supplied to the reac-
tor semi-continuously via two restricting valves and a
3-way tap. In the reactor, part of each monomer was
polymerized and the rest was discharged and measured
by a wet flowmeter. More details of the polymerization
system, its flowsheet and work-up of the product has
been described elsewhere [7].

Measurements of Viscosity
The viscosity of copolymers were determined in deca-
line (decahydrophthalene) at about 135°C ± 0.2 by
means of Ubbelohde suspended level dilution viscomet-
er, [7]. A volume of 15 mL of decaline containing 0.1%
w/v 2,6-di-tert-butyl-p-cresol antioxidant were placed
in the viscometer reservoir and after the attainment of
thermal equilibrium, the flow time, t_o, for pure decaline
was measured. Subsequently, an accurately weight
sample of copolymer (15 mg) was carefully dropped in
the reservoir and dissolved completely by bubbling dry
nitrogen and then the flowtime, t_p, was measured. Next
to it, several 5 mL aliquots of decaline were added and
each time after remixing, the new t_p was recorded. All
experiments were performed in duplicated manner and
timing for each experiment was recorded in triplicate.
The limiting viscosity numbers (LVN) were found
by extrapolation of the data obtained from double plot
of viscosity number and logarithmic viscosity number
versus polymer solution concentration on a single
graph as shown in Figure 1. The average of the two val-
ues was taken as the limiting viscosity number. Repeated experiments for the same sample and for

![Figure 1. Plot of η_sp/C or ln η_ref/C versus concentration.](http://www.SID.ir)
samples prepared under the same polymerization conditions was found to lie within 3.6% each other.

Direct application of Mark-Houwink equation of the form \([\eta] = 3.8 \times 10^{-4} M^0.74_v\) dL.g\(^{-1}\), displayed the so-called viscosity average molecular weight, \(M_v\) [8-13].

**RESULTS AND DISCUSSION**

Viscosity measurements and application of Mark-Houwink equation is the simplest and most rapid method for determining the relative molecular weight of polymer [8]. So far there are several Mark-Houwink equations in the literature for EP copolymers differing in their “\(\alpha\)” and “\(K\)” values [9-12]. We think that an important cause of the disagreements might be the type of copolymers of EP studied by different authors (statistic, graft, block and random). A widely employed equation was reported by Scholte et al. [11] and used by Pietikalnen and Seppala [12] for EP copolymers produced by the same catalyst system. This equation is that mentioned in experimental part and was used in this work. According to Maghami and Roberts, the \(K\) and \(\alpha\) parameters of this equation are almost constant over a wide range of propylene molar concentrations in the copolymer chains (20-45 mole%) and physical state of copolymers [13].

Depending on experimental polymerization conditions adopted in the present work, copolymers with a wide range of physical states from flowable and viscose to hard gels and solids were obtained indicating the serious effect of reaction conditions on life time of propagating species of \(\text{Cp}_2\text{ZrCl}_2\) in combination with methylaluminoxane. By changing the conditions, copolymers with viscosity average molecular weights in the range 4,000 to 22,000 g.mol\(^{-1}\) were resulted. All samples were also completely soluble in toluene between 25 and 60°C indicating that they were gel-free products.

The effect of main polymerization parameters on molecular weight was investigated by using the method outlined above in order to understand the magnitude and the type of termination processes which occur during the copolymerization since the molecular weight is in fact a consequence of competition between the chain growth and the chain termination reactions.

The variation of molecular weight with polymerization time is shown in Table 1. The effect is not significant, however, two opposing trends at moderate temperatures, e.g. 30°C, the \(M_v\) values increased slightly with polymerization time a behaviour that has also been observed by Chien and Wang for ethylene polymerization using the same catalyst system [14]. Such increase of molecular weight with polymerization time was suggested by these authors to be due to a decrease in the concentration of the active catalytic complexes as the polymerization proceeds. However, this behaviour becomes reverse for samples prepared at higher temperatures i.e., 60°C, since a continuous drop in molecular weight was detected with increasing polymerization time probably due to increase in the number of polymer chains produced per unit catalyst per unit time as a result of either chains transfer acceleration or time-dependence active center formation (or both).

A more detailed examination of the influence of temperature on molecular weight was carried out. As

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>30</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymerization Time (min)</td>
<td>([\eta]^*)</td>
<td>(M_v^{**} \times 10^{-3})</td>
<td>([\eta])</td>
</tr>
<tr>
<td>5</td>
<td>0.456</td>
<td>14.5</td>
<td>0.426</td>
</tr>
<tr>
<td>10</td>
<td>0.468</td>
<td>15.0</td>
<td>0.428</td>
</tr>
<tr>
<td>15</td>
<td>0.475</td>
<td>15.3</td>
<td>0.433</td>
</tr>
<tr>
<td>20</td>
<td>0.495</td>
<td>16.2</td>
<td>0.442</td>
</tr>
<tr>
<td>25</td>
<td>0.504</td>
<td>16.6</td>
<td>0.456</td>
</tr>
<tr>
<td>30</td>
<td>0.518</td>
<td>17.2</td>
<td>0.468</td>
</tr>
</tbody>
</table>

(*): Number average viscosity (dL g\(^{-1}\)). (**): viscosity average molecular weight (\(M_v\) g mol\(^{-1}\): polymerization conditions: \(C_3/C_2 = 50/50\); \([Zr] = 5 \times 10^{-6}\) (mol dm\(^{-3}\)), \([Al]/[Zr] = 3000\), solvent = toluene, and total pressure = 1 atm.
Table 2 shows, the polymerization temperature exerts a much stronger effect on the $\bar{M}_v$ since it dramatically decreased by about 70% with increasing the temperature from 25 to 60°C. The Arrhenius plot of $\bar{M}_v$ in Figure 2 confirms this dependency since its curve indicates a sharper slope at higher temperature regions. Therefore, it may be concluded that at low temperature the $\bar{M}_v$ is only a function of polymerization time, all other conditions being kept constant.

According to the related literature[15-16], there are two main transfer processes in absence of hydrogen addition. These are chain transfer to MAO with the rate constant $K_{tr,Al}^\beta$ and the spontaneous process of $\beta$-hydride elimination with the rate constant $K_{Al}^\beta$. The latter has been shown to be of more important for Cp$_2$ZrCl$_2$/MAO catalyst [16] (Scheme I).

$$\text{Zr-CH}_2\text{-CH-P} + \text{Zr-CH}_2\text{-CH}_3 \rightarrow \text{ZrH+CH}_2\text{-C-P}$$

$\beta$ – Hydride elimination

Scheme I

The relatively lower molecular weights obtained at higher temperatures must, therefore, be due to a decrease in the rate of olefin insertion or an increase in the rate of chain terminating transfer reactions and the average degree of polymerization is then determined by the ratio of chain propagation and chain termination.

Tsutsui et al. [17] have investigated the microstructures of EP copolymers prepared in the presence of Cp$_2$ZrCl$_2$/MAO by $^{13}$C NMR spectroscopy. According to their report, the chain transfer reaction is most probably caused by propylene monomer when the propagating chain end is propylene unit, viz (Scheme II):

$$\text{Zr-CH}_2\text{-CH-P} + \text{CH}_2=\text{CH}_3 \rightarrow \text{Zr-CH}_2\text{-CH}_2\text{-CH}_3$$

$\beta$ – Hydride elimination

Scheme II

Therefore, one can conclude that chain transfer reaction is most facilitated when the last added monomer into propagating chain is propylene.

[MAO]/[Zr] ratio is another influencing parameter on molecular weight as shown in Table 3. The molecular weight decreased slightly and almost linearly by keeping the MAO concentration constant and increasing the Cp$_2$ZrCl$_2$ concentration. Molecular weights are higher substantially at low zirconium concentrations. This might be due to dilution effects favoring the dissociated or olefin-separated ion pairs $C^*$ relative to their associated precursors $C$, and hence increasing the rate of chain propagation over that of chain termination. Kaminsky and co-workers advocated that a bimolecular reaction of the active complex with a second zirconocene species terminates growth of the polymer chain in a manner possibly related to the second-order deactivation process [18-19] (Scheme III).

$$\text{Cp}_2\text{ZrCl}_2 + \text{MAO} \rightarrow C^* + C^* \rightarrow \text{inactive species}$$

Scheme III

This behaviour may lead to the conclusion that for chain transfer reaction to occur, a bimetallic mechanism is necessary if one accepts that nearly all the Zr complexes are catalytically active. Further clarification of this behaviour can be expected from future studies on MAO-free metallocene polymerization catalysts.

In another series of polymerization experiments the concentration of MAO was changed at constant [Cp$_2$ZrCl$_2$]. The data collected in Table 4 indicate that a more intense effect arises from [MAO] than from [Cp$_2$ZrCl$_2$] because a sharper decrease in molecular weight was detected by increasing [MAO]/[Zr] from 1×10$^3$ to 3×10$^3$. The decline in $\bar{M}_v$ became then slight.
by further increase of this ratio.

This observation leads to assume two different roles for MAO in the present polymerization system. The first is to alkylate the zirconocene catalyst after initial complex formation as a result of which active species are formed and propagate (Scheme IV).

The second role of MAO is to function as chain transfer agent, viz, (Scheme V).

Therefore, this transfer to MAO should be competitive with chain transfer with propylene and by β-H elimination. However, the higher $M_v$ produced at low concentrations of MAO may be accounted for a slower transfer since the majority of these species are involved either in alkylated $\text{Cp}_2\text{ZrClMe.MAO}$ form or in propa-

![Scheme IV](image-url)

**Table 2.** Effect of polymerization temperature on $M_v$ at different mean residence times.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\eta]^*$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_v \times 10^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\eta]$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_v \times 10^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\eta]$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_v \times 10^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Polymerization conditions are shown in Table 1.

**Table 3.** Variation of $[\eta]$ and $M_v$ with $[\text{Zr}]$.

<table>
<thead>
<tr>
<th>$[\text{Zr}]$/mol dm$^{-3}$</th>
<th>$2 \times 10^{-6}$</th>
<th>$5 \times 10^{-6}$</th>
<th>$6.7 \times 10^{-6}$</th>
<th>$1.3 \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean residence time/min</td>
<td>$[\eta]$</td>
<td>$10^{-3} M_v$</td>
<td>$[\eta]$</td>
<td>$10^{-3} M_v$</td>
</tr>
<tr>
<td>10</td>
<td>0.450</td>
<td>14.2</td>
<td>0.428</td>
<td>13.3</td>
</tr>
<tr>
<td>20</td>
<td>0.433</td>
<td>14.7</td>
<td>0.433</td>
<td>13.9</td>
</tr>
<tr>
<td>30</td>
<td>0.480</td>
<td>15.5</td>
<td>0.461</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Polymerization conditions: $C_3/C_2 = 50/50$, $[\text{A}] = 1.5 \times 10^{-2}$ mol dm$^{-3}$, Temperature = 40°C, solvent = toluene, pressure = 1 atm.

**Table 4.** Effect of MAO concentration on $M_v$.

<table>
<thead>
<tr>
<th>$[\text{Al}]/[\text{Zr}]$ Ratio (mol/mol)</th>
<th>$1 \times 10^3$</th>
<th>$2 \times 10^3$</th>
<th>$3 \times 10^3$</th>
<th>$4 \times 10^3$</th>
<th>$5 \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\eta]$/$dL \ g^{-1}$</td>
<td>0.613</td>
<td>0.477</td>
<td>0.402</td>
<td>0.336</td>
<td>0.275</td>
</tr>
<tr>
<td>$M_v \times 10^{-3}$/g.mol$^{-1}$</td>
<td>21.6</td>
<td>15.4</td>
<td>12.2</td>
<td>9.6</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Polymerization conditions: $C_3/C_2 = 60/40$, Temperature = 40°C, $t = 20$ min, $[\text{Zr}] = 5 \times 10^{-6}$ mol dm$^{-3}$, solvent = toluene, total pressure = 1 atm.
Table 5. Effect of propylene mol % on $\bar{M}_v$ of copolymer.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[η]</td>
<td>$\bar{M}_v \times 10^{-3}$</td>
</tr>
<tr>
<td>C3 mol % in gas mixture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.442</td>
<td>13.9</td>
</tr>
<tr>
<td>60</td>
<td>0.402</td>
<td>12.2</td>
</tr>
<tr>
<td>70</td>
<td>0.349</td>
<td>10.1</td>
</tr>
<tr>
<td>80</td>
<td>0.241</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Polymerization conditions: [Zr] = 5×10^{-6} mol dm^{-3}, t = 20 min; [Al]/[Zr] = 3000, solvent = toluene, total pressure = 1 atm.

Table 5. Effect of propylene mol % on $\bar{M}_v$ of copolymer.

Table 5. Effect of propylene mol % on $\bar{M}_v$ of copolymer.

CONCLUSION

In conclusion, we have found that non-support, Cp2ZrCl2/MAO catalyst system produces almost low molecular weight EP copolymers. However, it is possible to rise the molecular weight of product by carefully adjusting the polymerization conditions such as propylene feed molar fraction, polymerization temperature, MAO concentration, etc. Both propylene and MAO act as chain transfer agents and as the polymerization temperature increases, these effects become more profound.

ACKNOWLEDGEMENTS

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