Determination of Active Centre Concentration for Polymerization of Propylene Using High Activity Ziegler Natta Catalyst

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ABSTRACT

Suspension polymerizations were carried out at 1 atm of propylene in pentamethyl heptane using Mg(OCC₂H₅)₂/di-n-butylphthalate/ThCl₄-AlEt₃/di-phenylidimethoxy silane catalyst system. Active centre concentration (C') was determined by quenching and radio-tagging methods using tritiated methanol and carbon monoxide, respectively. Effect of external donor on the C' was studied. An investigation in the effect of temperature (50-80 °C) on C', and propagation rate coefficient, k_p, was carried out using the catalyst system. The optimum values of C' were achieved at 65-70 °C. The maximum rate of polymerization as well as the k_p values increased steadily with increasing temperature. The preliminary investigation involved the time needed for the tritiated methanol and carbon monoxide to react with the active centres to stop the polymerization quickly and completely. The amount of carbon monoxide and alcohol which were able to stop the polymerization was also determined. In the present work a five-fold of tritiated alcohol concentration to alkylaluminium was used.

Key Words: polymerization, Ziegler-Natta catalyst, active centre, polypropylene, heterogeneous catalyst

INTRODUCTION

Determination of active centre concentration is an essential feature in the investigation of the kinetics and mechanisms of catalytic reactions. The active centre concentrations in Ziegler-Natta catalysts generally indicate the fraction of transition metal species which are able to act as centres for chain propagation. This determination allows comparison of the number of active centres for α-olefin polymerization using different catalysts. In fact, such determinations are necessary for the interpretation of polymerization...
activity. Unfortunately, no direct methods for the measurement of active centre concentrations have as yet been developed.

In the present work the determination was performed using two more common methods. Radio-tagging method using carbon monoxide (14CO), introduced by Yermakov et al. [1-3] and subsequently applied by Tait and coworkers [4-6]. In addition, the concentration of active centres was determined by quenching of the polymerization process using tritiated alcohol, a method first used by Feldman and Perry [7] and later developed by Tait et al. [8].

The objective of the study was to compare values of active centre concentrations obtained using two of the most commonly employed methods when polymerizations were carried out under carefully controlled conditions.

EXPERIMENTAL

Materials, preparation method of the catalyst and polymerization procedure have been described elsewhere [8].

Quenching of the Polymerization

In order to determine the active centre concentration using quenching method the amount of quenching agent added to the polymerization mixture must be sufficient to stop the polymerization quickly and completely.

An excess of about ten-fold of tritiated alcohol to metal polymer bond concentration has been used by researchers in the field [3,9 and 10]. In the present work a five-fold of tritiated alcohol concentration to alkylaluminium was used.

Quenching was achieved by injection of 1.0—1.5 cm³ of tritiated methanol, depending on the polymerization conditions employed, to the polymerization reactor. The contents of the reactor were left to react for a selected period of time (contact time) in the presence of monomer. At the end of the contact time, the reactor was evacuated and purged with nitrogen. The contents of the reactor were decontaminated. The amount of 14CO incorporated into the polymer was determined.

RESULTS AND DISCUSSION

Determination of Contact Time and C'

In order to employ radio-tagging methods such as the use of 14CO it is important to determine the length of time required for the 14CO to remain in contact with...
the polymerization system for its insertion into all growing chains to take place. Plots of the amount of $^{14}$CO incorporated into the polymer chains ($C_i$) against the contact time, $t_c$, were constructed. A value of $t_c = 40$ min was found for the catalyst system. This value is obtained by the extrapolation procedures shown in Figure 1 and represents the time required for the insertion of $^{14}$CO into all growing chains to take place, but before any significant amount of additional $^{14}$CO is introduced into polymer chains through copolymerization or other side reactions. The results of $C_i$ against $t_c$ are listed in Table 1.

The variations of $C_i$ with $t_c$ are depicted in Figure 1. The $C^*$ value was obtained from the intersection of two tangents constructed to the different parts of the $C_i$ versus contact time profile, where value of $16.3 \times 10^{-2} \text{ mol/mol Ti (16.3\%)}$ was obtained for the catalyst system. The contact time was evaluated to be 40 min and this value was used as the contact time for further studies.

Table 1. Variation of $C_i$ with $t_c$ for catalyst system Mg(OEt)$_2$/DNBP/TiCl$_4$/TEA/DPDMS.

<table>
<thead>
<tr>
<th>$t_c$ (min)</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>45</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>180</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_i$ (mol/mol Ti)</td>
<td>7.3</td>
<td>9.5</td>
<td>11.8</td>
<td>13.9</td>
<td>15.8</td>
<td>16.0</td>
<td>16.5</td>
<td>18.2</td>
<td>20.1</td>
<td>20.9</td>
</tr>
</tbody>
</table>

Polymerization conditions: [Ti]=0.060 mmol dm$^{-3}$; polymerization time=5 min; and [TEA]: [DPDS]: [Ti]=827:63:1 molar ratio.

Variation of $C^*$ and Propagation Rate Coefficient with Polymerization Time

The kinetic behaviour of the catalyst as demonstrated in its rate-time profile, showed a rapid change in the rate of polymerization with polymerization time [9]. Such behaviour highlights the importance of the possible variation of active centre concentrations ($C^*$) with polymerization time. To elucidate the relationships of the $C^*$ and propagation rate coefficient ($k_p$) with polymerization time a series of experiments were carried out and 5.0 cm$^3$ of $^{14}$CO was added at different polymerization times (5–120 min). The reactions were carried out in the presence of monomer. A contact time of 40 min was chosen.

The results are reported in Table 2. Figure 2 shows the variation of the $C^*$ and $k_p$ with polymerization time for the catalyst.

The propagation rate coefficient, $k_p$, was obtained using the eqn (1) and the rate of polymerizations ($R_p$) were determined as ref 9:

$$R_p = k_p C_p^* [M]$$

where:

- $R_p$: polymerization rate at the time of addition of $^{14}$CO; mol PP/mol Ti.s.
- $C_p^*$: active centre concentration at the polymerization time; $t_p$, mol/mol Ti.
- $K_p$: propagation rate coefficient; dm$^3$/mol.s.
- [M]: concentration of monomer, (mol/dm$^3$).

As can be seen from Table 2 and Figure 2, $C_p^*$ has remained almost constant (within experimental error) in relation with $t_p$. However, $k_p$ has decreased significantly with increasing $t_p$. Thus, the observed decay in $R_p$ was mainly due to a decrease in $k_p$ and not significantly to a decrease in $C_p^*$.

Variation of $C^*$ and $k_p$ with Temperature

The effect of temperature on $C^*$ and $k_p$ was studied in polymerization temperature range of 50–80 °C. The

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Table 2. Variation of \( C_p \) and \( k_p \) with the polymerization time for the MgCl₂ (ethoxide type)/DNBP/TiCl₄-TEA/DPDMS catalyst system.

<table>
<thead>
<tr>
<th>( t_p ) (min)</th>
<th>PP yield ( R_p ) (mol PP/mol Ti s)</th>
<th>( 10^2 \times C_p ) (mol/mol Ti)</th>
<th>( k_p ) (dm³/mol Ti s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.01</td>
<td>4.99</td>
<td>17.2</td>
</tr>
<tr>
<td>10</td>
<td>1.43</td>
<td>3.26</td>
<td>15.7</td>
</tr>
<tr>
<td>30</td>
<td>2.96</td>
<td>2.34</td>
<td>15.6</td>
</tr>
<tr>
<td>45</td>
<td>4.25</td>
<td>1.98</td>
<td>15.0</td>
</tr>
<tr>
<td>60</td>
<td>5.40</td>
<td>1.72</td>
<td>16.9</td>
</tr>
<tr>
<td>90</td>
<td>6.44</td>
<td>1.32</td>
<td>16.7</td>
</tr>
<tr>
<td>120</td>
<td>7.40</td>
<td>1.01</td>
<td>16.8</td>
</tr>
</tbody>
</table>

Polymerization conditions: \( \text{temp}=60 \, ^\circ \text{C}; \text{vol. of EC180}=0.250 \, \text{dm}^3; \) propylene=0.230 mol dm³; [Ti]=0.060 mmol dm³; contact time=40 min; [TEA]:[DPDMS][Ti]=827:53:1 molar ratio; \( ^{14}\text{CO}=5.0 \, \text{cm}^3 \), specific activity \( (\alpha)=2.65 \times 10^9 \, \text{dpm/mol} \).

The results of these polymerizations are listed in Table 3. \( ^{14}\text{CO} \) was added after 7 min of polymerization which produced the maximum activity for the catalyst. \( C' \) was quite low at 50 °C but increased with temperature, increasing to 70 °C. Then \( C' \) was decreased with further increase in temperature. The coefficient \( k_p \) was found to increase continuously with increase in temperature in the range of 50–80 °C.

**Determination of Metal-polymer Bond Concentration**

Determination of active centre concentration using a radio-quenching technique involved the quenching of polymerizations at different reaction times under constant conditions. The polymer was decontaminated and dried. From the determined polymer sample, the metal-polymer bond concentration in the catalyst system was evaluated using eqn (2) [6].

\[
[MPB] = \frac{KAG}{\alpha} \quad (2)
\]

where:

- [MPB]: concentration of metal-polymer bonds; mol/dm³.
- K: correction factor for kinetic isotopic effect.
- A: specific activity of the polymer decay per min; dpm/g.
- G: polymer yield at time of quenching; g/dm³.
- \( \alpha \): specific activity of the tritiated methanol; dpm/g.

Table 3. Variation of \( C_p \) and \( k_p \) with temperature using MgCl₂(ethoxide type)/DNBP/TiCl₄-TEA/DPDMS catalyst system.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( 10^2 \times K/T )</th>
<th>Yield of PP (g)</th>
<th>( R_p(\text{addition}) ) (mol PP/mol Ti s)</th>
<th>( 10^2 \times C_p ) (mol/mol Ti)</th>
<th>[M] (mol/dm³)</th>
<th>( k_p ) (dm³/mol Ti s)</th>
<th>( \ln(R_p(\text{addition}))/[M] \times C_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>3.096</td>
<td>0.72</td>
<td>3.44</td>
<td>9.8</td>
<td>0.28</td>
<td>125.4</td>
<td>4.83</td>
</tr>
<tr>
<td>60</td>
<td>3.003</td>
<td>0.72</td>
<td>4.99</td>
<td>16.1</td>
<td>0.23</td>
<td>134.3</td>
<td>4.90</td>
</tr>
<tr>
<td>70</td>
<td>2.916</td>
<td>1.12</td>
<td>5.63</td>
<td>17.2</td>
<td>0.18</td>
<td>182.4</td>
<td>5.21</td>
</tr>
<tr>
<td>80</td>
<td>2.833</td>
<td>1.00</td>
<td>5.18</td>
<td>14.4</td>
<td>0.13</td>
<td>276.7</td>
<td>5.62</td>
</tr>
</tbody>
</table>

Polymerization conditions: [Ti]=0.08 mmol/dm³; vol of EC180=0.250 dm³; co-catalyst=TEA; TEA:DPDMS:Ti=827:53:1 molar ratio; polymerization time= 5 min.
Table 4. Variation of [MPB] with polymerization time, $t_p$, for the MgCl$_2$ (ethoxide type)/DNBP/TiCl$_4$-TEA catalyst system.

<table>
<thead>
<tr>
<th>$t_p$ (min)</th>
<th>Yield (g PP/dm$^3$)</th>
<th>$10^5$[MPB] (mol/dm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4.69</td>
<td>0.9</td>
</tr>
<tr>
<td>10</td>
<td>7.20</td>
<td>1.0</td>
</tr>
<tr>
<td>20</td>
<td>14.08</td>
<td>1.3</td>
</tr>
<tr>
<td>30</td>
<td>14.24</td>
<td>1.6</td>
</tr>
<tr>
<td>45</td>
<td>19.20</td>
<td>1.6</td>
</tr>
<tr>
<td>60</td>
<td>24.16</td>
<td>1.8</td>
</tr>
<tr>
<td>90</td>
<td>32.40</td>
<td>2.0</td>
</tr>
<tr>
<td>120</td>
<td>37.76</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Polymerization conditions: temp=60 °C; vol. of EC180=0.125 dm$^3$; [propylene]=0.230 mol/dm$^3$; [Ti]=0.060 mmol/dm$^3$; [TEA]/[Ti]=224:1 molar ratio; residence time=20 min; specific activity ($a$) =1.08$\times10^{11}$ dpm/mmol.

Preliminarily, the amount of quenching agent which is sufficient to react with all metal-polymer bonds were determined. Different quantities of quench reagents have been used to stop the polymerization. Figure 3 shows the effect of addition of tritiated methanol on polymerization process.

Variation of [MPB] with Polymerization Time and Determination of Active Centre Concentration

[MPB] was studied for the catalyst system under optimum conditions at 60 °C. The results obtained and conditions used, are reported in Tables 4 and 5. Figures 4 and 5 show the variation of [MPB] with polymerization time for the catalyst systems.

Plots of [MPB] versus $t_p$ were found to consist of two periods: an initial acceleration period and then a period in which the [MPB] increased continuously with time. The initial increase in the [MPB] indicated the formation of active centres, assuming that chain transfer to alkylaluminium was negligible during the early stages of polymerization, or, that the formation of active centres and chain transfer occurred simul-
Table 6. Result of $C^*$ using tritium for the Mg(OEt)$_2$/DNBP/TiCl$_4$-TEA/DPDMS catalyst system.

<table>
<thead>
<tr>
<th>TEA:ED:TI molar ratio</th>
<th>$10^2 \times 14^{14}$CO (mol Ti)$^{-1}$</th>
<th>$10^8 R_p$ (mol dm$^{-3}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>224:0:1</td>
<td>22.0</td>
<td>13.3</td>
</tr>
<tr>
<td>627:63:1</td>
<td>20.8</td>
<td>6.0</td>
</tr>
</tbody>
</table>

taneously. The later linear increase of [MPB] with $t_p$ was believed to be due to chain transfer reactions with alkylaluminium as the polymerization proceeded.

Values of $C_o$ were determined by extrapolation of the linear parts of plots of [MPB] versus $t_p$ to zero polymerization time. Polymerization rate constants, $k_p$, were calculated assuming that propagation occurred with the total bulk monomer concentration using eqn (3):

$$R_p = k_p C^* [M]$$

(3)

where:

$C^*$: active centre concentration at zero time of polymerization in mol/mol Ti.

The linear increase in the [MPB] with $t_p$ occurs as a result of chain transfer with alkylaluminium. The rate of chain transfer, $R_{tr}$, with alkylaluminium may be obtained from the eqn (4):

$$[MPB] = C^* + \int_0^t R_{tr} dt$$

(4)

Assuming that the rate of chain transfer with alkylaluminium is constant with $t_p$, eqn (5) can be expressed as:

$$[MPB] = C^* + R_{tr} t$$

(5)

Plots of [MPB] versus $t_p$ possessed a linear region whose slope represented the rate of chain transfer whose intercept represents $C^*$. Table 6 represents the results obtained.

CONCLUSION

The rapid change in the rate of polymerization with polymerization time (the decay observed) [9] was mainly due to a decrease in $k_p$ and not significantly in $C^*$.

Only a relatively small percentage of the Ti loaded is involved in active centres.

There is an optimum value of $C^*$ with respect to temperature of polymerization.

REFERENCES