AN INFRARED INVESTIGATION OF THE CATALYST FORMATION
IN THE SYSTEM Ni(acac)₂, C₃H₄, (iBu)₃Al FOR PROPADIENE
POLYMERIZATION

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Summary

The catalyst formation in the system Ni(acac)₂, C₃H₄, (iBu)₃Al was
investigated by means of infrared spectroscopy. It was found that the
Al(acac)₃ and (iBu)₂Al(acac) formed are both by-products of catalyst forma-
tion without a catalytic activity. Ni(acac)₂ loses its acac groups forming the
unstable (iBu)₂Ni compound; without C₃H₄ being present, this compound
disproportionates to Ni metal and isobutane and isobutene. In the presence
of C₃H₄ an allyl-nickel complex is formed, which reacts with (iBu)₃Al to give the
actual catalyst, possibly a bimetallic allyl-nickel–aluminium complex. Catalysts
such as Ni(acac)₂, C₃H₄, (iBu)₃Al and (ηC₃H₅)₂Ni with or without (iBu)₃Al all
selectively give 1, 2, 1, 2-polypropadiene. A Lewis base like pyridine not only
decreases the polymerization rate but also changes the selectivity towards the
formation of 1, 2, 2, 1-polymer.

Introduction

Van den Enk and van der Ploeg [1, 2] propose a mechanism for the
catalyst formation in the Ni(acac)₂, C₃H₄, (iBu)₃Al* system, which they used
for the polymerization of propadiene. This mechanism is given in eqns. (1) -
(3).

\[
\begin{align*}
\text{Ni(acac)}₂ + (iBu)₃\text{Al} & \rightarrow [X] \\
[X] & \rightarrow \text{Ni}^{(0)} \\
[X] + C₃H₄ & \rightarrow \text{C}_₁\text{yellow} \quad \text{Al/Ni} \leq 2 \\
C₁ + (iBu)₃\text{Al} & \rightleftharpoons \text{C}_2\text{red} \quad \text{Al/Ni} > 2
\end{align*}
\]

*Ni(acac)₂ is nickelacetylacetonate; nickel, bis(2,2-pentane-dionato-0,0').
C₃H₄ is allene; propadiene.
(iBu)₃Al is triisobutylaluminium; aluminium, tris(2-methyl-propyl).
C₂ is the actual catalyst for the polymerization of C₃H₄.

The authors mention two most remarkable points in the mechanism:
(1) The presence of propadiene or another olefin is absolutely necessary before the addition of (iBu)₃Al to the Ni(acac)₂ solution, otherwise the inactive Ni metal is formed.
(2) Polymerization only takes place provided Al/Ni > 2.
This infrared investigation of this catalyst is performed to obtain more information about the structure of X, C₁ and C₂.

Experimental

All reactions, unless stated otherwise, are performed at room temperature in a benzene solution under a nitrogen atmosphere. The apparatus for working in a nitrogen atmosphere, free from oxygen and water (< 1 ppm), is described by De Liefde Meyer [3]. The concentration of the Ni(acac)₂ solution used is about 0.1 mole/l.

All infrared spectra are recorded from benzene solutions, unless stated otherwise, and compensated with pure benzene for the solvent absorptions.
Bis-π-allyl-nickel is synthesized via an allylgrignard according to the method described by Bogdanovic [4].
The polymerization experiments are carried out as described by van den Enk and van der Ploeg [1, 2].

Results and discussion

Aluminium components formed
When (iBu)₃Al reacts with Ni(acac)₂ only two different aluminium compounds can be formed: Al(acac)₃ and (iBu)₂Al(acac) [5, 6].
According to Kroll et al. [5, 6], (iBu)Al(acac)₂ is unstable, for it disproportionates immediately into (iBu)₂Al(acac) and Al(acac)₃. The authors showed by synthesizing R₂Al(acac) (R = methyl, ethyl or isobutyl) from Al(acac)₃ and R₂Al that a fast exchange of the acac groups takes place between these two components.
The results of our experiments are given in Tables 1 and 2. They show that if Ni(acac)₂ reacts with (iBu)₃Al, whether or not in the presence of propadiene, the same aluminium compounds appear as reaction products. When Al/Ni ≤ 2/3 only Al(acac)₃ is formed (characteristic absorptions: 1288 cm⁻¹, 490 cm⁻¹). If more (iBu)₃Al is added, (iBu)₂Al(acac) is formed until the ratio Al/Ni = 2 is reached. At this ratio all the Al(acac)₃ is converted into (iBu)₂Al(acac); the 1288 cm⁻¹ absorption is shifted to 1294 cm⁻¹ and instead of the strong absorption at 490 cm⁻¹ a weak one has appeared at 500 cm⁻¹. In addition to the Al(acac)₃ and the (iBu)₂Al(acac) formation, isobutene and isobutane are isolated gas chromatographically in equal amounts. This confirms the results of Pisher et al. [7].
Obviously the following reactions occur:

1. When \( \text{Al}/\text{Ni} \leq 2/3 \):

\[
\text{Ni(acac)}_2 + 2/3(i\text{Bu})_3\text{Al} \rightarrow \text{Ni}^{(0)} \downarrow + 2/3\text{Al(acac)}_3 + \text{C}_4\text{H}_8 + \text{C}_4\text{H}_{10}
\]

\( \text{C}_4\text{H}_8 \) is isobutene,
\( \text{C}_4\text{H}_{10} \) is isobutane.

(2) When \( 2/3 \leq \text{Al}/\text{Ni} \leq 2 \), the following reaction also takes place:

\[
\text{Al(acac)}_3 + 2(i\text{Bu})_3\text{Al} \rightarrow 3(i\text{Bu})_2\text{Al(acac)}.
\]

If more \( (i\text{Bu})_3\text{Al} \) is added so that the ratio \( \text{Al}/\text{Ni} > 2 \), this compound remains visible in the IR spectrum (1360, 1320, 1015, 635 cm\(^{-1}\)).

Neither the separate reactants of the catalyst system nor combinations of \( \text{Ni(acac)}_2 \) and \( (i\text{Bu})_3\text{Al} \) are capable of polymerizing the propadiene added. Obviously, the presence of propadiene during catalyst formation is essential. This is in agreement with the observation of van den Enk and van der Ploeg [1, 2].

**Experiments with (iBu)_2Al(acac)**

Van den Enk and van der Ploeg [1, 2] found that for \( \text{Al}/\text{Ni} \leq 2 \) a yellow \( \text{C}_1 \) complex is formed in the \( \text{Ni(acac)}_2, \text{C}_3\text{H}_4, (i\text{Bu})_3\text{Al} \) system, which is not active for polymerization.

As is shown above, at \( \text{Al}/\text{Ni} = 2 \) all the \( \text{Al(acac)}_3 \) formed has reacted with \( (i\text{Bu})_3\text{Al} \), forming \( (i\text{Bu})_2\text{Al(acac)} \) (see reaction B). One may suggest therefore, that \( (i\text{Bu})_2\text{Al(acac)} \) is either a catalyst poison or an indifferent by-product of the catalyst formation and \( (i\text{Bu})_3\text{Al} \) is necessary to activate the \( \text{C}_1 \) complex. We studied these possibilities by measuring the polymerization activity of the \( \text{Ni(acac)}_2 \) solution in benzene, saturated with propadiene in the presence of \( (i\text{Bu})_2\text{Al(acac)} \), instead of \( (i\text{Bu})_3\text{Al} \).

This system has a very low activity even if \( \text{Al}/\text{Ni} = 10 \). The acac groups from \( \text{Ni(acac)}_2 \) were exchanged for isobutyl groups, because we observed the infrared bands of \( \text{Al(acac)}_3 \) and the disappearance of \( \text{Ni(acac)}_2 \) bands, indicating that the \( \text{C}_1 \) complex is presumably formed. By adding an amount of \( (i\text{Bu})_3\text{Al} \) the propadiene polymerization became very fast at \( (i\text{Bu})_3\text{Al}/\text{Ni} \geq 2 \) and the 1, 2, 1, 2-polypropadiene was formed. These experiments show no clear poisoning effects from the excess of \( (i\text{Bu})_2\text{Al(acac)} \), so it can be regarded as a byproduct of the catalyst formation. From these experiments we may conclude that for the formation of an active catalyst at least part of the aluminium compound must be present in the reaction mixture without acac groups, in order to activate the \( \text{C}_1 \) complex.

**The formation of the catalyst in the presence of propadiene**

The results of the series of experiments in which the ratio \( \text{Al}/\text{Ni} \) was varied (Table 2) show that the same reactions occur between \( \text{Ni(acac)}_2 \) and \( (i\text{Bu})_3\text{Al} \) as far as aluminium is concerned, whether or not propadiene is present. The acac groups are exchanged and until \( \text{Al}/\text{Ni} = 2/3 \), \( \text{Al(acac)}_3 \) (1288, 490 cm\(^{-1}\)) is formed. When more \( (i\text{Bu})_3\text{Al} \) is added until \( \text{Al}/\text{Ni} = 2 \),
### TABLE 1

<table>
<thead>
<tr>
<th>Components</th>
<th>Characteristic infrared absorptions of the pure catalyst components and their reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni(acac)}_2 )</td>
<td>1500(vs) 1510(vs) 1450(sh) 1400(vs) 1260(s) 1190(w)</td>
</tr>
<tr>
<td>( \text{Al(acac)}_2 )</td>
<td>1582(s) 1524(s) 1379(s) 1282(m) 1196</td>
</tr>
<tr>
<td>( \text{Al(acac)}_2 )</td>
<td>1590(vs) 1530(vs) 1460(sh) 1388(vs) 1288(s) 1190(w)</td>
</tr>
<tr>
<td>( \text{(iBu)}_2 \text{Al(acac)} [5] )</td>
<td>1587(s) 1529(s) 1379(s) 1320(m) 1294(m)</td>
</tr>
<tr>
<td>( \text{(iBu)}_2 \text{Al(acac)} )</td>
<td>1585(vs) 1525(vs) 1460(sh) 1375(vs) 1320(m) 1294(s) 1178(s)</td>
</tr>
<tr>
<td>( \text{(iBu)}_2 \text{Al} )</td>
<td>1460(s) 1450(sh) 1395(sh) 1375(s) 1360(s) 1320(s) 1175(s)</td>
</tr>
<tr>
<td>( \text{C}_7\text{H}_8 ) (isobutene)</td>
<td>1653(s) 1455(s) 1435(s) 1372(s) 1275(w) 1170(m)</td>
</tr>
<tr>
<td>( \text{C}<em>8\text{H}</em>{10} ) (isobutane)</td>
<td>1459(s) 1388(m) 1365(s) 1225(m)</td>
</tr>
<tr>
<td>( \text{Ni(acac)}_2 ) : ( \text{(iBu)}_2 \text{Al} )</td>
<td>1 : 1/3 1580(vs) 1510(vs) 1450(sh) 1400(vs) 1288(s) 1260(s) 1190(w)</td>
</tr>
<tr>
<td>1 : 2/3 1600(w) 1590(vs) 1510(vs) 1450(sh) 1400(vs) 1320(w) 1288(s) 1260(m) 1190(m)</td>
<td></td>
</tr>
<tr>
<td>1 : 1 1655(w) 1590(vs) 1510(vs) 1450(sh) 1400(vs) 1320(m) 1290(m) 1260(w) 1175(m)</td>
<td></td>
</tr>
<tr>
<td>1 : 2 1650(w) 1580(s) 1525(s) 1455(sh) 1375(vs) 1318(m) 1292(m) 1260(w) 1175(m)</td>
<td></td>
</tr>
<tr>
<td>1 : 4 1650(w) 1580(s) 1525(s) 1460(sh) 1375(vs) 1318(s) 1294(w) 1175(m)</td>
<td></td>
</tr>
<tr>
<td>1 : 8 1650(w) 1580(s) 1525(s) 1460(s) 1375(vs) 1318(s) 1294(w) 1175(m)</td>
<td></td>
</tr>
<tr>
<td>1 : 10 ibid</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2

Infrared absorptions* of the reaction products of nickel catalyst systems in benzene

| \( \text{C}_7\text{H}_8 \) | 1945(s) | 1675(w) | 1385(m) |
| \( \text{2,4-dimethylpentene} \) | 1650(s) | 1385 - 1365(s) |

| \( \text{Ni(acac)}_2 \) : \( \text{C}_7\text{H}_8 \) : \( \text{(iBu)}_2 \text{Al} \) | 1 : 15 0.25 1945(s) 1675(w) 1350(sh) | 1288(w) 1260(s) |
| 1 : 3 0.3 1940(m) 1680(w) 1635(sh) 1360(sh) 1320(w) 1289(s) 1275(w) 1258(w) |
| 1 : 2 1 1940(vw) 1650(sh) 1635(sh) 1360(sh) 1320(m) 1292(m) |
| 1 : 3 2 1635(m) 1360(sh) 1318(m) 1292(m) |
| 1 : 4 1 1635(sh) 1360(sh) 1318(w) 1288(s) 1275(w) 1260(vw) |
| 1 : 4 2 1640(sh) 1360(sh) 1314(w) 1288(s) 1275(w) 1260(vw) |
| 1 : 4 8 1648(m) 1635(sh) 1360(sh) 1315(s) 1291(m) 1275(vw) |
| 1 : 4 10 1650(m) 1655(sh) 1359(s) 1317(m) 1293(w) 1275(vw) |
| \( \text{Ni(acac)}_2 \) : \( \text{C}_7\text{H}_8 \) : \( \text{(iBu)}_2 \text{Al(acac)} \) | 1 : 4 10.50(m) 1655(w) 1360(sh) 1320(w) 1288(s) |
| 1 : 6 10 1950(s) 1675(w) 1360(sh) 1320(w) 1291(s) |
| \( \text{C}_8\text{H}_{10} \) : \( \text{Ni} \) | 1755(w) 1690(vw) 1485(m) 1448(w) |
| 1 : 6 1655(w) 1630(sh) 1360(s) 1315(s) 1275(w) |

* The absorptions between 1590 - 1400 are not present in this table because this part of the spectrum was not recorded.

**N.R. = not recorded. Spectrum recorded until 650 cm\(^{-1}\).
mixtures in absence of propadiene. All components are solved in benzene

<table>
<thead>
<tr>
<th>170(sh)</th>
<th>100(s)</th>
<th>925(s)</th>
<th>765(m)</th>
<th>575(w)</th>
<th>415(m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1031(m)</td>
<td>935(m)</td>
<td>778(m)</td>
<td>593(sh)</td>
<td>577(m)</td>
<td>490(s)</td>
</tr>
<tr>
<td>1035(m)</td>
<td>939(m)</td>
<td>782(m)</td>
<td>595(w)</td>
<td>511(m)</td>
<td>500(m)</td>
</tr>
<tr>
<td>155(sh)</td>
<td>100(s)</td>
<td>935(m)</td>
<td>815(s)</td>
<td>635(s)</td>
<td>545(m)</td>
</tr>
<tr>
<td>155(sh)</td>
<td>1015(s)</td>
<td>945(m)</td>
<td>815(s)</td>
<td>635(s)</td>
<td>425(m)</td>
</tr>
<tr>
<td>1055(w)</td>
<td>915(w)</td>
<td>785(w)</td>
<td>882(vs)</td>
<td>795(w)</td>
<td>520(vs)</td>
</tr>
</tbody>
</table>

The spectrum is dominated by the acac-groups and there are no changes.
this Al(acac)₃ is completely converted into (iBu)₂Al(acac) (490 cm⁻¹ disappears, 1288 cm⁻¹ shifts to 1294 cm⁻¹). A remarkable difference is that no nickel precipitate is formed and the C₃H₄ present reacts (disappearance of 1945, 1675, 835 cm⁻¹). Moreover, isobutene (C₄H₈, 1650, 1275, 885 cm⁻¹) and C₇H₁₄ (1650, 890 cm⁻¹) were isolated with the aid of preparative gas chromatography. Infrared, H-N-M.R. and mass spectra of the latter compound showed it to be 2,4-dimethylpentene.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_3.
\end{align*}
\]

This compound is apparently formed from propadiene and an isobutyl group.

K. Fisher *et al.* [7] showed that by the reduction of Ni(acac)₂ with aluminium alkyls, nickel hydrides could be formed as an intermediate. This suggests that from NiH₂ and C₃H₄ a bis-\(\pi\)-allyl-nickel complex is formed (see Table 4), which is known to be a catalyst for the polymerization of propadiene [8]. We may therefore expect that, if bis \(\pi\) allyl-nickel is formed, the yellow C₁ complex should polymerize propadiene. According to van den Enk and van der Ploeg [1], this is not the case. We found, however, that, for instance, at Al/Ni = 1 propadiene was polymerized very slowly. The rate of polymerization is comparable with that of bis-\(\pi\)-allyl-nickel (see Table 3).

The C₁ complex might therefore be bis-\(\pi\)-allyl-nickel. In the infrared spectra from the catalyst mixture we could not detect the adsorptions of bis-\(\pi\)-allyl-nickel as given by Bogdanovic [4]. Neither was isolation of bis-\(\pi\)-allyl-nickel from this reaction mixture possible, because the C₁ complex, freed from solvent, gives, in the presence of the aluminium compound also formed, an oily mixture which is difficult to separate and purify. In addition to the absorption bands of the compounds known to be present, we observed a band at 1635 cm⁻¹ a \(\nu(C=\text{CH}_2)\) stretch and at 885 cm⁻¹ \(\nu(=\text{CH}_2)\) deformation. For C₂ these did not disappear after evaporation of the solvent and renewed addition of it to the compounds. They might indicate the presence of a \(\sigma\)-allyl group [9, 10].

Aiming to improve the detection of propadiene and \(\sigma\)- or \(\pi\)-allyl groups we tried to compensate all the absorption bands of the respective aluminium compounds by adding them to the benzene in the reference cell. The spectra only showed the 1650 - 1635 cm⁻¹ and 885 cm⁻¹ absorptions from a vinylidene group. No \(\pi\)-coordinate bond of propadiene to nickel and no \(\pi\)-allyl group was observed. When more propadiene was added it was still possible to isolate C₄H₈, but no 2,4-dimethylpentene. Within 5 minutes all added propadiene was consumed and the spectra gradually changed into those of 1, 2, 1,2-polypropadiene (1640, 1435, 1340, 1005, 889 cm⁻¹), which could be isolated.

Possible explanations for the phenomena observed, are:

(a) as long as Al/Ni < 2, bis-\(\pi\)-allyl-nickel is formed of which the rather weak infrared absorptions cannot be detected;

(b) if Al/Ni > 2, bis-\(\pi\)-allyl is transformed under the influence of (iBu)₂Al into a binuclear \(\sigma\)-allyl, which shows absorptions at 1635 cm⁻¹ and 890 cm⁻¹.
The catalyst system bis-π-allyl-nickel plus triisobutylaluminium

When bis-π-allyl-nickel has reacted with triisobutylaluminium (Al/Ni = 8), the infrared spectrum of the reaction mixture is similar to that of the catalyst system Ni(acac)₂ + 2C₃H₄ + 8(iBu)₃Al (see Table 2), apart from the absorptions of the acac groups. This means that also in this case no π-allyl absorptions can be detected. The characteristic absorptions of a vinylidene group are present (1650 - 1630, 890 cm⁻¹), which could belong to isobutene and/or to a σ-allyl group. Apparently triisobutylaluminium reacts with the bis-π allyl nickel complex, transforming the π-allyl into a σ-allyl structure and/or releasing part of the isobutyl groups, forming isobutene. The isolation of this complex has not been successful up till now, as the bimetallic complex is very unstable [11].

Polymerization of propadiene by various catalyst systems

Various systems have been used as polymerization catalysts (see Table 3). The polymerization rate with bis-π-allyl-nickel is of the same order of magnitude as that of the system Ni(acac)₂, C₃H₄, (iBu)₃Al, Al/Ni ≲ 2. The polymerization rates of both catalysts are increased enormously by the addition of (iBu)₃Al provided Al/Ni > 2 for the latter. In all these four cases the 1, 2, 1, 2-polypropadiene is formed exclusively, see Figs. 1 and 2. The polymer, however, obtained with bis-π-allyl-nickel has a lower melting point (80 - 92 °C) than the polymers obtained in the other 3 cases (melting point: 120 - 125 °C).

Fig. 1. 1, 2, 1, 2-polypropadiene; catalyst Ni(acac)₂ + C₃H₄ + (iBu)₃Al. [Ni] = 0.02 mol l⁻¹ Al/Ni = 5.

Fig. 2. 1, 2, 1, 2-polypropadiene; catalyst bis-π-allyl-nickel. [Ni] = 0.02 mol l⁻¹.
In the spectrum of the 1, 2, 1, 2-polymer of Otsuka [8] there is also an absorption at 1600 cm\(^{-1}\), which must be attributed to the 1, 2, 2, 1-polypropadiene [1, 2, 12].

In Table 3 and Fig. 3, it is shown that we get the same two kinds of structural elements in the polymer, if we use the Ni(acac)$_2$-2 pyridine complex, instead of Ni(acac)$_2$ in our catalyst system. Bromide may have the same effect as pyridine, acting as a Lewis base, which could cause the formation of 1, 2, 2, 1-polypropadiene, shown in the spectra of the polymers obtained by Otsuka [8].

**Discussion of the reaction scheme (Table 4)**

We shall now discuss the reaction scheme, as given in Table 4, in more detail.

The total exchange of the ligands between (iBu)$_3$Al and Ni(acac)$_2$ indicates that (iBu)$_3$Ni can be formed as an intermediate. In the infrared spectra of the catalyst reaction mixtures no Ni-C bonds are found. If these bonds have a lifetime long enough to be detected by infrared, the absorption will be very weak and will lie in the far infrared between 650 and 250 cm\(^{-1}\). It is more likely that these bonds are so unstable [13] that, if no propadiene is present, the (iBu)$_3$Ni formed will disproportionate immediately into nickel metal and isobutene and isobutane [5]. Even at $-124 \, ^\circ\text{C}$ we observed the formation of nickel metal from the reactants Ni(acac)$_2$ and (iBu)$_3$Al.

(iBu)$_3$Ni formed in this way disproportionate via nickel hydride [5, 14, 15]. If propadiene is present this nickel hydride can form a \(\pi\)-allyl-nickel complex which is relatively stable. In literature this type of reaction has been described for the Pd-H bond with propadiene or butadiene [16].

Evidence of the disproportionation of (iBu)$_3$Ni into a Ni-H bond can be seen in the fact that in the presence of propadiene only isobutene could be detected and no isobutane. Not only this reaction occurs, but also a small amount of propadiene inserts into a nickel-isobutyl bond, as is shown by the formation of a small amount of 2,4-dimethylpentene.
TABLE 3

Activity and selectivity of various catalyst systems for the polymerization of propadiene at 1 atm and 20 °C in benzene

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni (mmol/ml)</th>
<th>Al/Ni (mmole)</th>
<th>C₃H₄ (mmole)</th>
<th>Time (h)</th>
<th>Solvent volume (ml)</th>
<th>C₃H₄ conversion (%)</th>
<th>Structure of the polymer by infrared spectrum</th>
<th>Melting point (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(acac)₂ + C₃H₄ + (iBu)₃Al</td>
<td>0.2</td>
<td>1</td>
<td>6</td>
<td>67</td>
<td>5</td>
<td>50</td>
<td>1, 2, 1, 2</td>
<td>120 - 130</td>
<td></td>
</tr>
<tr>
<td>Ni(acac)₂ + C₃H₄ + (iBu)₃Al</td>
<td>0.2</td>
<td>10</td>
<td>6</td>
<td>0.08</td>
<td>5</td>
<td>95</td>
<td>1, 2, 1, 2</td>
<td>120 - 130</td>
<td></td>
</tr>
<tr>
<td>Ni(acac)₂ + (iBu)₃Al + C₃H₄</td>
<td>0.2</td>
<td>10</td>
<td>6</td>
<td>17</td>
<td>5</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ni(acac)₂ + C₄H₆ + (iBu)₃Al</td>
<td>0.2</td>
<td>3</td>
<td>6</td>
<td>0.08</td>
<td>5</td>
<td>80</td>
<td>1, 2, 1, 2</td>
<td>120 - 130</td>
<td></td>
</tr>
<tr>
<td>Co(acac)₂ + C₃H₄ + (iBu)₃Al</td>
<td>0.2</td>
<td>1</td>
<td>6</td>
<td>0.08</td>
<td>5</td>
<td>90</td>
<td>1, 2, 1, 2</td>
<td>120 - 130</td>
<td></td>
</tr>
<tr>
<td>Co(acac)₃ + C₃H₄ + (iBu)₃Al</td>
<td>0.2</td>
<td>1</td>
<td>6</td>
<td>0.08</td>
<td>5</td>
<td>90</td>
<td>1, 2, 1, 2</td>
<td>120 - 130</td>
<td></td>
</tr>
<tr>
<td>Ni(acac)₂2pyr + C₃H₄ + (iBu)₃Al</td>
<td>0.2</td>
<td>2</td>
<td>2</td>
<td>48</td>
<td>5</td>
<td>90</td>
<td>1, 2, 1, 2 + 1, 2, 1</td>
<td>120 - 130</td>
<td></td>
</tr>
<tr>
<td>(πC₃H₅)₂Ni</td>
<td>0.0025</td>
<td>-</td>
<td>23.6</td>
<td>67</td>
<td>20</td>
<td>25**</td>
<td>1, 2, 1, 2</td>
<td>80 - 92</td>
<td></td>
</tr>
<tr>
<td>(πC₃H₅)₂Ni + (iBu)₃Al</td>
<td>0.06</td>
<td>10</td>
<td>1.4</td>
<td>0.08</td>
<td>1.2</td>
<td>95</td>
<td>1, 2, 1, 2</td>
<td>120 - 125</td>
<td></td>
</tr>
<tr>
<td>Ni(acac)₂ + C₃H₄ + (iBu)₃Al</td>
<td>0.002</td>
<td>10</td>
<td>37.5</td>
<td>0.08</td>
<td>50</td>
<td>36.0**</td>
<td>1, 2, 1, 2</td>
<td>113 - 122</td>
<td>1</td>
</tr>
<tr>
<td>Ni(acac)₂ + (iBu)₃Al</td>
<td>0.002</td>
<td>-</td>
<td>24</td>
<td>-</td>
<td>-</td>
<td>16.7**</td>
<td>1, 2, 1, 2 + 1, 2, 1</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>(πC₃H₅)₂Ni</td>
<td>0.002</td>
<td>-</td>
<td>24 - 28</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1, 2, 1, 2 + 1, 2, 2, 1</td>
<td>60 - 61</td>
<td>8</td>
</tr>
<tr>
<td>(πC₃H₅)NiBr</td>
<td>0.002</td>
<td>-</td>
<td>24</td>
<td>-</td>
<td>-</td>
<td>67.5**</td>
<td>1, 2, 1, 2 + 1, 2, 2, 1</td>
<td>60 - 61</td>
<td>8</td>
</tr>
</tbody>
</table>

*Butadiene. **Conversions in % based on polypropadiene isolated.
TABLE 4
Reaction scheme of the catalyst formation

\[
\begin{align*}
\text{Al/Ni} \leq 2/3 & \quad 3\text{Ni(acac)}_2 + 2\text{(iBu)}_3\text{Al} \rightarrow 3\text{(iBu)}_2\text{Ni} + 2\text{Al(acac)}_3 \\
\text{green} \\
\frac{2/3 < \text{Al/Ni} < 2}{2/3 < \text{Al/Ni} < 2} & \quad 2\text{Al(acac)}_3 + 4\text{(iBu)}_3\text{Al} \rightarrow 6\text{(iBu)}_2\text{Al(acac)} \\
\text{[5]} \\
\text{Al/Ni} = 2 & \quad \text{Ni(acac)}_2 + 2\text{(iBu)}_3\text{Al} \rightarrow \text{(iBu)}_2\text{Ni} + 2\text{(iBu)}_2\text{Al(acac)} \\
\text{(iBu)}_2\text{Ni} & \rightarrow \text{iBuNiH} + \text{C}_4\text{H}_8 \quad \text{[7]} \\
\end{align*}
\]

By repeated reaction with propadiene the following complexes could be formed as \(C_1\):

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 \quad \quad \quad \quad \text{CH}_2 & \quad \quad \quad \quad \text{CH}_2 \\
\text{CH}_2 & \quad \quad \quad \quad \text{CH}_2 \\
\text{CH}_2 & \quad \quad \quad \quad \text{CH}_2 \\
\text{(yellow)}
\end{align*}
\]

If \(\text{Al/Ni} > 2\) we obtain, for instance:

\[
\begin{align*}
\text{(\pi\text{C}_3\text{H}_5)}_2\text{Ni} + \text{(iBu)}_3\text{Al} & \rightarrow \text{C}_2\text{-complex} + \text{C}_4\text{H}_8 \\
\text{orange-red}
\end{align*}
\]

\(\text{C}_2\) is possibly a bimetallic \(\sigma\)-allyl-nickel-aluminium complex.

If \(\text{C}_3\text{H}_4\) is not present \((\text{iBu})_2\text{Ni}\) disproportionates:

\[
\begin{align*}
(\text{iBu})_2\text{Ni} & \rightarrow \text{Ni}^{[0]} \quad \downarrow \quad + \text{C}_4\text{H}_8 + \text{C}_4\text{H}_{10} \quad \text{[7]} \\
\text{black}
\end{align*}
\]

In the infrared spectra (Table 2) it is shown that in the preparation of the catalyst with twice the equivalent amount of propadiene relative to nickel, this propadiene quickly disappears, even if \(2/3 \leq \text{Al/Ni} \leq 2\). While the propadiene absorptions in the infrared spectra disappear, vinylidene absorptions appear (1650 - 1635 and 890 cm\(^{-1}\)). This may point to the polymerization of propadiene to 1, 2, 1, 2-polypropadiene, which gives the same absorptions. However, no polymers and no oligomers (other than the small amount of \(\text{C}_7\text{H}_{14}\)) could be isolated in this case. So there must be another explanation for these absorptions. For \(\text{Al/Ni} \leq 2\) the presence of isobutene explains the absorptions observed (isobutene 1650; 885 cm\(^{-1}\)). For \(\text{Al/Ni} > 2\) these absorptions are still present after evaporation of the solvent and therefore they
cannot be caused by isobutene. An explanation for these bands is that they may find their origin in $\sigma$-allyl groups. For instance, $\sigma$-allyl-mercury [9] shows infrared absorptions at almost the same positions, i.e., 1623 cm$^{-1}$, 881 cm$^{-1}$. $\sigma$-allyl-nickel complex could have been formed under the influence of (iBu)$_3$Al.

The same changes in the infrared absorptions were observed after the reaction between bis-$\pi$-allyl-nickel and (iBu)$_3$Al. It may therefore be possible that in this case, and in the case of the C$_2$ complex, a bimetallic nickel–aluminium complex is formed. Complex formation between bis-$\pi$-allyl-nickel and (iBu)$_3$Al can cause one vacant coordination place if both $\pi$-allyl-groups rearrange to $\sigma$-allyl groups. The polymerization can occur via a coordination-insertion mechanism.

The promotor action of (iBu)$_3$Al in the bimetallic complex must be sought in its electron-attracting character, as (iBu)$_3$Al is a Lewis acid. The stabilization of a $\pi$-allyl bond by back-donation will be less strong, making $\pi$-allyl more feasible to transform into the $\sigma$-allyl configuration. Also the Ni–C bond is destabilized by electron attraction of (iBu)$_3$Al, thus making it easier for the propadiene to insert into the Ni–C bond in its presence. If the coordination of propadiene to the metal is the rate-determining step during the polymerization reaction, then the electron-attracting capacity of (iBu)$_3$Al is an advantage too, because in this case the $\pi$-electron donation can take place more easily.

Lewis acids such as (iBu)$_3$Al enhance the polymerization rate, while bases like pyridine decrease the rate. Moreover, the selectivity becomes lower, because not only 1, 2, 1, 2-polypropadiene is formed, but also 1, 2, 2, 1-polypropadiene.

The influence of Lewis acids and bases as well as the kinetics of the propadiene polymerization will be the subject of a future publication.

Conclusions

(1) The unstable compound [X] in the reaction mechanism shown by van den Enk and van der Ploeg (see Introduction), may be (iBu)$_2$Ni. In the absence of propadiene this compound disproportionates by releasing isobutene and isobutane. Most likely this disproportionation goes via a nickel hydride bond. If propadiene is present a $\pi$-allyl-nickel complex and isobutene are formed probably via the nickel hydride intermediate.

(2) Al(acac)$_3$ formed in the reaction between Ni(acac)$_2$ and (iBu)$_3$Al, reacts with (iBu)$_3$Al forming (iBu)$_2$Al(acac). Both aluminium compounds are catalytically non-active by-products of the catalyst formation.

(3) The simultaneous formation of (iBu)$_2$Al(acac) and an allyl-nickel complex until the ratio Al/Ni = 2 is reached, is responsible for the fact that, up to this ratio, the catalytic activity of the catalyst as found by van den Enk and van der Ploeg, is as low as the activity found for bis-$\pi$-allyl-nickel.

(4) The reaction between bis-$\pi$-allyl-nickel and (iBu)$_3$Al gives a catalyst of the same activity as the Ni(acac)$_2$ system with Al/Ni > 2. So (iBu)$_3$Al is not only a reactant but also a promotor.
(5) The C₂ complex (see Introduction) possibly is a bimetallic allyl-nickel-aluminium complex.

(6) The Lewis base pyridine not only decreases the polymerization rate, but also changes the selectivity of the catalyst towards the formation of the 1,2,2,1-polymer.

References