

## AN INFRARED INVESTIGATION OF THE CATALYST FORMATION IN THE SYSTEM $\text{Ni}(\text{acac})_2$ , $\text{C}_3\text{H}_4$ , $(\text{iBu})_3\text{Al}$ FOR PROPADIENE POLYMERIZATION

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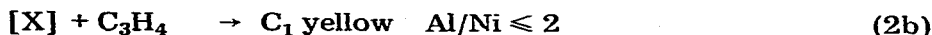
(Received October 18, 1976)

### Summary

The catalyst formation in the system  $\text{Ni}(\text{acac})_2$ ,  $\text{C}_3\text{H}_4$ ,  $(\text{iBu})_3\text{Al}$  was investigated by means of infrared spectroscopy. It was found that the  $\text{Al}(\text{acac})_3$  and  $(\text{iBu})_2\text{Al}(\text{acac})$  formed are both by-products of catalyst formation without a catalytic activity.  $\text{Ni}(\text{acac})_2$  loses its acac groups forming the unstable  $(\text{iBu})_2\text{Ni}$  compound; without  $\text{C}_3\text{H}_4$  being present, this compound disproportionates to Ni metal and isobutane and isobutene. In the presence of  $\text{C}_3\text{H}_4$  an allyl-nickel complex is formed, which reacts with  $(\text{iBu})_3\text{Al}$  to give the actual catalyst, possibly a bimetallic allyl-nickel-aluminium complex. Catalysts such as  $\text{Ni}(\text{acac})_2$ ,  $\text{C}_3\text{H}_4$ ,  $(\text{iBu})_3\text{Al}$  and  $(\pi\text{C}_3\text{H}_5)_2\text{Ni}$  with or without  $(\text{iBu})_3\text{Al}$  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  $\text{Ni}(\text{acac})_2$ ,  $\text{C}_3\text{H}_4$ ,  $(\text{iBu})_3\text{Al}^*$  system, which they used for the polymerization of propadiene. This mechanism is given in eqns. (1) - (3).



\* $\text{Ni}(\text{acac})_2$  is nickelacetylacetonate; nickel, bis(2,2-pentane-dionato-0,0').  
 $\text{C}_3\text{H}_4$  is allene; propadiene.  
 $(\text{iBu})_3\text{Al}$  is triisobutylaluminium; aluminium, tris(2-methyl-propyl).

$C_2$  is the actual catalyst for the polymerization of  $C_3H_4$ .

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  $Al/Ni \geq 2$ .

This infrared investigation of this catalyst is performed to obtain more information about the structure of X,  $C_1$  and  $C_2$ .

## 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- $\pi$ -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*

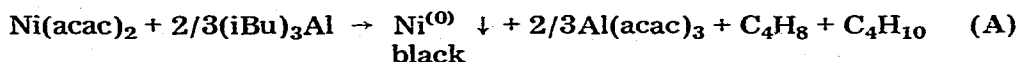
When  $(iBu)_3Al$  reacts with  $Ni(acac)_2$  only two different aluminium compounds can be formed:  $Al(acac)_3$  and  $(iBu)_2Al(acac)$  [5, 6].

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  $R_2Al(acac)$  ( $R =$  methyl, ethyl or isobutyl) from  $Al(acac)_3$  and  $R_3Al$  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  $Al/Ni \leq 2/3$  only  $Al(acac)_3$  is formed (characteristic absorptions:  $1288\text{ cm}^{-1}$ ,  $490\text{ cm}^{-1}$ ). 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  $1288\text{ cm}^{-1}$  absorption is shifted to  $1294\text{ cm}^{-1}$  and instead of the strong absorption at  $490\text{ cm}^{-1}$  a weak one has appeared at  $500\text{ cm}^{-1}$ . 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 Fisher *et al.* [7].

Obviously the following reactions occur:

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



$\text{C}_4\text{H}_8$  is isobutene,

$\text{C}_4\text{H}_{10}$  is isobutane.

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



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

Neither the separate reactants of the catalyst system nor combinations of  $\text{Ni}(\text{acac})_2$  and  $(\text{iBu})_3\text{Al}$  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 $(\text{iBu})_2\text{Al}(\text{acac})$*

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

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

This system has a very low activity even if  $\text{Al/Ni} = 10$ . The acac groups from  $\text{Ni}(\text{acac})_2$  were exchanged for isobutyl groups, because we observed the infrared bands of  $\text{Al}(\text{acac})_3$  and the disappearance of  $\text{Ni}(\text{acac})_2$  bands, indicating that the  $\text{C}_1$  complex is presumably formed. By adding an amount of  $(\text{iBu})_3\text{Al}$  the propadiene polymerization became very fast at  $(\text{iBu})_3\text{Al/Ni} \geq 2$  and the 1, 2, 1, 2-polypropadiene was formed. These experiments show no clear poisoning effects from the excess of  $(\text{iBu})_2\text{Al}(\text{acac})$ , 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  $\text{Al/Ni}$  was varied (Table 2) show that the same reactions occur between  $\text{Ni}(\text{acac})_2$  and  $(\text{iBu})_3\text{Al}$  as far as aluminium is concerned, whether or not propadiene is present. The acac groups are exchanged and until  $\text{Al/Ni} = 2/3$ ,  $\text{Al}(\text{acac})_3$  ( $1288, 490 \text{ cm}^{-1}$ ) is formed. When more  $(\text{iBu})_3\text{Al}$  is added until  $\text{Al/Ni} = 2$ ,

TABLE 1

Characteristic infrared absorptions of the pure catalyst components and their reaction

Components										
Ni(acac) <sub>2</sub>		1590(vs)	1510(vs)	1450(sh)	1400(vs)				1260(s)	1190(w)
Al(acac) <sub>3</sub> [5]		1582(s)	1524(s)		1379(s)			1282(m)		1196
Al(acac) <sub>3</sub>		1590(vs)	1530(vs)	1460(sh)	1388(vs)			1288(s)		1190(w)
(iBu) <sub>2</sub> Al(acac) [5]		1587(s)	1529(s)		1379(s)	1320(m)	1294(m)			1193(m)
(iBu) <sub>2</sub> Al(acac)		1585(vs)	1525(vs)	1460(sh)	1375(vs)	1320(m)	1294(s)			1178(s)
(iBu) <sub>3</sub> Al		1460(s)	1450(sh)	1395(sh)	1375(s)	1360(s)	1320(s)			1175(s)
C <sub>4</sub> H <sub>8</sub> (isobutene)	1653(s)		1455(s)	1435(s)	1372(s)			1275(w)		
C <sub>4</sub> H <sub>10</sub> (isobutane)			1459(s)	1388(m)	1365(s)	1325(m)				1170(m)
Ni(acac) <sub>2</sub> : (iBu) <sub>3</sub> Al										
1 : 1/3		1590(vs)	1510(vs)	1450(sh)	1400(vs)	-		1288(s)	1260(s)	1190(w)
1 : 2/3	1650(w)	1590(vs)	1510(vs)	1450(sh)	1400(vs)	1320(w)		1288(s)	1260(m)	1190(m)
1 : 1	1655(w)	1590(vs)	1510(vs)	1450(sh)	1400(vs)	1320(w)	1290(m)		1260(w)	1175(m)
1 : 2	1650(w)	1580(s)	1525(s)	1455(sh)	1375(vs)	1318(m)	1292(m)		1260(vw)	1175(m)
1 : 4	1650(w)	1580(s)	1525(s)	1460(s)	1375(vs)	1318(m)	1293(w)			1175(m)
1 : 8	1650(w)	1580(s)	1525(s)	1460(s)	1375(vs)	1318(s)	1294(w)			1175(s)
1 : 10		<i>ibid</i>								

TABLE 2

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

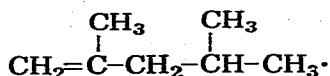
C <sub>3</sub> H <sub>4</sub>		1945(s)	1675(w)			1385(m)				
2,4-dimethylpentene				1650(s)		1385 - 1368(s)				
Ni(acac) <sub>2</sub> + C <sub>3</sub> H <sub>4</sub> + (iBu) <sub>3</sub> Al										
1   15   0.25		1945(s)	1675(w)			1360(sh)		1288(w)		1260(s)
1   3   0.3		1940(m)	1680(w)			1635(sh)	1360(sh)	1288(s)	1275(vw)	1260(s)
1   2   1		1940(vw)		1650(sh)		1635(sh)		1289(s)	1275(vw)	1258(w)
1   3   2						1635(m)	1360(sh)	1318(m)	1292(m)	
1   4   1						1635(sh)	1360(sh)	1318(w)	1288(s)	1275(vw)
1   4   2						1640(sh)	1360(sh)	1314(w)	1288(s)	1275(vw)
1   4   8				1648(m)		1635(sh)	1360(sh)	1315(s)	1291(m)	1275(vw)
1   4   10				1650(m)		1635(sh)	1359(s)	1317(m)	1293(w)	1275(vw)
Ni(acac) <sub>2</sub> + C <sub>3</sub> H <sub>4</sub> + (iBu) <sub>2</sub> Al(acac)										
1   4   2		1950(m)				1360(sh)	1320(sh)	1288(s)		
1   6   10		1950(s)	1675(w)			1360(sh)	1320(w)	1291(s)		
( $\pi$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Ni		1755(vw)	1690(vw)	1485(m)	1448(w)					1205(m)
( $\pi$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Ni + (iBu) <sub>3</sub> Al										
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

\*\*N.R. = not recorded. Spectrum recorded until 650 cm<sup>-1</sup>.



this  $\text{Al}(\text{acac})_3$  is completely converted into  $(\text{iBu})_2\text{Al}(\text{acac})$  ( $490\text{ cm}^{-1}$  disappears,  $1288\text{ cm}^{-1}$  shifts to  $1294\text{ cm}^{-1}$ ). A remarkable difference is that no nickel precipitate is formed and the  $\text{C}_3\text{H}_4$  present reacts (disappearance of  $1945, 1675, 835\text{ cm}^{-1}$ ). Moreover, isobutene ( $\text{C}_4\text{H}_8$ ,  $1650, 1275, 885\text{ cm}^{-1}$ ) and  $\text{C}_7\text{H}_{14}$  ( $1650, 890\text{ cm}^{-1}$ ) 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.



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

K. Fisher *et al.* [7] showed that by the reduction of  $\text{Ni}(\text{acac})_2$  with aluminium alkyls, nickel hydrides could be formed as an intermediate. This suggests that from  $\text{NiH}_2$  and  $\text{C}_3\text{H}_4$  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  $\text{C}_1$  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  $\text{Al}/\text{Ni} = 1$  propadiene was polymerized very slowly. The rate of polymerization is comparable with that of bis- $\pi$ -allyl-nickel (see Table 3).

The  $\text{C}_1$  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  $\text{C}_1$  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  $1635\text{ cm}^{-1}$  a  $\nu(\text{C}=\text{CH}_2)$  stretch and at  $885\text{ cm}^{-1}$   $\nu(=\text{CH}_2)$  deformation. For  $\text{C}_2$  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  $1650 - 1635\text{ cm}^{-1}$  and  $885\text{ cm}^{-1}$  absorptions from a vinylidene group. No  $\pi$ -coordinative bond of propadiene to nickel and no  $\pi$ -allyl group was observed. When more propadiene was added it was still possible to isolate  $\text{C}_4\text{H}_8$ , 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 ( $1640, 1435, 1340, 1005, 889\text{ cm}^{-1}$ ), which could be isolated.

Possible explanations for the phenomena observed, are:

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

(b) if  $\text{Al}/\text{Ni} > 2$ , bis- $\pi$ -allyl is transformed under the influence of  $(\text{iBu})_3\text{Al}$  into a binuclear  $\sigma$ -allyl, which shows absorptions at  $1635\text{ cm}^{-1}$  and  $890\text{ cm}^{-1}$ .

### *The catalyst system bis- $\pi$ -allyl-nickel plus triisobutylaluminium*

When bis- $\pi$ -allyl-nickel has reacted with triisobutylaluminium (Al/Ni = 8), the infrared spectrum of the reaction mixture is similar to that of the catalyst system  $\text{Ni}(\text{acac})_2 + 2\text{C}_3\text{H}_4 + 8(\text{iBu})_3\text{Al}$  (see Table 2), apart from the absorptions of the acac groups. This means that also in this case no  $\pi$ -allyl absorptions can be detected. The characteristic absorptions of a vinylidene group are present ( $1650 - 1630, 890 \text{ cm}^{-1}$ ), which could belong to isobutene and/or to a  $\sigma$ -allyl group. Apparently triisobutylaluminium reacts with the bis- $\pi$ -allyl-nickel complex, transforming the  $\pi$ -allyl into a  $\sigma$ -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- $\pi$ -allyl-nickel is of the same order of magnitude as that of the system  $\text{Ni}(\text{acac})_2, \text{C}_3\text{H}_4, (\text{iBu})_3\text{Al}, \text{Al/Ni} \leq 2$ . The polymerization rates of both catalysts are increased enormously by the addition of  $(\text{iBu})_3\text{Al}$  provided  $\text{Al/Ni} > 2$  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- $\pi$ -allyl-nickel has a lower melting point ( $80 - 92^\circ\text{C}$ ) than the polymers obtained in the other 3 cases (melting point:  $120 - 125^\circ\text{C}$ ).

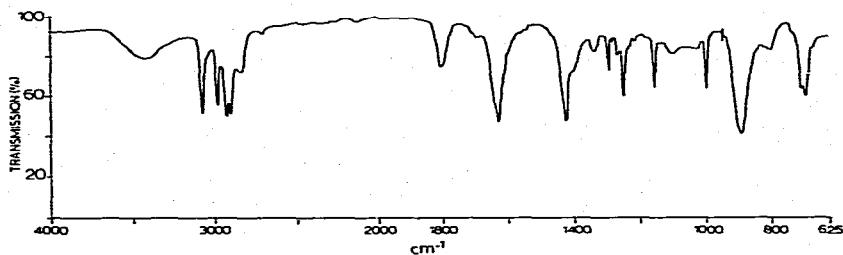


Fig. 1. 1, 2, 1, 2-polypropadiene; catalyst  $\text{Ni}(\text{acac})_2 + \text{C}_3\text{H}_4 + (\text{iBu})_3\text{Al}$ .  $[\text{Ni}] = 0.02 \text{ mol l}^{-1}$   
Al/Ni = 5.

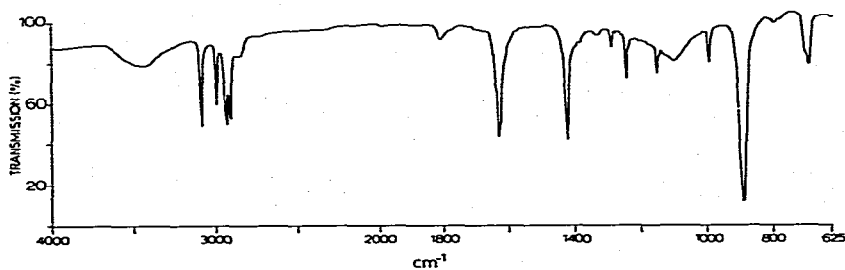


Fig. 2. 1, 2, 1, 2-polypropadiene; catalyst bis- $\pi$ -allyl-nickel.  $[\text{Ni}] \approx 0.02 \text{ mol l}^{-1}$ .

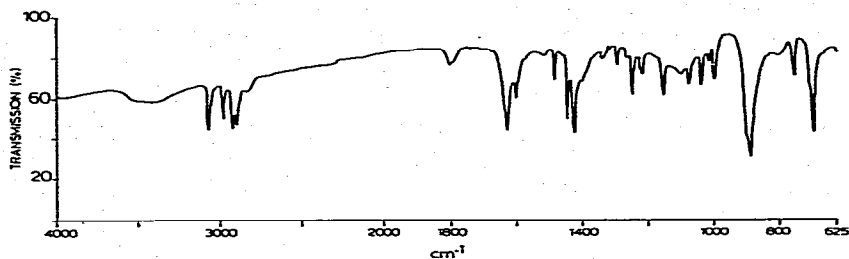


Fig. 3. 1, 2, 1, 2 + 1, 2, 2, 1-polypropadiene; catalyst  $\text{Ni}(\text{acac})_2\text{2pyr} + \text{C}_3\text{H}_4 + (\text{iBu})_3\text{Al}$ .  $[\text{Ni}] = 0.2 \text{ mol l}^{-1}$ .  $\text{Al/Ni} = 2$ .

In the spectrum of the 1, 2, 1, 2-polymer of Otsuka [8] there is also an absorption at  $1600 \text{ cm}^{-1}$ , 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  $\text{Ni}(\text{acac})_2 \cdot 2$  pyridine complex, instead of  $\text{Ni}(\text{acac})_2$  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  $(\text{iBu})_3\text{Al}$  and  $\text{Ni}(\text{acac})_2$  indicates that  $(\text{iBu})_2\text{Ni}$  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  $250 \text{ cm}^{-1}$ . It is more likely that these bonds are so unstable [13] that, if no propadiene is present, the  $(\text{iBu})_2\text{Ni}$  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  $\text{Ni}(\text{acac})_2$  and  $(\text{iBu})_3\text{Al}$ .

$(\text{iBu})_2\text{Ni}$  formed in this way disproportionates *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  $(\text{iBu})_2\text{Ni}$  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

Catalyst	Ni (mmol/ml)	Al/Ni (mmole) (mmole)	C <sub>3</sub> H <sub>4</sub> (mmole)	Time (h)	Solvent volume (ml)	C <sub>3</sub> H <sub>4</sub> conversion (%)	Structure of the polymer by infrared spectrum	Melting point (°C)	Refer- ence
Ni(acac) <sub>2</sub> + C <sub>3</sub> H <sub>4</sub> + (iBu) <sub>3</sub> Al	0.2	1	6	67	5	50	1, 2, 1, 2	120 - 130	
Ni(acac) <sub>2</sub> + C <sub>3</sub> H <sub>4</sub> + (iBu) <sub>3</sub> Al	0.2	10	6	0.08	5	95	1, 2, 1, 2	120 - 130	
Ni(acac) <sub>2</sub> + (iBu) <sub>3</sub> Al + C <sub>3</sub> H <sub>4</sub>	0.2	10	6	17	5	0	-	-	
Ni(acac) <sub>2</sub> + C <sub>4</sub> H <sub>6</sub> * + (iBu) <sub>3</sub> Al	0.2	3	6	0.08		80	1, 2, 1, 2	120 - 130	
Co(acac) <sub>2</sub> + C <sub>3</sub> H <sub>4</sub> + (iBu) <sub>3</sub> Al	0.2	1	6	0.08	5	90	1, 2, 1, 2	120 - 130	
Co(acac) <sub>3</sub> + C <sub>3</sub> H <sub>4</sub> + (iBu) <sub>3</sub> Al	0.2	1	6	0.08	5	90	1, 2, 1, 2	120 - 130	
Ni(acac) <sub>2</sub> 2pyr + C <sub>3</sub> H <sub>4</sub> + (iBu) <sub>3</sub> Al	0.2	2	2	48	5	90	1, 2, 1, 2 + 1, 2, 2, 1		
(πC <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Ni	0.0025	-	23.6	67	20	25**	1, 2, 1, 2	80 - 92	
(πC <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Ni + (iBu) <sub>3</sub> Al	0.06	10	1.4	0.08	1.2	95	1, 2, 1, 2	120 - 125	
Ni(acac) <sub>2</sub> + C <sub>3</sub> H <sub>4</sub> + (iBu) <sub>3</sub> Al	0.002	10	37.5	0.08	50	36.0**	1, 2, 1, 2	113 - 122	1
Ni(acac) <sub>2</sub> + (iBu) <sub>3</sub> Al	0.002			24		16.7**	1, 2, 1, 2 + 1, 2, 2, 1		8
(πC <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Ni	0.002	-		24 - 28			1, 2, 1, 2 + 1, 2, 2, 1	60 - 61	8
(πC <sub>3</sub> H <sub>5</sub> )NiBr	0.002	-		24		67.5**	1, 2, 1, 2 + 1, 2, 2, 1	60 - 61	8

\*Butadiene.

\*\*Conversions in % based on polypropadiene isolated.



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.*,  $1623\text{ cm}^{-1}$ ,  $881\text{ cm}^{-1}$ .  $\sigma$ -allyl-nickel complex could have been formed under the influence of  $(i\text{Bu})_3\text{Al}$ .

The same changes in the infrared absorptions were observed after the reaction between bis- $\pi$ -allyl-nickel and  $(i\text{Bu})_3\text{Al}$ . It may therefore be possible that in this case, and in the case of the  $\text{C}_2$  complex, a bimetallic nickel-aluminium complex is formed. Complex formation between bis- $\pi$ -allyl-nickel and  $(i\text{Bu})_3\text{Al}$  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  $(i\text{Bu})_3\text{Al}$  in the bimetallic complex must be sought in its electron-attracting character, as  $(i\text{Bu})_3\text{Al}$  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  $(i\text{Bu})_3\text{Al}$ , 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  $(i\text{Bu})_3\text{Al}$  is an advantage too, because in this case the  $\pi$ -electron donation can take place more easily.

Lewis acids such as  $(i\text{Bu})_3\text{Al}$  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  $(i\text{Bu})_2\text{Ni}$ . 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)  $\text{Al}(\text{acac})_3$  formed in the reaction between  $\text{Ni}(\text{acac})_2$  and  $(i\text{Bu})_3\text{Al}$ , reacts with  $(i\text{Bu})_3\text{Al}$  forming  $(i\text{Bu})_2\text{Al}(\text{acac})$ . Both aluminium compounds are catalytically non-active by-products of the catalyst formation.

(3) The simultaneous formation of  $(i\text{Bu})_2\text{Al}(\text{acac})$  and an allyl-nickel complex until the ratio  $\text{Al}/\text{Ni} = 2$  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  $(i\text{Bu})_3\text{Al}$  gives a catalyst of the same activity as the  $\text{Ni}(\text{acac})_2$  system with  $\text{Al}/\text{Ni} > 2$ . So  $(i\text{Bu})_3\text{Al}$  is not only a reactant but also a promotor.

(5) The  $C_2$  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.

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