European Polymer Journal, Vol. 16, pp. 745 to 752

0014-3057/80/0801-0745$02.00/0

THE POLYMERIZATION OF PROPADIENE BY $Ni(acac)_2$, C_3H_4, R_nAlX_{3-n} CATALYSTS

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(*Received* 30 *October* 1979)

Abstract—Catalyst formation in the system $Ni(acac)_2$, C_3H_4, R_nAlX_{3-n} was studied. Polymerization experiments showed that, by replacing ionic groups such as $acac^-$, Br^-, Cl^- with alkyl or hydride groups, an active catalyst is obtained. Electrolysis of $Ni(acac)_2$ in tetrahydrofuran also gives an active catalyst. Lewis acids like $(iBu)_3Al$ and Et_3Al increase the polymerization rate, while Lewis bases like pyridine and triphenylphosphine not only decrease the rate but also change selectivity. The selectivity is not changed if different transition metals (e.g. Co, Pd, Ni) are used. Kinetic measurements show a first order dependence on Ni. The dependence on $(iBu)_3Al$ changes from first to zero order with increasing Al/Ni ratio. This can be explained by assuming that the very active catalyst is formed via an equilibrium between a nickel complex and $(iBu)_3Al$. A first order deactivation of the nickel catalyst is observed; it is faster during polymerization than during ageing of the catalyst.

INTRODUCTION

The polymerization of propadiene by a catalyst consisting of $Ni(acac)_2$ and Et_3Al dissolved in benzene was discovered by Otsuka [1, 2]. He stated that this catalyst system has little activity and gives a gelled insoluble polymer. This in contrast with the polymers formed by π-allylnickel complexes, which are readily soluble.

van den Enk and van der Ploeg [3] found that, by changing the sequence of trialkylaluminium and monomer addition, a highly active catalyst for propadiene polymerization is formed. They also showed [4] that it is essential that a stabilizing ligand is present before the trialkylaluminium is added, otherwise inactive nickel metal is formed. Wilke [5] stated that different catalytic behaviour could possibly be found by the use of $(iBu)_3Al$ [3, 4] instead of Et_3Al [1].

The polymer obtained by van den Enk and van der Ploeg [3, 4] is slightly soluble in boiling toluene, chlorobenzene and xylene. The low solubility may be due to the high crystallinity [6]. The high solubility of the polymer prepared using a π-allylnickel catalyst by Otsuka [1] can be caused by 1.2.2.1 structural elements being present together with the 1.2.1.2 structural elements as shown by the i.r.-spectrum [7, 8].

van Ommen *et al.* [8] found that bis-π-allylnickel gives a polymer with the same 1.2.1.2.-structure as the system based on $Ni(acac)_2$ but the bis-π-allylnickel catalyst is much less active. It was shown that the activity of the bis-π-allylnickel can be increased to the same level as that of the $Ni(acac)_2$ based catalyst by adding $(iBu)_3Al$. They concluded from i.r.-investigations that in the mechanism proposed by van den Enk and van der Ploeg [3]:

$$
\begin{aligned}
&Ni(acac)_2 + (iBu)_3Al \rightarrow X\\
&X \rightarrow Ni\ (metal)\\
&X + C_3H_4 \rightarrow C_1\\
&C_1 + (iBu)_3Al \rightleftarrows C_2\\
&C_2 + nC_3H_4 \rightarrow 1.2.1.2\ polypropadiene
\end{aligned}
$$

X could be $(iBu)_2Ni$ (decomposing in the absence of propadiene to Ni-metal, isobutane and isobutene) and C_1 might possibly be a π-allylnickel complex. The formation and structure of C_2 remained obscure.

The aim of this study was 2-fold, namely to find whether or not the structure and reactivity of the aluminium alkyl [5] is essential for the activity and selectivity of the catalysts, and also to perform kinetic measurements as a function of C_{Ni} and C_{Al}, in order to learn more about composition and structure of the complex C_2 [3].

EXPERIMENTAL

Materials

$Ni(acac)_2$ (Baker) was sublimed at 190° before use. R_nAlX_{3-n} (Schuchardt, purity 93–95%) was used without further purification. Propadiene (L'air liquide, purity 99%) was freed from O_2 and H_2O by bubbling through triisobutylaluminium. Toluene and benzene (Merck, pro analysis) were dried on molecular sieve 13X (Union Carbide) and degassed and saturated with purified N_2. The N_2 was freed from O_2 with a BTS-catalyst (BASF) and dried with molecular sieve 13X, the resulting O_2 and H_2O contents being less than 1 ppm.

Procedures

Unless stated otherwise, all reactions were performed under N_2. The kinetic measurements were performed at 21° and 25° in the way described earlier [9, 10]. The rate was not limited by the dissolution of the propadiene. The Hatta number at 21° is $\sqrt{k_r D}/k_{sol} = 4 \times 10^{-3}$ (k_r is reaction rate constant; D is diffusion constant of propadiene in benzene and toluene, k_{sol} is rate constant of dissolution). This number must be larger than 0.3 for the dissolution process to influence the reaction rate [11]. The solubility of propadiene in toluene or benzene at 21.5° is 1.2 ± 0.2 mol l^{-1}. The polymer obtained was isolated as described by van den Enk and van der Ploeg [3] and characterized by means of i.r. spectroscopy. The ESR-samples were transferred with a syringe into a quartz-tube fitted with a stopcock and serum cap. The ESR-spectra were recorded on a Varian-E ESR-spectrometer.

Table 1. Polymerization of propadiene with various catalyst systems at 1 atm, unless stated otherwise, and 21°. Propadiene is added before the second component x. Solvent benzene or * toluene. Crossl. = crosslinked polymer

Catalyst Ni	x	C_{Ni} or C_{Pd} ($mol \cdot l^{-1}$)	C_x ($mol \cdot l^{-1}$)	$\frac{x}{Ni}$	C_3H_4 (mmol)	Time (hr)	Volume (ml)	Conversic (%C_3H_4	Structure of polym (i.r. spect)
$Ni(acac)_2$	$(iBu)_3Al$	0.002	0.002	1	6	1	5	6	1.2.1.2
$Ni(acac)_2$	$(iBu)_3Al$	0.002	0.02	10	6	1	5	25	1.2.1.2
$Ni(acac)_2$	$iBu)_2Alacac$	0.004	0.05	11	7.7	2	6.4	5	1.2.1.2
$Ni(acac)_2$	iBuMgBr	0.002	0.5	250	6	1	5	ND	1.2.1.2
—	iBuMgBr	—	0.5	—	6	48	5*	—	—
$Ni(acac)_2$	Et_3Al	0.002	0.02	10	6	1.1	5*	6	1.2.1.2
$Ni(acac)_2$	Et_2AlCl	0.002	0.02	10	6	1	5*	12	1.2.1.2 and crossl.
$Ni(acac)_2$	$EtAlCl_2$	0.002	0.02	10	6	0.8	5*	11	1.2.1.2 and crossl.
—	$EtAlCl_2$	—	0.06	—	6	1	5*	6	crossl.
—	$AlBr_3$	—	30	—	513	24	100	ND	crossl. (under pressure)
$Ni(acac)_2$	$LiAlH_4$	0.02	0.02	1	12	10	1 ml THF 10 ml Toluene	ND	1.2.1.2
$Ni(acac)_2$	Electrolysis with Al electrodes	0.2	—	—	125	72	THF 250	50§	1.2.1.2 (50% oligomers of the 1.2.2.1-type)
$Ni(acac)_2 2Pyr$	$(iBu)_3Al$	0.2	0.4	2	2	48	5	90§	1.2.1.2/1.2.2.1
$Ni(acac)_2$	½bipy‡ $(iBu)_3Al$	0.02	0.04	2	6	1.1	5*	8§	1.2.1.2
$Ni(acac)_2$	½bipy‡ $(iBu)_3Al$	0.02	0.10	5	6	1.1	5	8§	1.2.1.2
$Ni(acac)_2$	½bipy $(iBu)_3Al$	0.04	0.14	3.5	6	1.1	5*	16§	1.2.1.2
$NiCl_2$	$(iBu)_3Al$	Suspension 0.087	0.024	3.6	142	0.2	120*	80§	1.2.1.2
$NiBr_2$	$(iBu)_3Al$	Suspension 0.5	1.3	2.5	40	21	52	48§	1.2.1.2
$Pd(acac)_2$	$(iBu)_3Al$	0.024	0.24	10	60	2	50*	7§	1.2.1.2
$Pd(acac)_2PPh_3$	$(iBu)_3Al$	0.024	0.24	10	60	2	50*	1§	1.2.1.2/1.2.2.1
πC_3H_5NiCl†	—	0.001	—	—	2.450	23	797*	89§	1.2.1.2/1.2.2.1 (under pressure)
$(\pi C_3H_5)_2Ni$	—	0.0025	—	—	23.6	67	20*	25§	1.2.1.2

† Unpublished results of van den Enk.
‡ bipy = bipyridyl.
§ Conversions based on the amount of polymer isolated.
ND = not determined.

Table 2. Influence of different aluminium alkyls on the polymerization rate [Ni(acac)$_2$] = 0.002 mol·l^{-1}. Volume is 5 ml toluene. r in ml/min. The toluene is saturated with C_3H_4 at 1 atm and this concentration is maintained during polymerization

Aluminium alkyl	Al/Ni	r_5^*	r_{10}^*	r_{40}^*
$(iBu)_3Al$	2	0.18	0.10	0.08
	5	0.74	0.57	0.37
	10	0.80	0.66	0.45
Et_3Al	5	0.20	0.14	0.11
	10	0.21	0.16	0.12
Et_2AlCl	5	0.64	0.39	0.18
	10	0.61	0.45	0.11
$EtAlCl_2$	5	0.51	0.27	0.10
	10	0.53	0.27	0.11
$EtAlCl_2$	$C_{Al} = 0.06$	0.47	0.30	0.10

*r_i means polymerization rate after i min of polymerization.

RESULTS

Survey and discussion of polymerization experiments

Table 1 shows catalysts for the polymerization of C_3H_4 to polypropadiene. To obtain an active catalyst, it is essential that C_3H_4 is present before the activating agent is added. When Et_3Al is used instead of $(iBu)_3Al$, the catalyst has a lower activity. When an Al–chloride bond is present, anionic polymerization is also possible and a crosslinked product as well as the 1.2.1.2-polymer is obtained. Surprisingly this Al–hal bond must already be present; when it is formed during the reaction in the case of $NiCl_2$ or $NiBr_2$, only 1.2.1.2-polypropadiene is formed. $LiAlH_4$ can only be used as an activator if a polar solvent, such as tetrahydrofuran in which it is soluble, is used. All ways of activation have the common feature of being able to remove the acac-groups from Ni(acac)$_2$.

Pd(acac)$_2$, C_3H_4, $(iBu)_3Al$ also give the 1.2.1.2 polymer although with low efficiency. This shows that it is not the Pd-atom itself which is responsible for the 1.2.2.1 polymer formation in the $Pd(NO)_3$, PPh_3, HAc (acetic acid) system of Shier [12]. It appears that the ligands of the transition metal influence the selectivity. This view is supported by the earlier observation [8] that pyridine can change the selectivity of our system towards 1.2.2.1 polymer formation. The result (Table 1) with π-allylnickel chloride, where a mixture of 1.2.1.2 and 1.2.2.1 structural elements in the polymer has also been found, substantiates this.

$(iBu)_3Al$(bipy), $(iBu)_2Al$(acac), Et_3Al, $LiAlH_4$ and electrolysis with Ni(acac)$_2$ give catalysts of low activity compared with Ni(acac)$_2$ and $(iBu)_3Al$ for Al/Ni > 2. Their activity is of the same order of magnitude as Ni(acac)$_2$ and $(iBu)_3Al$ for Al/Ni < 2 (see Table 2), probably because in these cases a bimetallic C_2 complex cannot be formed. It is also shown in this table that, if an aluminium alkyl containing Cl atoms is used, a polymerization rate is obtained which is the average of the 1.2.1.2 polymerization rate for C_1 and that for the chlorine containing aluminium alkyl itself, which gives a crosslinked polymer (Table 1).

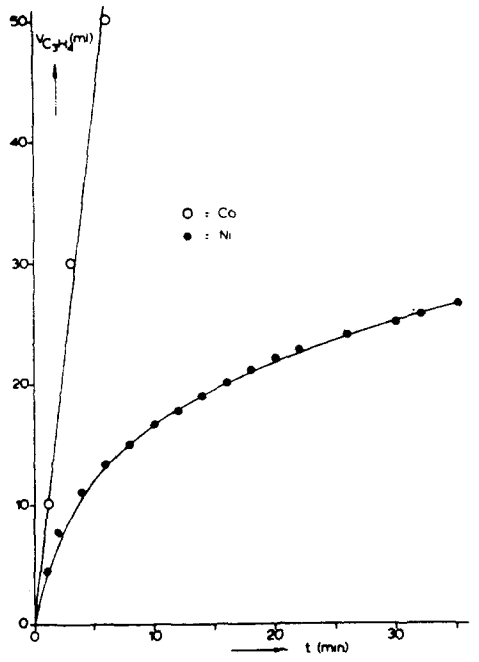


Fig. 1. The volume of C_3H_4 consumed as a function of time: O for $C_{Co(III)} = 2.8 \times 10^{-3}$ mol·l^{-1}, $C_{Al} = 1.60 \times 10^{-3}$ mol·l^{-1}, $T = -3.5°$ [10]; ● for $C_{Ni} = 2 \times 10^{-3}$ mol·l^{-1}, $C_{Al} = 588 \times 10^{-3}$ mol·l^{-1}, $T = 21.5°$, reaction volume 5 ml.

Kinetic results

Figure 1 shows a typical plot of the volume of C_3H_4 consumed as a function of time. In contrast with what is found for Co [10], the rate is not constant but decreases with time. This is also found when the reaction temperature is lowered to −15°.

ESR-measurements during polymerization (see Table 3) show that decomposition to Ni(I) and/or Ni(metal) cannot be the cause of the deactivation, as no ESR-signal is observed. If Ni(acac)$_2$ reacts with $(iBu)_3Al$ in the absence of C_3H_4, the broad ESR-

Table 3. ESR-signals in catalyst mixtures, solvent benzene

C_{Ni} (mol l^{-1})	C_3H_4 (mol l^{-1})	C_{Al} (mol l^{-1})	Temp. (°C)	ESR g.value	Solvent volume	Polymerization time (hr)	% Conversion of C_3H_4	Structure of the polymer by i.r.
0.2	—	0.07	20	2.2	5 ml	—	—	—
0.2	—	0.4	20	2.2	i.d.	—	—	—
0.2	—	1.6	20	2.2	i.d.	—	—	—
0.002	1.2	0.0013	20	None	50 ml	24	0.2	1.2.1.2
0.002	1.2	0.003	20	None	i.d.	24	1.8	1.2.1.2
0.002	1.2	0.006	20	None	i.d.	24	4.1	1.2.1.2

Table 4. Influence of ageing of the catalyst on the polymerization rate, solvent benzene, $T = 21°$

Concentration during ageing				Concentration during polymerization (reaction volume 5 ml)				
C_{Ni} (mmol ml^{-1})	$C_{C_3H_4}$ (mmol ml^{-1})	C_{Al} (mmol ml^{-1})	Time (hr)	C_{Ni} (mmol ml^{-1})	$C_{C_3H_4}$ (mmol ml^{-1})	C_A (mmol ml^{-1})	r initial (ml min^{-1})	r after 47 min (ml min^{-1})
0.009	0.028	2.73	0.3	0.002	1.2	0.59	1.25	0.20
i.d.	i.d.	i.d.	5.6	i.d.	i.d.	i.d.	1.20	0.20
i.d.	i.d.	i.d.	24.7	i.d.	i.d.	i.d.	0.88	0.22
i.d.	i.d.	i.d.	28.5	i.d.	i.d.	i.d.	0.67	0.22
i.d.	i.d.	i.d.	96.6	i.d.	i.d.	i.d.	0.55	0.20

signal at g = 2.2 [13] is in accordance with disproportionation to Ni(metal), which is known to occur [5, 8].

It was also observed that deactivation of the catalyst took place more quickly during polymerization than when stoichiometric catalyst mixtures were allowed to age without polymerization (see Table 4). The mechanism of ageing must be different from that of deactivation, although the process must lead to the same final product because the residual activities are identical.

To determine the polymerization rate as a function of the Ni and/or Al concentration, initial rates must be used. In practice this is rather difficult because upon adding the last catalyst component [where it makes no difference whether this is $(iBu)_3Al$ or $Ni(acac)_2$], the catalyst is formed, releasing its heat of formation, while C_3H_4 dissolves in the added $(iBu)_3Al$. It is thus not known exactly what is measured at very short times. Therefore the rate at $t = 10$ min is chosen as the pseudo-initial rate.

In Fig. 2 this quantity is plotted as a function of the Ni concentration in the presence of a large excess of $(iBu)_3Al$ $59 < Al/Ni < 590$. The order with respect to Ni is found to be unity, as found for Co [10]. From the slope of this line, a rate constant of 2.4 min^{-1} at 21.5° is obtained which is considerably smaller than the value for Co of 29 min^{-1} at −3.5°.

Figure 3 shows that a large excess of $(iBu)_2Al(acac)$, which is a by-product of the catalyst formation as shown by i.r.-spectra [8], has no influence on the rate of polymerization within experimental error. There is however a slight tendency for decrease of activity with increasing $(iBu)_2Al(acac)$ concentration which could be caused by the reaction of a small part of the $(iBu)_3Al$ with the increasing amount of acac-groups [14, 15]. Figures 4 and 5 show the rate of C_3H_4 consumption at $t = 10$/min as a function of the Al-concentration over a wide range. The Ni concentration is constant but in practically all cases small compared with the Al-concentration. From Fig. 4 it appears that up to $Al/Ni = 2$ there is a small increase in rate. From $Al/Ni > 2$ the rate increases sharply. Figure 5 shows that, when $Al/Ni > 8$–100, the increase of rate with $(iBu)_3Al$ concentration is less than proportional and approaches zero.

DISCUSSION OF THE KINETIC RESULTS

From the mechanism proposed by van den Enk and van der Ploeg [2], it follows that at high $(iBu)_3Al$

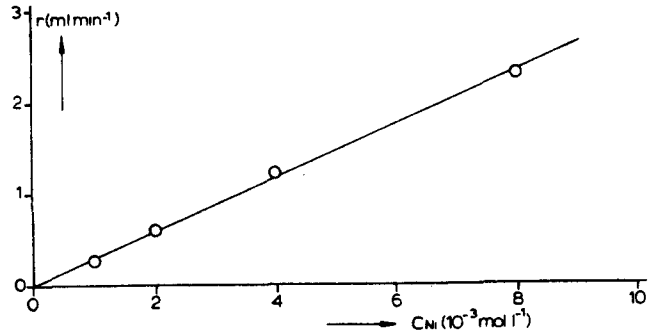


Fig. 2. The rate of C_3H_4 polymerization as a function of $Ni(acac)_2$ concentration. $C_{Al} = 588 \times 10^{-3}$ mol·l^{-1}, $T = 21.5°$, reaction volume 5 ml, $t = 10$ min.

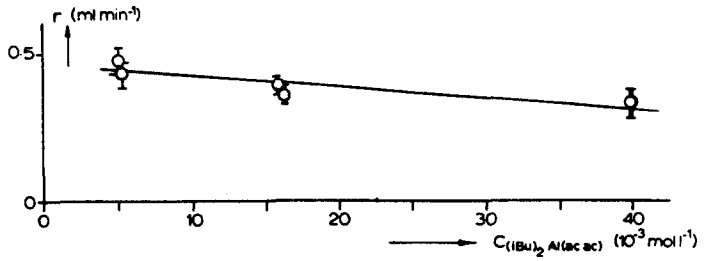


Fig. 3. The rate of C_3H_4 polymerization as a function of $(iBu)_2Al(acac)$ concentration. $C_{Ni} = 2.10^{-3}$ mol·l^{-1}, $C_{Al} = 20{\cdot}10^{-3}$ mol·l^{-1}, $T = 21.5°$, reaction volume 5 ml.

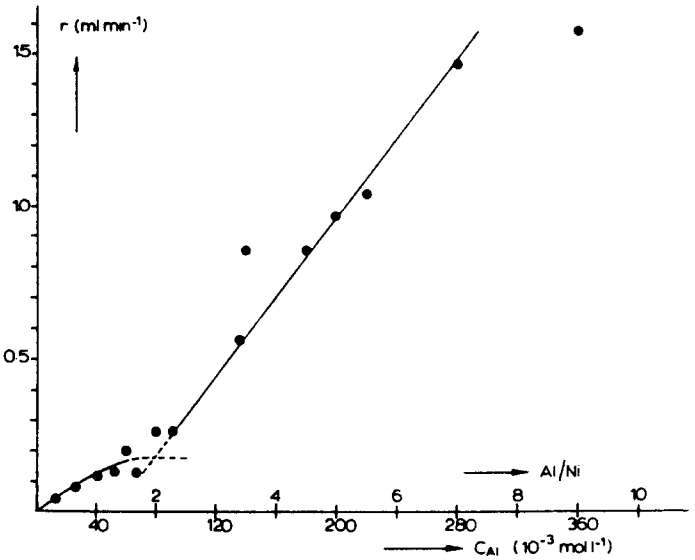


Fig. 4. The rate of C_3H_4 polymerization as a function of $(iBu)_3Al$ concentration. $C_{Ni} = 40 \cdot 10^{-3}$ mol·l^{-1}, $T = 21.5°$, reaction volume 2 ml.

(Al/Ni ≥ 30) concentrations the rate of the polymerization should be first order in the Ni-concentration in agreement with Fig. 2. This means that the concentration of the active catalyst is proportional to the original concentration of nickel acetylacetonate. That $(iBu)_2Al(acac)$ has no influence on the catalyst activity, as shown in Fig. 3, is also in agreement with their mechanism. Figure 4 shows that, up to Al/Ni = 2, a catalyst is obtained with low activity. In agreement with an earlier publication [8], it is observed that there is a small increase in rate up to Al/Ni = 2. This rate increase is small because part of the $(iBu)_3Al$ reactions with $Al(acac)_3$ to give $(iBu)_2Al(acac)$ which, as shown in Fig. 3, does not influence the rate. Above Al/Ni = 2 the rate increases again sharply with Al-concentration, because then all $Al(acac)_3$ has been converted to $(iBu)_2Al(acac)$ and excess $(iBu)_3Al$ for the formation of the more active catalyst C_2 is available. From the bending of the curve (Fig. 5) at high Al/Ni ratios, it is deduced that a bimetallic C_2 catalyst is formed via an equilibrium.

Table 4 shows a low but constant polymerization rate at long polymerization times. Thus two other types of catalytically active species may be involved; such an effect is not unusual with this type of catalyst [16]. To explain the observations, the following mechanism is proposed*:

$$\text{Al/Ni} \leq 2 \quad \text{Ni} + 2\text{Al} \longrightarrow C_1$$

$$C_1 + C_3H_4 \xrightarrow{k_1} \text{1.2.1.2 polypropadiene}$$

$$\text{Al/Ni} > 2 \quad C_1 + \text{Al} \overset{K_e}{\rightleftharpoons} C_2$$

$$C_2 + C_3H_4 \xrightarrow{k_2} \text{1.2.1.2 polypropadiene}$$

$$C_2 \xrightarrow{k_4} C_3$$

$$C_3 + C_3H_4 \xrightarrow{k_3} \text{1.2.1.2 polypropadiene}$$

* r is rate of polymerization; k_1, k_2, k_3 are rate constants of polymerization by C_1, C_2, C_3; k_4 is rate constant of deactivation $C_2 \rightarrow C_3$; Ni and Al are $Ni(acac)_2$ and $(iBu)_3Al$ respectively.

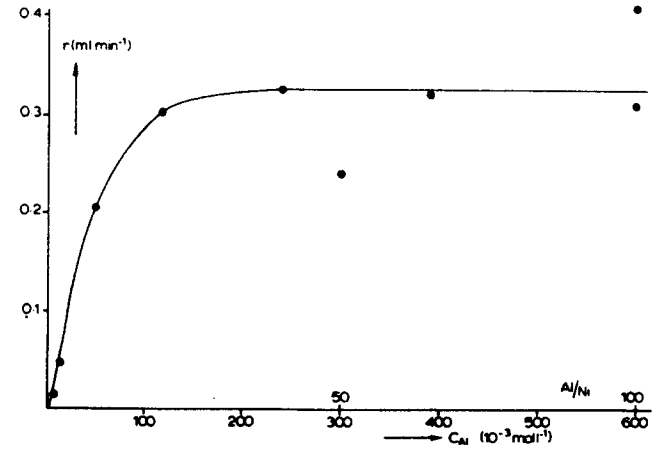


Fig. 5. The rate of C_3H_4 polymerization as a function of $(iBu)_3Al$ concentration. $C_{Ni} = 6.10^{-3}$ mol·l^{-1}, $T = 25°$, reaction volume 1 ml.

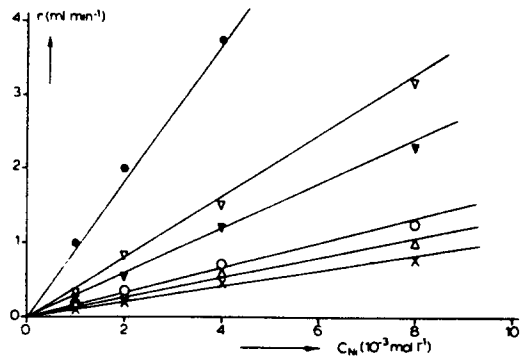


Fig. 6. The rate of C_3H_4 polymerization as a function of $Ni(acac)_2$ concentration at various times. $C_{Al} = 588 \cdot 10^{-3}$ mol·l^{-1}, reaction volume 5 ml. ● $t = 2$ min; ▽ $t = 6$ min; ▼ $t = 10$ min; ○ $t = 16$ min; △ $t = 20$ min; × $t = 28$ min.

The rate of polymerization is then given by [17,18]:

$$r = k_1 C_1 + k_2 C_2 + k_3 C_3 \quad (1)$$

$$C_1 = Ni_0 - C_2 - C_3 \quad (2)$$

C_2 can be calculated from

$$K_e = \frac{C_2}{C_1 + Al}. \quad (3)$$

Figure 1 shows a decreasing rate with time. For a first order process, the rate at different times must be a linear function of C_{Ni} which is actually the case (see Fig. 6). The deactivation is then described by

$$\frac{dC_2}{dt} = k_d C_2 . \quad (4)$$

By elimination of C_1 and C_2 and integration, a rather complicated equation is obtained for the volume of C_3H_4 consumed as a function of time, C_{Ni} and C_{Al}. From the data of Fig. 4 it follows that $k_1 = 0.15$ min^{-1} and from those of Table 4 that $k_3 = 0.83$ min^{-1} and from Fig. 5 $K_e = 33$ mol^{-1}·l. After differentiation of the integrated rate equation with respect to K_e/k_2, k_3 and k_d, a set of equations is obtained which is fitted with the rate measurements using a least squares method by adjusting k_2, k_d and k_3 leading to the following results:

Set of measurements	K_e mol^{-1}·l	k_1 min^{-1}	k_2 min^{-1}	k_3 min^{-1}	k_d min^{-1}	$\frac{\sum_i (\hat{V}_{i,t} - V_{i,t})^2}{\Sigma Ni - 1}$ Sum of squares of deviations
Fig. 6	33	0.15	4.2	0.84	0.14	$5.02\ 10^{-1}$
Fig. 5	33	0.15	5.54	1.0	0.13	$3.73\ 10^{+1}$
Fig. 4	33	0.15	1.0	0.3	0.12	$4.93\ 10^{+1}$

From Figs 5 and 6, the average value of k_2 is 4.7 ± 1.5 min^{-1} in reasonable agreement with the results obtained from the data of Fig. 2 at $t = 10$ min.

The lines shown in Fig. 6 give the best fit with the experimental points. These are also the most reproducible results, possibly caused by the high Al/Ni ratio, so that impurities such as O_2 or H_2O had negligible effect on the rate of the reaction.

The rather big deviation of k_2 and k_3 calculated from the data in Fig. 4 could be caused by catalyst poisoning by O_2 and H_2O because in that case C_{Al} is smallest, so that the protection of the catalyst by the excess of $(iBu)_3Al$ is also slight. This poisoning would decrease the active Ni concentration leading to an apparent decrease of k_2 and k_3 by a factor of about 3–4.

A fitting procedure using all five constants simultaneously is unfortunately too complicated and does not lead to unequivocal results. On the other hand this mechanism does give a reasonable description of the overall kinetic curves.

DISCUSSION OF THE CATALYST STRUCTURE

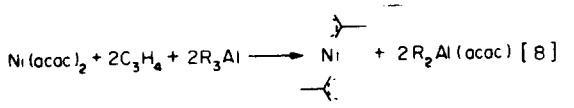
The i.r. spectra and the polymerization experiments [8] indicate that the C_1 complex formed up to Al/Ni = 2 is an allylnickel complex (see Scheme 1). The rate measurements show that $(iBu)_2Al(acac)$ is only a by-product of the catalyst formation. The experiments with different alkylating agents show that it is possible to obtain an active catalyst when ionic groups such as $acac^-$, Br^-, Cl^- are replaced by alkyl or hydride groups. However, $Ni(hal)_2$ does not dissolve in benzene or toluene so that probably only part of the $Ni(hal)_2$ is converted to the active soluble catalyst, and only a very small amount of Al–hal bonds is formed. The concentration of Al–hal bonds is obviously too low for creating a detectable amount of crosslinked polypropadiene (compare Table 1). Insertion of C_3H_4 into the Ni–alkyl or Ni–hydride bond then gives a relatively stable allylnickel complex. If no protection olefin, which can form a π-allyl group, is present, Ni metal precipitates and an active catalyst is not obtained.

An explanation of Otsuka's observation of a low 1.2.1.2-polymer yield when using a [$Ni(acac)_2$ + Et_3Al] system as catalyst and our observation that [$Ni(acac)_2$ + $(iBu)_3Al$] is not active, is that in our case (and probably also in Otsuka's experiment) the trialkyl aluminium compound is added before the monomer. In that case Ni metal is formed which is inactive for polymerization. If C_3H_4 is added directly after (within half a minute) the aluminium alkyl, not all the Ni has precipitated and some catalyst can still be formed. We performed one experiment in this way and obtained a very small yield of 1.2.1.2 polypropadiene.

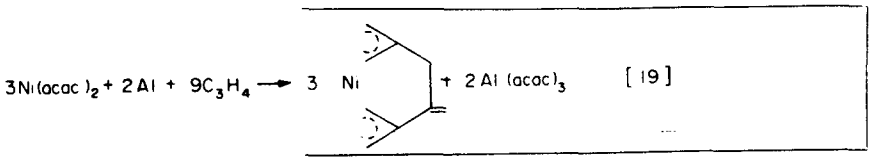
Even the electrolysis fits in this scheme. It is known [19, 20] that, via oxidative addition of propadiene, π-allylnickel complexes can be formed. Also it is known that transition metal atoms react with suitable olefins to form complexes [22]. By reduction of $Ni(acac)_2$ by electrolysis in an aprotic solvent, Ni atoms can be formed subsequently reacting with propadiene, to form, via oxidative addition, an allylnickel complex.

SCHEME 1

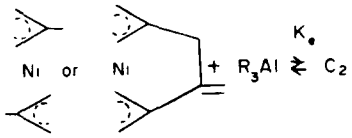
Chemical formation of C_1



Formation of C_1 by electrolysis.
The overall cell reaction, using Al-electrodes is:



followed by



The catalyst thus obtained has low activity, comparable with that of bis-π-allylnickel. $(iBu)_3Al$ is needed as a Lewis acid to form a bimetallic catalyst with high activity. Kinetic measurements show that a bimetallic catalyst containing Ni and Al is formed in an equilibrium step. Co-ordinatively saturated aluminium alkyls, such as $(iBu)_2Al(acac)$, $(Et_2AlCl)_2$ or $(iBu)_3Al(bipy)$, are unable to form such a complex and therefore show the low activity of the C_1 complex. The anionic polymerization activity of the chlorinated aluminium alkyls makes it more difficult to see what takes place. From Table 2 it appears that the rate of the anionic and of the (1.2.1.2) C_1 polymerization are almost additive. So a possible explanation is that these two types of polymerization take place independently.

The increase in rate caused by $(iBu)_3Al$ forming the C_2 complex is considerable (a factor of 30, compare k_1 and k_2). It can be explained in the same way as proposed previously [8]. The electron attracting character of the Lewis acid $(iBu)_3Al$ destabilizes the π-allyl bond so that it becomes more like a σ-allyl bond and insertion of C_3H_4 in this destabilized bond will be easier. When this is the rate determining step, the rate of the polymerization increases. When co-ordination of C_3H_4 to the metal is rate determining, a low electron density on the Ni is also an advantage because π-electron donation of the propadiene can take place more easily. From the present results, it is not possible to choose between these alternatives. Measurement of the order in C_3H_4 may clarify this.

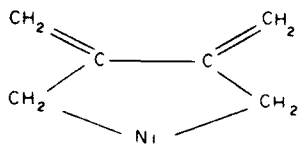
It is more difficult to explain why Et_3Al is not such a good co-catalyst as $(iBu)_3Al$. The inability of Et_3Al to form a Ni–Al bimetallic complex, as stated previously for $(iBu)_2Al(acac)$, $(Et_2AlCl)_2$ and $(iBu)_3Al(bipy)$, could be the cause. However, Et_3Al is a better Lewis acid than $(iBu)_3Al$ and is expected to form bimetallic complexes more readily as shown by its dimerization. On the other hand this could also be the cause of its lower activity: the dimers being so stable that the formation of a Ni–Al bimetallic complex has a smaller equilibrium constant of complex formation. From published data [23] it can be calculated that the dissociation constant of $(Et_3Al)_2$ is $3 \cdot 10^{-3}$ at 298° in mesitylene, which will lower K_e considerably. $(iBu)_3Al$ does not dimerize, predominantly because of steric hindrance. To form a complex with Ni could be easier because Ni (0.72 Å) is larger than Al (0.50 Å). Also steric hindrance is smaller because one of the groups is a σ-allyl which is less bulky than an isobutyl-group and only two groups are present (see Scheme 1). In the same way, $(iBu)_3Al$ forms a complex with $Et(iBu)_2Al$ where steric hindrance is also smaller [24, 25].

In agreement with our results, Wilke [5] suggested that $Ni(acac)_2$, Et_3Al could give a catalyst with a lower activity than $Ni(acac)_2$, $(iBu)_3Al$.

The i.r.-spectra of the catalyst [8] do not show the presence of π-allyl groups, possibly because the allyl group is mainly present as a σ-allyl group or has an intermediate structure giving an open co-ordination site for a propadiene molecule, in this way initiating the polymerization. The next step is the insertion of C_3H_4 in one of the σ-allyl bonds. After the insertion, the allyl group can stabilize again as a π-allyl. Repetition of this process leads to the formation of 1.2.1.2 polypropadiene. This C_2 complex has less stable allyl-bonds than the bis-π-allyl complex and it does not decompose as easily as $(iBu)_2Ni$: the C_2 complex balances between stability and instability.

Some Lewis bases decrease the selectivity as shown by the results of Table 1. In this case a polymer with 1.2.2.1 structural elements is obtained. The electron donation of a Lewis base to the Ni can cause this decrease in selectivity but it is not possible to exclude the steric hindrance caused by the occupation by the Lewis base of one co-ordination site of the metal as another explanation. The chloride in π-allyl-nickel chloride can also act as a Lewis base as follows from the dimeric structure of this compound [26] and in this case also 1.2.2.1 structural elements are formed. This was also found by Otsuka [1, 7] who claims that bis-π-allylnickel gives the same polymer as π-allyl-nickel chloride in contrast to our observation that it gives the 1.2.1.2-polymer [8].

A possible explanation for the change in polymerization mechanism caused by Lewis bases is the following. Theoretical calculations of nickel and palladium π-allyl complexes showed that Lewis bases increase the strength of a π-allyl bond [26]. As a consequence the insertion will be less easy, so the rate of insertion and consequently the rate of polymerization will decrease. If exchange [28] bound and dissolved C_3H_4 is still possible, this process can become relatively more important. From quantum-chemical calculations [27], it follows that in this process bond formation between the central C-atoms of C_3H_4 is probable, increasing the number of 1.2.2.1 structural elements in the polymer chain:



The nature of the C_3 complex is still obscure although this complex must be rather stable (the yellow colour of the catalyst solution after polymerization is maintained for weeks in the absence of O_2 and H_2O). It is also reasonably certain that it is not the encapsulation of the catalyst by the polymer formed, because in the case of Co (see Fig. 1, [10]) more polymer of the same structure is formed and with Co there is no decrease in activity in the same time. Furthermore only a small part of the Ni was found in the polymer. Poisoning with O_2 and H_2O of the catalyst is ruled out for the first mentioned reason. Because the temperature was maintained with 0.1°, temperature changes cannot explain this effect.

CONCLUSIONS

(i) Different alkylating agents can be used to form an active catalyst from $Ni(acac)_2$ and C_3H_4 for the polymerization of C_3H_4 selectivity to 1.2.1.2 polypropadiene.

(ii) $(iBu)_2Al(acac)$ is only a by-product of catalyst formation in the system $Ni(acac)_2$, C_3H_4, $(iBu)_3Al$.

(iii) The active catalyst is bimetallic.

(iv) Deactivation occurs during polymerization to a less active catalyst, which gives the same polymer.

(v) Lewis acids increase and Lewis bases decrease the activity of the catalyst, the latter also change the selectivity so that 1.2.2.1 structural elements are found in the polymer.

(vi) Et_2AlCl, $EtAlCl$ and $AlCl_3$ give an anionic polymerization of C_3H_4 to a crosslinked polypropadiene.

Acknowledgements—We thank J. G. M. van Rens and P. Mars for valuable discussions and H. Bosch for assistance with the computer calculations of the kinetic parameters.

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