

**MICROHETEROGENEOUS CATALYTIC SYSTEM  
Ni(0)<sub>col</sub>-Ni(I)-Ni(II) FOR LOW PRESSURE POLYMERIZATION  
OF BUTADIENE. IV.\***

**THE STRUCTURE OF AN ACTIVE CENTRE**

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A trimetallic complex  $(\text{acac})\text{BF}_2\cdot\text{Ni(I)(C}_2\text{H}_5)_2\cdot\text{FAl(C}_2\text{H}_5)_2$  fixed to the colloid nickel  $\text{Ni(0)}_{\text{col}}$  surface is an active centre of the catalytic system  $\text{Ni(II) (acac)}_2\text{-BF}_3\cdot\text{O(C}_2\text{H}_5)_2\text{-Al(C}_2\text{H}_5)_3$  for the stereospecific polymerization of butadiene. The absolute number of paramagnetic products of  $\text{Ni(II)}$  reduction proceeds through a maximum when changing the  $[\text{Al}]/[\text{Ni}]$  molar ratio. The rate of polymerization, conversion and molecular weight follow the same dependence. The polybutadiene synthesized by using catalysts where  $[\text{Al}]/[\text{Ni}]$  ratio was 4–8 is highly stereoregular and it contains as much as 98% of 1,4-*cis* isomer. The ESR signal of the catalyst with a maximum polymerization activity is greatly asymmetrical and it characterizes a number of magnetically anisotropic  $\pi$ -complexes of butadiene with  $\text{Ni(I)}$  as well as number and size of  $\text{Ni(0)}_{\text{col}}$  particles. The delocalization of an unpaired  $3d^9$  electron over the antibonding butadiene orbital together with the delocalization of electron density of the central  $\text{Ni(I)}$  atom over the three fluorine ligands in the complex weakens a  $\text{Ni-C}$  bond. This creates a favourable condition for the insertion of monomer between the metal and carbon which finally leads to the oriented grow of a polymer chain. The aluminium atom "pushes" the propagating polymer end during the insertion act thus controlling the molecular weight. The average molecular weight  $\overline{M}_w$  depends upon the size of  $\text{Ni(0)}_{\text{col}}$  microcrystals on which the trimetallic active centre together with a  $\pi$ -complex of monomer is adsorbed.

The mechanism operative during the reduction of nickel acetylacetonate in non-polar medium in the presence of a Lewis acid is different from that when the acid is absent<sup>1-3</sup>. In the latter case the olefins present are transformed (dimerization, cyclization)<sup>4-7</sup>. Also small amounts of oligomers<sup>8</sup> or co-oligomers<sup>9</sup> can be formed. On the other hand the reduction of acetates, naphthenates,  $\text{Ni(II)}$  oxalates in the presence of a protolytic<sup>10</sup> or Lewis<sup>11</sup> acid such as  $\text{BF}_3$  gives stereoselective catalysts for butadiene polymerization. According to Yoshimoto and co-workers<sup>11</sup> the active centre of the catalytic system  $\text{Ni(II) naphthenate-BF}_3\text{O(C}_2\text{H}_5)_2\text{-Al(C}_2\text{H}_5)_3$  is nickel in its "reduced form", the Lewis acid being the source of fluorine anions for the catalytic complex. Stereoregularity can be substantially influenced by donor — acceptor properties of the anion of protolytic acid or by the exchange of ligands attached to nickel. The mechanism of polymer chain propagation is visualized by the authors as the insertion of monomer between the transition metal and the last polymerization unit. We have found<sup>1</sup> that the active centre of a  $\text{Ni(acac)}_2\text{-}$

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$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2\text{-Al}(\text{C}_2\text{H}_5)_3$  catalyst is not of an ion character<sup>3</sup> and that its basic component are paramagnetic Ni(I) species and ferromagnetic colloid nickel  $\text{Ni}(0)_{\text{col}}$ .

In this work we present a correlation of catalytic activity during 1,4-*cis* polybutadiene polymerization with the number of unpaired electrons of different types examined by the ESR method. The structure of an active centre, the mechanism of a stereoregular "coupling" of butadiene on the trimetallic complex attached to colloid nickel as well as the function of aluminium atom during the molecular weight control of the polymer is suggested.

## EXPERIMENTAL

Chemicals, their purification and toluene solutions preparation under an inert atmosphere, resp. have already been described in our previous papers<sup>1-3</sup>. Butadiene, chromatographically pure was dried by 5% NaOH, sodium hydroxide pellets and molecular sieves (5 Å); it was condensed at  $-15^\circ\text{C}$  into a vessel containing  $\text{Al}(\text{C}_2\text{H}_5)_3$  and the catalyst; it was distilled at  $20^\circ\text{C}$  and again condensed at  $-10^\circ\text{C}$ . The hydride  $\text{NaH}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$  (sodium dihydro-bis(2 methoxyethoxy)aluminate) was supplied in form of 70% toluene solution by the Institute of Inorganic Syntheses, Czechoslovak Academy of Sciences, Prague-Řež. When studying the catalytic activity dependence on the  $[\text{Al}]/[\text{Ni}]$  molar ratio, keeping  $[\text{B}]/[\text{Ni}]$  ratio constant (6.5), the following procedure was performed: 20% solution of butadiene ( $[\text{butadiene}]/[\text{Ni}] = 20-40$ ) was added to the solution of  $\text{Ni}(\text{acac})_2$  (0.135 mol) at  $30^\circ\text{C}$ ; then the solution of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_3$  (0.848 mol) was added followed, after 10 min, by the solution of  $\text{Al}(\text{C}_2\text{H}_5)_3$  (0.678 mol) which was added dropwise while stirring vigorously.

The rate of polymerization at  $40^\circ\text{C}$  (closed system) was measured as follows: to 5 ml of 20% toluene solution of butadiene 0.5 ml of catalytic mixture (30 min after its preparation) was added; at the same time the ESR spectra of the catalyst used were taken. The measure of polymerization rate was the reciprocal value of time  $\tau$  that had to elapse until a glass coated magnetic stirrer could not move in the reaction mixture<sup>12</sup>. The catalyst was then decomposed by 0.25 ml of 0.1% methanol-toluene (4 : 3) solution of an antioxidant. A viscous polymer solution was washed with 1% phosphoric acid and water; the catalyst-free polymer was dried to constant weight at  $40^\circ\text{C}$  under a vacuum of  $10^{-1}$  Torr. The conversion was determined gravimetrically. Isomer content in polymer films was determined by IR spectrometry<sup>13,14</sup> using a UR 10 Zeiss instrument (1,4-*cis* component according to the  $740\text{ cm}^{-1}$  band, 1,3-*trans* component by means of the  $970\text{ cm}^{-1}$  band and vinyl groups using the absorption at  $910\text{ cm}^{-1}$  band). Molecular weight was determined by light-scattering<sup>15</sup> of 0.3-0.003% cyclonexane solutions, the values being compared with those of the limiting viscosity number determined at  $20^\circ\text{C}$  by an Ubbelohde viscometer. ESR spectra were taken using closed cells of 4 mm in diameter under an atmosphere of nitrogen employing a Varian E-3 spectrometer with 100 kHz modulation. For the purpose of ESR signals study of dried catalysts, the system was evacuated down to  $5 \cdot 10^{-2}$  Torr at room temperature or at  $80^\circ\text{C}$ . The integration of the derivation signals was performed on a Varian Spectrossystem SS-100 spectral counter.

## RESULTS

The standard catalyst (SC) with a maximum catalytic activity was prepared in the presence of butadiene ( $[\text{Ni}] : [\text{B}] : [\text{Al}] : [\text{butadiene}] = 1 : 6.5 : 6.3 : 20$ ). Its asymmetrical ESR signal (Fig. 1) is substantially different from that observed in systems prepared in the absence of mono-

mer. The reduction of Ni(II) in the absence of butadiene yields predominantly colloid nickel  $\text{Ni}(0)_{\text{col}}$  which gives an ESR signal at  $g = 2.24 \pm 0.02$  ( $\Delta H_{1/2} = 300-600$  Oe) superposed on a weak singlet due to Ni(I),  $g = 2.05$  ( $\Delta H_{1/2} = 35$  Oe)<sup>1</sup>. If the reduction is carried out in the presence of allenes, 1-pentene and 1-decene, resp. only a broad symmetrical signal due to colloid nickel is seen, the highest intensity being observed when methylacetylene is present (Table I).

It follows from the comparison of the catalytic activity (characterized by the value of  $\tau$ ) with the antibonding  $\pi$ -orbitals energy of corresponding unsaturated hydrocarbons calculated by Otsuka<sup>16</sup> that no direct relationship is observed between the catalytic activity and the supposed stability of Ni(I)- $\pi$ -complexes with monoolefins. The catalytic activity is high in such cases where Ni(I) formation predominates over that of  $\text{Ni}(0)_{\text{col}}$ . Butadiene plays an important role during the reduction by maintaining relatively high level of Ni(I) and suppressing the formation of colloid centres. If this is not so, *e.g.* in the presence of other unsaturated hydrocarbons, then the activity markedly decreases or the polymerization does not proceed at all, this being in agreement with the observation of Ryoza Sakatu and coworkers<sup>17</sup>.

During the reduction without monomer but in the presence of traces of moisture the signal due to colloid nickel is overlapped with a weak triplet ( $g \approx 2.05$ ); the latter is probably due to hydrated Ni(I). The standard catalysts when dried *in vacuo* at room temperature exhibits in the solid state an equal ESR spectrum similar to that obtained in solution. This suggests that butadiene is relatively strongly bonded to Ni(I) forming a  $\pi$ -complex whose  $g = 2.14 \pm 0.02$  (dried material has a light-pink colour). Dried catalyst that was prepared without butadiene has a grey colour

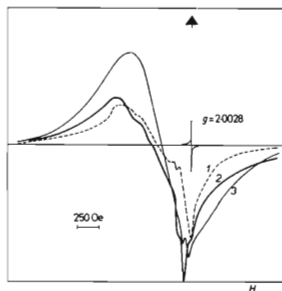


FIG. 1

Superposed ESR Signals of Catalyst at the Molar Ratio Ni : B : Al = 1 : 6.5 : 6.3 in the Presence and in the Absence of  $\pi$ -Complex, respectively

Reduction of  $\text{Ni}(\text{acac})_2$  1 in the presence of butadiene at  $[\text{Ni}] : [\text{butadiene}] = 1 : 20$ , 2 toluene solution without monomer, 3 signal 1 after bubbling gaseous methylacetylene through the solution.

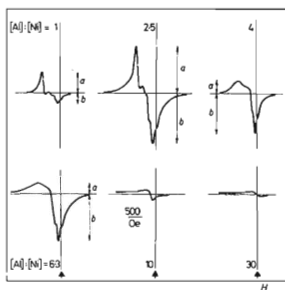


FIG. 2

The Symmetry Change ( $a/b$ ) of Superposed ESR Signals of Catalysts Prepared at Various Molar Ratio  $[\text{Al}]/[\text{Ni}] = 1-30$  Maintaining  $[\text{Ni}]/[\text{B}] = 6.5$  and  $[\text{Ni}]/[\text{Butadiene}] = 20$

The signals  $[\text{Al}]/[\text{Ni}] = 6.3, 10$  and  $30$  were taken at doubled sensitivity of spectrometer.

and gives an ESR signal corresponding to  $\text{Ni}(0)_{\text{col}}$  onto which a weak Ni(I) singlet is superposed. The  $\pi$ -complex can be removed from the surface of the active complex also by purging the dried catalyst with water vapour or by drying at  $80^\circ\text{C}$  *in vacuo*. During this procedure the pink colour of the material becomes grey while the asymmetry of the ESR signal disappears. Similar effect can be observed also in the solution of standard catalyst if gaseous methylacetylene is bubbled through the latter (Fig. 1). Simultaneously with the disappearance of the ESR signal of the  $\pi$ -complex also the catalytic activity is lost.

The character of ESR signals as well as an overall number of paramagnetic species during the reduction of Ni(II) in the presence of butadiene at constant concentration of boron fluoride etherate is changing with the molar ratio of [Al]/[Ni] (Fig. 2). When [Al]/[Ni] < 1 then no ESR signals are observed. Symmetrical signals are seen at molar ratio 1–3. The symmetry disappears when this ratio exceeds the value of 4, the greatest asymmetry being observed at the molar ratio [Al]/[Ni] = 6.3. At this point the system exhibits the maximum activity. Further increasing of the aluminium amount leads to the reduction of the overall area of signals and finally, at the molar ratio equal to 30, the catalytic complex is practically destroyed, the activity being zero. The deciphering of resulting envelope-curve of ESR signals could be done by analysis of absorption (integral) curves and after an approximate graphical decomposition of superposed signals due to four types of paramagnetic particles. Whereas the integral curves of catalytic systems prepared in the absence of butadiene are symmetrical, having a maximum at  $g = 2.23 \pm 0.02$  which corresponds to the  $\text{Ni}(0)_{\text{col}}$  ferromagnetic resonance (Fig. 3) the systems prepared in the presence of butadiene exhibit asymmetrical signals. This is characteristic for complexes having anisotropic  $g$ -value and symmetry axis ( $g_x = g_y \neq g_z$ )<sup>26</sup>. The asymmetry is caused by the superposition of components  $g_{\parallel} \approx 6-5$  and  $g_{\perp} = 2.14 \pm 0.02$  whose orientation is different with regard to direction of static magnetic field. The first differentiation of asymmetrical absorption curves gives also asymmetrical curve which shows unresolved hyperfine structure. It is probably a triplet which is formed as a consequence of interaction of an unpaired electron with two protons on carbons in position 2 and 4 of butadiene bonded in form of a  $\pi$ -complex. An asymmetrical signal due to  $\pi$ -complex with Ni(I) was observed also during the reduction of  $\text{Ni}(\text{acac})_2$  with triethylaluminium in the absence of a Lewis acid. The signal had a very similar  $g$ -value ( $g \approx 2.1$ ).

TABLE I

Relative Amount of Colloid Nickel  $\text{Ni}_{\text{col}}^{\text{R}}$  During the Reduction of  $\text{Ni}(\text{acac})_2$  by Triethylaluminium in the Presence of Unsaturated Hydrocarbons and Without Monomer Respectively, Compared with the Energy of  $\pi^*$  Antibonding Orbital of Olefins, Catalytic Activity and Symmetry of ESR Signals ([Ni] : [B] : [Al] : [Hydrocarbon] = 1 : 6.5 : 6.3 : 20)

Hydrocarbon	$\pi^*$ , eV	$\text{Ni}_{\text{col}}^{\text{R}}$	ESR signal	Activity $\tau$ , min
Without monomer		1.00	symmetrical	35
Methylacetylene	-4.9	30.00	symmetrical	does not polymerize
1-Decene	-2.0	20.00	symmetrical	trace polymerization
1-Pentene	-2.0	1.20	symmetrical	trace polymerization
1,3-Butadiene	-3.4	0.12	asymmetrical	12

The second factor determining the shape of the differential envelope curve is the superposition of a Ni(I)  $\pi$ -complex,  $g_{\perp} = 2.14$  ( $\Delta H_{1/2} = 250$  Oe) with that of colloid nickel. The band-width depends upon the size of nickel microcrystals and its  $g$ -value changes according to the character of Ni(0)<sub>col</sub> interactions *i.e.* whether the latter interacts with the monomer forming a  $\pi$ -complex or with the Ni(I) central atom in the trimetallic complex. At the early stage of reduction process ( $[Al]/[Ni] = 2$ ) when colloid centres are relatively small and when they interact with butadiene the envelope curve is symmetrical (Fig. 4a) and the signal  $g = 2.34 \pm 0.02$  ( $\Delta H_{1/2} = 300$  Oe) is seen. When colloid particles are bigger, the trimetallic complex being adsorbed on their surface, the ferromagnetic resonance is observed at lower  $g = 2.24$ , the bandwidth being greater ( $\Delta H_{1/2} = 400$  Oe), (Fig. 4b).

The catalytic activity expressed as a reciprocal of time ( $1/\tau$ ) when plotted against the catalyst composition proceeds through a maximum at the  $[Al]/[Ni]$  ratio = 5–7. It coincides with the biggest asymmetry of ESR signal (Fig. 5). The overall number of all paramagnetic particles present in the system expressed as an overall area of all three superposed signals does not coincide with the maximum activity. Moreover, when the polymerization rate reaches its maximum the lowest electric conductivity is observed<sup>3</sup>. Although intense ESR signals (predominantly those of Ni(I) and a septet due to the ligand free radical<sup>1</sup> resp.), are observed during the reduction

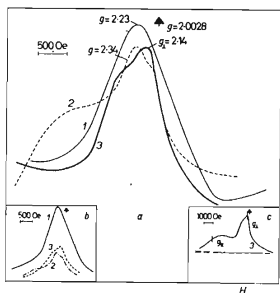


FIG. 3

Absorption ESR Signal of Products of Ni(acac)<sub>2</sub> Reduction by Triethylaluminium in the Absence of (curve 1) and in the Presence of Butadiene (curves 2, 3)  $[Al]/[Ni] = 2$  (curve 3, only Higher Magnetic Field Region) and  $[Al]/[Ni] = 6.3$  (1 and 2) at Constant Ratio  $[Ni]/[B] = 6.5$

*a* Equal amplitude independent of absolute number of paramagnetic particles, *b* real ratio of areas proportional to overall number of paramagnetic particles, *c* integration curve of asymmetrical line (3) over the whole region of magnetic field.

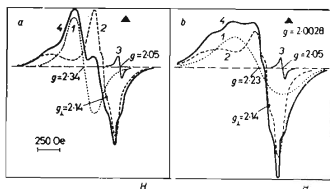


FIG. 4

Theoretical Decomposition of Superposed ESR Signals

*a* symmetrical — catalyst  $[Ni] : [B] : [Al] : [butadiene] = 1 : 6.5 : 2 : 20$ , *b* asymmetrical  $[Ni] : [B] : [Al] : [butadiene] = 1 : 6.5 : 6.3 : 20$ .

1  $\pi$ -complex of colloid nickel with butadiene  $g_{\perp} = 2.34 \pm 0.02$ , 2  $\pi$ -complex of monomer with Ni(I)  $g_{\perp} = 2.14$ , 3 Ni(I), 4 resulting superposed signal.

of  $\text{Ni}(\text{acac})_2$  by alkylaluminium ( $[\text{Al}]/[\text{Ni}] < 1$ ) in the absence of a Lewis acid, no polymer is formed.

Not only the catalytic activity and the yield but also the molecular weight (Fig. 6) proceeds through a maximum, when examined in dependence on the  $[\text{Al}]/[\text{Ni}]$  ratio. Over the whole range of  $[\text{Ni}]/[\text{Al}]$  ratios, where ESR signals are seen, also polymerization proceeds, the resulting polymer containing high concentration of a geometric isomer (up to 98% 1,4-*cis* structure) independently of the molecular weight achieved.

The activity of catalyst is a function of more parameters such as time, traces of moisture and oxygen, respectively. After 1 hour after the catalyst preparation the activity of catalyst is the highest; it does not change in the course of another 2 hours. Whereas traces of oxygen prevent a complete reduction of  $\text{Ni}(\text{I})$  to  $\text{Ni}(\text{0})_{\text{col}}$ , greater amount of oxygen leads to an immediate dis-

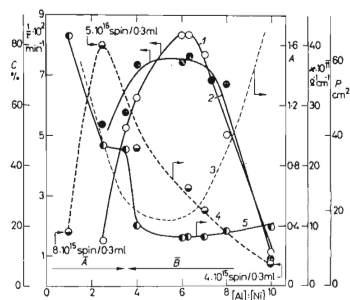


FIG. 5

Dependence of Catalytic Activity ( $1/\tau$ ), Conversion ( $C$ ), ESR Signal Area ( $P$ ) Proportional to the Number of Unpaired Electrons, Asymmetry of ESR Signal ( $A$ ) and Electric Conductivity ( $\kappa$ ) upon the Molar Ratio  $[\text{Al}]/[\text{Ni}]$  at Constant  $[\text{Ni}]:[\text{B}]:[\text{butadiene}]$  Ratio Being  $1:6.5:20$

Curves: 1  $1/\tau$  (20% toluene solution of butadiene at  $40^\circ\text{C}$  with 10% vol. of catalyst), 2  $C$  (inactivation of catalyst immediately after elapsing of  $\tau$ ), 3  $\kappa$  (room temperature), 4  $P$  (0.3 ml of sample, superposed ESR signals  $\text{Ni}(\text{0})_{\text{col}} + \text{Ni}(\text{I}) + \pi$ -complex with  $\text{Ni}(\text{I})$  and  $\pi$ -complex with  $\text{Ni}(\text{0})_{\text{col}}$  respectively), 5  $A = a/b$  ( $\bar{A}$  region of symmetrical signal of low catalytic activity for the formation of polymer,  $\bar{B}$  high catalytic activity, asymmetrical signal).

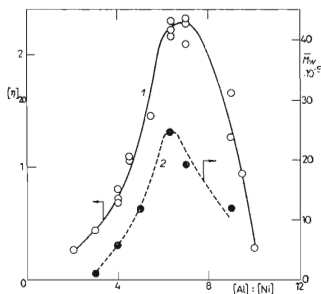


FIG. 6

The Molecular Weight Dependence  $\bar{M}_w$  (1) and Relative Viscosity  $[\eta]$   $20^\circ\text{C}$  2 of 1,4-*cis* Polybutadiene Upon the Ratio  $[\text{Al}]/[\text{Ni}]$  in the Catalyst at Constant Ratio  $[\text{Ni}]:[\text{B}]:[\text{Butadiene}] = 1:6.5:20$

appearance of paramagnetic species and thus to the loss of polymerization activity. If the triethylaluminium is substituted by aluminium hydride, the system is not catalytically active in polymerization. When the hydride is added in amount of 1% to the standard catalyst, the polymerization activity is substantially lowered so that only 80% conversion is achieved after 12 hours.

## DISCUSSION

The presence of paramagnetic species is essential for the catalyst examined to be active in polymerization. This condition is, however, not a sufficient one; the catalytic activity is not determined by the absolute number of unpaired electrons but it is determined by the number of  $\pi$ -complexes (Ni(I)-butadiene) with regard to the number of colloid particles of Ni(0)<sub>col</sub> of a suitable size. The paramagnetic species Ni(I) or Ni(0)<sub>col</sub> are themselves not active centres of stereoselective polymerization and do not facilitate the formation of polymer with sufficiently high molecular weight. The formation of a  $\pi$ -complex with Ni(I) in the process of Ni(II) reduction restricts the growth of colloid nickel centres. The ESR signal of the complex has a higher  $g$ -value ( $g \approx 2.14$ ) but this value is close to that for Ni(I)(2.05). The effective  $g$ -value observed in the case of Ni<sup>+</sup> ions that were generated by X-ray irradiation of nickel acetate tetrahydrate<sup>18</sup> was in good agreement with our experiments, having the value of  $g = 2.06 - 2.1$ ; this signal was attributed to the  $3d^9$  electron arrangement.  $\pi$ -complexes of dienes with catalysts on the basis of Ti(III) and alkylaluminium ( $g = 1.983$ ) possessing an unpaired  $3d^1$  electron and their ESR spectra have been described by Hirai and coworkers<sup>19</sup>. The authors observed hyperfine structure of the signal due to the spin-spin interaction of unpaired electron with protons of the growing chain on the coordinated polybutadiene catalysts. The complicated superposed spectra seen in our case do not facilitate to discern the hyperfine structure that is expressed only by a  $\pi$ -complex splitting. The interaction of ligands, as well as the formation of  $\pi$ -complexes with unpaired electron, was ESR spectroscopically proven also by other authors<sup>20,21</sup>. From the point of view of the theory of orientation according to Fukui<sup>17</sup> the  $\pi$ -orbital symmetry is favourable for overlap stabilization due to the fact that the  $\psi_{xz}$  orbital of the Ni(I) unpaired electron is a donor for a  $\pi_4^*$  antibonding orbital of butadiene. The direction of electron flow is from the highest occupied Ni(I) orbital (HO) towards the lowest unoccupied orbital (LU) of butadiene<sup>22,23</sup>. The role of the highest occupied orbital is played by the  $3d^9$  orbital (SO) possessing one electron; this orbital can generally function both as (HO) and (Lu). The experimentally observed magnetic anisotropy of the  $\pi$ -complexes is the reason why we presume that the highest level containing an unpaired electron is the  $d_{xz}$  orbital and not the  $d_{z^2}$  interacting with the antibonding  $\pi_3^*$  orbital as assumed in the case of perfectly symmetrical octahedral ligand field.

High stereospecificity of the studied catalyst is in connection with the formation of an axis-symmetrical  $\pi$ -complex having an anisotropic  $g$ -value. If, however, the  $\pi$ -complex of monomer with nickel is strongly bonded then the polymerization does

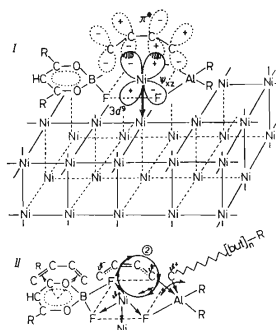
not occur, as suggested by Sakata and coworkers<sup>17</sup>. It is well known<sup>4</sup> that unsaturated hydrocarbons can be coordinated in form of a  $\pi$ -complex also to Ni(0) and Ni(0)<sub>col</sub>, respectively. The geometrical analysis of differential ESR signals and corresponding absorption curves at the [Al]/[Ni] ratio being 1 to 3 has indicated that colloid nickel centres that interact with monomer are formed from the very beginning of the Ni(II) reduction. Elementary centres are of the size of at least one domain (100 Å). Whereas they exhibit ferromagnetic resonance<sup>1</sup> whose line width is 300 Oe bigger colloid particles formed at [Al]/[Ni] = 6 have the latter 400–500 Oe wide. Narrower signals with  $g_{\perp} = 2.34$ ,  $g_{\parallel} = 5.4-6.7$  can be accounted for by the bonding of butadiene to colloid nickel centres which can lead to the suppression of the dipolar interaction between individual domain regions. When sufficiently big microcrystals of the colloid carrier on which the original  $\pi$ -complex can be substituted by a trimetallic B—Ni(I)—Al complex are not formed, only low molecular products are produced. The character of the ESR signal changes from the symmetrical to asymmetrical one as a consequence of Ni(0)<sub>col</sub> line broadening and  $g$ -value shift from 2.34 to 2.24 whenever the [Al]/[Ni] ratio exceeds the value of 4. A maximum polymerization activity is observed at the greatest asymmetry of the signal, *i.e.* at the moment when colloid particles reached a certain optimum size and became carriers of the active complex. Under these conditions the probability of bonding two butadiene molecules to one Ni(I) centre is substantially lowered because one coordination site is blocked by the carrier. This also lowers the probability of cyclization and oligomer formation. A favourable situation is created for a space bonding of monomer to polymer up to  $\bar{M}_w = 2 \cdot 10^6$ . The excess of aluminium ( $[Al]/[B] > 1$  and  $[Al] : [Ni] > 8$ ) affects the active centre. If the reduction is carried out in the absence of butadiene, substantially bigger colloid particles are formed thus suppressing Ni(I) in the system and the activity of the system is *c.* 3 times lower ( $\pi$ -complex is formed in the process of polymerization). The length of a resulting polymer chain achieved on one active centre is also dependent on microheterogeneity of the system and on the redox-equilibrium between various forms of nickel. The colloid carrier can be interpreted as a ligand of different size. When the colloid particles are too big then the microheterogeneous character of catalyst becomes, after certain time, heterogeneous and metallic nickel precipitates. Only during the first hour after the synthesis the system appears homogeneous.

The area corresponding to the ESR signal of  $\pi$ -complex with Ni(I) was tentatively defined as a criterium for the determination of the number of active centres. The error of this estimate is the same as that caused by the deciphering of superposed ESR signals. We have selected the difference between the area of the standard catalyst signal and that seen after the disappearance of  $\pi$ -complex caused by bubbling of methylacetylene through the system (Fig. 1). The number of active centres found by this way was  $7 \cdot 10^{15} \pm 30\%$  per 0.5 ml of the catalyst which corresponds to the concentration of approximately  $10^{-4}$  mol/l. The active centre is formed as an inter-





on nickel and carbon causes an increase in the distance between the two atoms. A space distortion analogous to the Jahn–Teller effect observed in the case<sup>18</sup> of  $\text{Ni}^+$  creates suitable steric condition for the insertion to the “semi-ion biradical” between the weakened Ni–C bond. The aluminium atom in complex keeps the fragment of homolytic fission sufficiently close to the active centre until the insertion occurs. A subsequent insertion of monomer between the  $\text{Ni}\cdots\text{C}$  bond leads to the oriented growth of polymer chain. The other metal in complex, aluminium, can thus function as a “pusher” of the growing end of polymer. During the insertion the excess of spin density from the  $\pi_4^*$  antibonding orbital is transferred back to the Ni central atom while the  $\psi_{xz}$  orbital of the  $3d^9$  unpaired electron forms a new  $\pi$ -complex with another monomer. Charge transfer appears as a consecutive cycle directed from Ni(I) towards the  $\pi$ -complex with butadiene and after the insertion between Ni–C bond the charge is transferred back to the central atom. This hypothesis could account for the driving force of the propagation process while preserving high stereoregularity. The monomer is during the whole process suitably oriented allowing only 1,4-*cis* space configuration.



It can be assumed that in the first stage the monomer is oriented on the surface of a colloid carrier in vicinity of the active centre before the formation of  $\pi$ -complex with Ni(I) occurs. In this stage favourable conditions are created for dimerization, trimerization and cyclization, respectively, in the absence of Lewis acid. The activation energy of polymerization is thus lowered. Further orientation which facilitates the occupation of a free coordination site of Ni(I) by the monomer after the insertion can be connected with the effect of nonbonding electrons on two oxygen atoms of the acetylacetonate cycle which is positioned in the plane of complex. This leads to a stepwise lowering of the activation energy. The analysis of a model suggests that bulky ethyl groups from the side of  $\text{Al}(\text{C}_2\text{H}_5)_3$  sterically hinder the access of monomer to an active centre. Thus an optimum space configuration is formed where the monomer is 1,4-*cis* oriented, this being favourable for the  $\pi$ -complex formation suitably oriented for insertion.

The periodic "binding" of monomer on an active centre proceeds until the insertion cycle is interrupted by the formation of solid hydride through a random hydrogen abstraction according to mechanism already published<sup>25,26</sup>. A similar effect was achieved when Al-hydride was added to SC while polymerization rate was substantially lowered. We assume that even at  $[Al]/[Ni] < 6.5$  (when  $[Al] > [B]$ ) the occupation of active centre by alkylmetal (insertion blocking) will effectively lower the polymerization activity thus leading to the molecular weight decrease. This can account for the dependence of  $\bar{M}_w$  on  $[Al]/[Ni]$  ratio which proceeds through a maximum. It seems that the molecular weight depends also on the size of colloid "carrier" of the active centre on which a bulky polymers cluster grows. At the molecular weight approximately  $2 \cdot 10^6$  the monomer cannot diffuse to the active centre, the polymer cluster being torn off as a consequence of thermal movement. The centre becomes free to start a new polymerization.

From the number of active centres at 80% conversion and mean molecular weight  $2 \cdot 10^6$  it can be calculated how many times one centre can participate in polymerization. This value was found to be 10–30 (distribution curve shape has only a slight influence). At 40°C approximately  $10^5$  monomer units are bonded stereoregularly on one active centre during 1–3 minutes. An elementary insertion act takes c.  $10^{-5}$  seconds to happen. If we take into account that molecular vibrations take  $10^{-13}$  seconds it follows that the formation of polymer chain *via* the  $\pi$ -complex should be regarded as a simultaneous reaction of a complex with limited lifetime. The estimated insertion time is sufficient for the aluminium component in a trimetallic complex to play a role of "pusher" of a growing polymer end thus controlling the molecular weight. The boron atom in complex influences the orientation of monomer and through fluorine atoms it contributes to the Ni–C bond weakening.

Since no ESR signals due to monomer or polymer free radicals ( $g \approx 2.00$ ) were detected during polymerization while the conductivity is minimum at maximum polymerization activity (3 orders of magnitude decrease<sup>3</sup>) we feel that it is plausible to assume that the active centre is a hybrid between radical ion and a coordination centre which can be a general property of other organometallic catalytic complexes of Ziegler-Natta type.

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