Complex catalysis. Part XLVI [1]. The mechanism of mol mass regulation in the allyl nickel complex catalyzed 1,4-*cis* polymerization of butadiene

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Abstract

For the industrially important 1,4-*cis* polymerization of butadiene the polymerization degree $\bar{n}$ can be regulated in a theoretically founded way with the C_{12}-allyl nickel(II) complex $[Ni(C_{12}H_{19})][B(C_6H_3(CF_3)_2)_4]$ **1** as the catalyst. A proper kinetic reaction model has been derived with the insertion reaction of butadiene into the allyl nickel bond and the β-hydride elimination from the growing polybutadienyl chain as the rate determining reaction steps for the chain propagation and for the transfer reaction of the catalyst to the monomer, respectively, by which a new polymer chain is formed.

Keywords: Allyl; Butadiene; 1,4-Cis polymerization; Mol mass regulation; Nickel

1. Introduction

With the synthesis and characterization of the cationic C_{12}-allyl nickel(II) complex $[Ni(C_{12}H_{19})][B(C_6H_3(CF_3)_2)_4]$ **1** [1,2] as a highly active catalyst for the industrially important 1,4-*cis* polymerization of butadiene [3] we have proved conclusively, that in accordance with the reaction model derived by us for the allyl nickel complex catalyzed butadiene polymerization [4,5], the cationic polybutadienyl butadiene nickel(II) complex $[RC_3H_4Ni(C_4H_6)]^+$ is the real catalyst for the 1,4-*cis* polymerization of butadiene, cf. the reaction scheme in Fig. 1 [6,7].

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[1] For Part XLV, see [14].

Accordingly, the cation $[Ni(C_{12}H_{19})]^+$, which is present mainly in the thermodynamically more stable *syn*-form **b**, reacts during a very short initiation period via the less stable but more reactive *anti*-form **a** under insertion of butadiene to the *anti*-polybutadienyl complex **c**. As a result of the very rapid *anti–syn* isomerization [8] this complex also does exist in equilibrium – cf. K_3 – with the more stable *syn*-complex **d**, which must be regarded as the stable store complex under the conditions of polymerization.

With butadiene the polybutadienyl butadiene complexes **e** and **f** are formed as the real catalysts. By the much higher reactivity of the less stable *anti*-complex **e** the formation of *cis*-units are catalyzed in accordance to the so called *anti–cis* and *syn–trans* correlation. Since all the equilibria can supposed to be rapid the insertion reaction of buta-
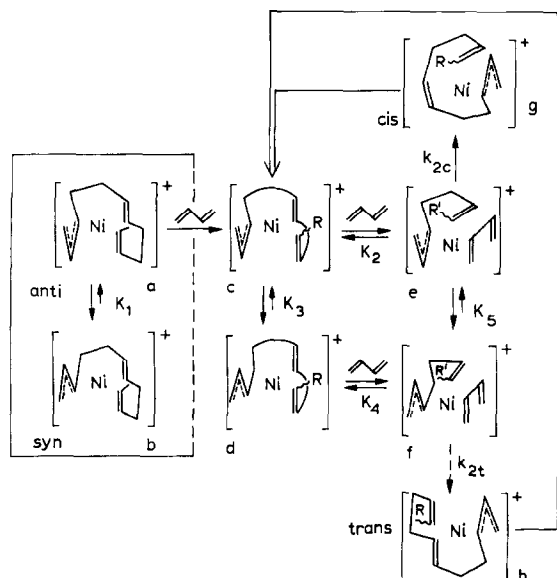
Fig. 1. Reaction scheme for the catalysis of the 1,4-*cis* polymerization of butadiene with the C_{12}-allyl nickel(II) cation from the complex **1** as precatalyst in a non-coordinating solvent like toluene, benzene, dichloroethane or without solvent in liquid butadiene. For detailed explanations see text.

diene k_{2c} has to be taken as rate determining step in the catalytic cycle. Thus, the catalytic activity is determined thermodynamically by the concentration of the η^4-*cis*-butadiene complex in the *anti*-form **e** and kinetically by its reactivity k_{2c}. Therefore a natural limit to catalytic activity is given by the coordination of π-bonds from the growing chain to the nickel, which have to be substituted by the coordination of butadiene according to the equilibrium K_2.

The insertion reaction of butadiene into the allyl nickel(II) bond takes place under formation of a σ-bond between the terminal C-atoms of both components in a correspondingly modified π-coordinated state [7], and the new η^3-butenyl group is obtained in the *anti*-configuration, cf. complex **g**, in accordance to the principle of strongest interaction and least structure variation, respectively. Furthermore, to avoid a highly unstable transition state for the insertion step by coordinative unsaturation at the nickel, it has to be supposed, that the next π-bond from the growing chain is coordinated to the nickel and supports the insertion step energetically thereby essentially. For sterical reasons the coordination of the next

double bond could take place more easily in the *anti*-complex **e** than in the *syn*-complex **f** giving rise to the *cis* selectivity, for which from the Curtin–Hammett principle [9], the relation $S_{c/t} = k_{2c}(k_{2t} \cdot K_5)^{-1}$ can be derived [6,10].

Besides catalytic activity and selectivity the mol mass regulation is the third important aspect in controlling the polymer properties. In this paper we complete our reaction model on the allyl nickel complex catalyzed 1,4-*cis* polymerization of butadiene by elucidating also the mechanism of the mol mass regulation [11].

2. Experimental

2.1. Butadiene polymerization

With the C_{12}-allyl nickel(II) complex $[Ni(C_{12}H_{19})][B(C_6H_3(CF_3)_2)_4]$ **1** as the catalyst [1] the polymerization of butadiene was investigated in toluene as solvent under the following variations of the experimental conditions:
Butadiene concentration,
$[BD]_0$:   1.3–5.1 M
Nickel concentration,
$[Ni]$:   0.45–2.7·10^{-4} M
Conversion,
$C = ([BD]_0 - [BD])[BD]$: 0.30–0.55

Reaction temperature T and reaction time t: 25°C (30, 60 min); 0°C (30, 180, 240 min), 40°C (3, 5, 7, 10 min), 50°C (5 min).

Besides the turnover number $TON = [BD]_0 C[Ni]^{-1} t^{-1}$ in mol BD (mol Ni·h)$^{-1}$, as the measure of catalytic activity, the *cis–trans* selectivity $S_{c/t}$, the conversion C and the polymerization degree $\bar{n}$ has been determined. For experimental details see precedent publications [1,6,12].

2.2. β-Hydride elimination

The formation of the diene group at the chain end by β-hydride elimination according to the reaction scheme in Fig. 3 has been proved by trapping the diene in a Diels–Alder reaction with the

azodicarbonic acid diethyl ester $C_2H_5OC(O)N=N(O)COC_2H_5$, known as a strong dieneophile [13], and identification of the formed tetrahydro-1,2-diazine derivative by ^{13}C-NMR spectroscopy.

To generate the diene end group in a proper high concentration a short chain polybutadiene with $M_n \approx 500{-}600$ g mol^{-1} was synthesized by using the less active C_{12}-allylnickel(II) complex $[Ni(C_{12}H_{19})][FB(C_6F_5)_3]$ **2** [14] as the catalyst.

11.3 mg of the complex **2** were added to a solution of butadiene in 150 ml toluene with $[BD]_0 = 0.1$ M (Ni:BD = 1:1000). The polymerization was carried out under shaking at room temperature. After 4 h the reaction was stopped by adding 10 μl concentrated HCl$_{aq}$, and all the solvent was distilled off. From the obtained polybutadiene 0.4 g were solved in 10 ml toluene, 0.15 ml (1 mmol) of the azodicarbonic acid diethyl ester was added, and the yellow reaction solution was boiled 4–5 h up to nearly complete decolouration. Then the solvent was removed, the remaining viscous oil was washed several times with methanol and solved in CDCl$_3$ to get a 0.1 M solution of the tetrahydro-1,2-diazine derivative, which was identified by its ^{13}C NMR spectrum in comparison with the spectrum of the same Diels–Alder product prepared under identical conditions with penta-1,3(E)-diene. ^{13}C NMR (CDCl$_3$, 22.1 MHz, 25°C) δ 156.0, 154.0, 128.6, 124.9, 67.6, 61.7, 61.4, 38.4, 13.8, 13.7; Diels–Alder product from penta-1,3(E)-diene δ 155.1, 154.6, 128.7, 121.9, 49.7, 61.6, 61.3, 42.0, 13.4, 13.4, 17.8 [15].

3. Results and discussion

3.1. The catalytic properties of $[Ni(C_{12}H_{19})][B(C_6H_3(CF_3)_2)_4]$ **1**

Under standard conditions, which means $[Ni] = 2 \cdot 10^{-4}$ M, $[BD]_0 \approx 2$ M, $T = 25°C$ and $t = 30$ min, the polymerization in toluene gives the following results: $C \approx 0.5$; TON $\approx 1.2 \cdot 10^4$ mol BD(mol Ni·h)$^{-1}$; $S_{c/t}$: 93% cis, $M_w \approx 7.5 \cdot 10^4$ g mol^{-1}, $M_n \approx 3.2 \cdot 10^4$ g mol^{-1}, and $M_w/M_n \approx 2$.

For the mechanistic investigations the stability of complex **1**, which can be handled on air for a short time without decomposition, and its relatively good solubility is very useful, but by high activity some limits in the variation of the reaction conditions – for example to keep the temperature constant at the used concentrations – were given.

3.2. The rate of the chain propagation

If in the reaction mechanism of the allyl nickel complex catalyzed 1,4-cis polymerization of butadiene (cf. the reaction scheme in Fig. 1) all the equilibria are rapid and the insertion reaction of butadiene via the reaction channel k_{2c} is the rate determining step the rate of chain propagation r_p can be described by the rate law $r_p = k_p[Ni][BD]$, where k_p is the propagation rate constant.

Provided that the whole amount of nickel in the used catalyst **1** is catalytically active and that there is no deactivation during the reaction time t, then with the relation $[Ni] = [Ni]_{tot} = $ const. the rate law takes pseudo first order $r_p = k[BD]$ where $k = k_p[Ni]$. Since the concentration of butadiene is given by $[BD] = [BD]_0 e^{-kt}$ the conversion of butadiene $C = ([BD]_0 - [BD])[BD]_0^{-1}$ is described by Eq. (1):

$$C = 1 - e^{-kt} = 1 - e^{-k_p[Ni]t} \qquad (1)$$

From Eq. (1) follows Eq. (2) for the propagation rate constant k_p by simple transformation:

$$k_p = \frac{2.3}{[Ni]t}\lg\frac{1}{1-C} \qquad (2)$$

Fig. 2. shows the determined dependence of $\lg(1(1-C)^{-1})$ on the product of catalyst concentration and reaction time $[Ni]t(2.3)^{-1}$. From the slope of the regression line the propagation constant $k_p \approx 3$ l mol^{-1} s^{-1} is found and the correctness of Eq. (2) is proved. At 0°C the propagation constant decreases to $k_p \approx 0.5$ l mol^{-1} s^{-1} and at 50°C it increases to $k_p \approx 11$ l mol^{-1} s^{-1}.
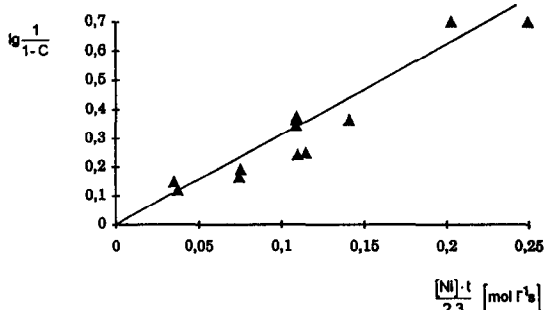
Fig. 2. The dependence of the conversion $C = ([BD]_0 - [BD])[BD]_0^{-1}$ from the product of the nickel concentration [Ni] in mol l^{-1} and the reaction time t in seconds for 12 runs of polymerization at 25°C according to Eq. (2).

3.3. The rate of the transfer reaction

Without any transfer reaction the polymerization degree $\bar{n}$ should be given by the so called theoretical chain length ν accordingly to Eq. (3):

$$\nu = \frac{[BD]_0 C}{[Ni]} \qquad (3)$$

Since a ratio $\nu(\bar{n})^{-1} \approx 5\text{--}12$ was found in dependence of the reaction conditions a transfer reaction of the catalyst to the monomer must take place giving rise to the formation of more than one polymer chain per nickel during the reaction time t.

The most probable course of the transfer reaction is outlined schematically in Fig. 3. After the formation of the σ-C(3) polybutadienyl complex **A** a hydrido-diene complex **B** can be formed by β-hydride elimination. The hydrido-diene complex **B** reacts quickly with butadiene under substitution of the polybutadiene from the nickel and formation of a crotylnickel(II) complex **C** by butadiene insertion into the hydrido–nickel bond.
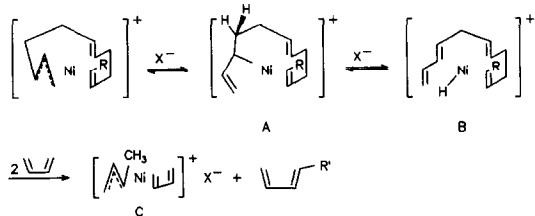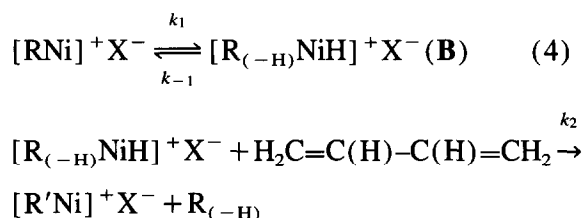

Fig. 3. Reaction scheme for the β-hydride elimination as the rate determining step of the transfer reaction of the catalyst to the monomer.

The formation of the 1,3-diene end group could be established unequivocally by trapping the diene in a Diels–Alder reaction with the azodicarbonic acid diethyl ester as already described above (cf. Experimental section).

The existence of a η^3-allyl–η^4-cis-butadiene complex was supported by proving ^{13}C-NMR spectroscopically the formation of the η^3-1,3-dimethallyl(η^4-cis-hexa-2(E),4(E)-diene) nickel(II) tetrafluoroborate $[(CH_3)_2C_3H_3Ni(CH_3C_4H_4CH_3)]BF_4$ from $[(CH_3)_2C_3H_3NiBr]_2$, the hexadiene and $AgBF_4$ in CD_2Cl_2 at $-70°C$ [15].

The transfer reaction can be described kinetically by the following reaction scheme (4):

$$[RNi]^+X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [R_{(-H)}NiH]^+X^- \ (B) \qquad (4)$$

$$[R_{(-H)}NiH]^+X^- + H_2C=C(H)-C(H)=CH_2 \overset{k_2}{\rightarrow}$$
$$[R'Ni]^+X^- + R_{(-H)}$$

If the β-hydride elimination k_1 is assumed to be the rate determining step in the transfer reaction followed by the more rapid substitution and insertion reaction k_2, then by application of the Bodenstein principle for the hydrido-diene complex **B** the rate law for the transfer reaction $r_{\ddot{u}} = k_1[Ni]$ can be derived. The preposition is that complex **B** is a very reactive intermediate, whose concentration can be regarded as constant in the stationary state of the reaction course, and whose reversed reaction can be neglected correspondingly to the relation $k_{-1} \ll k_2[BD]$.

With the rate of the transfer reaction also the formation rate of the polymer chains is given, which is defined by $r_{\ddot{u}} = d[X]/dt$, where [X] is the molar concentration of the polymer chains. After the reaction time t the concentration of polymer chains generated by the transfer reaction is given by $[X] = k_{\ddot{u}}[Ni]t$ with $k_{\ddot{u}} = k_1$. Additionally every catalyst molecule bears one growing chain. Therefore the polymerization degree $\bar{n}$ is obtained as the ratio of the converted amount of butadiene $[BD]_0 C$ and the total concentration of the formed
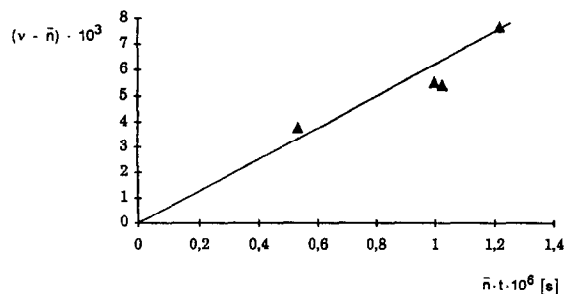
Fig. 4. Relation between the theoretical chain length $\nu = [BD]_0 C[Ni]^{-1}$ and the polymerization degree $\bar{n}$ according to Eq. (6) for 4 runs of polymerization under standard conditions at 25°C.

polymer chains bonded to nickel or being free $[Ni] + [X]$, according to Eq. (5):

$$\bar{n} = \frac{[BD]_0 C}{[Ni] + [X]} = \frac{[BD]_0 C}{[Ni](1 + k_{ü}t)} \qquad (5)$$

By introducing the theoretical chain length ν – cf. Eq. (3) – and after the proper transformation, Eq. (6) is obtained for the rate constant $k_{ü}$ of the transfer reaction:

$$k_{ü} = \frac{\nu - n}{\bar{n}t} = \left(\frac{\nu}{\bar{n}} - 1\right)t^{-1} \qquad (6)$$

Fig. 4 shows the relation between the parameters $\nu - \bar{n}$ and $\bar{n}t$ for 4 polybutadienes, which were prepared under standard conditions at 25°C.

From the slope of the regression line the rate constant $k_{ü} \approx 6 \cdot 10^{-3}$ s^{-1} is obtained. For 0°C and 50°C the values of the rate constant are $k_{ü} \approx 5 \cdot 10^{-4}$ s^{-1} and $k_{ü} \approx 1.5 \cdot 10^{-2}$ s^{-1}, respectively. Thus, $k_{ü}$ shows a similar dependence on temperature as k_p. Therefore, the ratio of both rate constants $k_p/k_{ü}$ is only slightly dependent on temperature and can be regarded to a good approximation as independent of temperature in the range of the given reaction conditions.

3.4. The control of the polymerization degree $\bar{n}$

Elimination of the reaction time t by combination of Eq. (2) and (6) gives Eq. (7) or Eq. (8) for the polymerization degree or the average chain length $\bar{n}$:

$$\frac{\nu}{\bar{n}} - 1 = \frac{k_{ü}}{k_p} \cdot \frac{2.3 \lg(1/(1-C))}{[Ni]} \qquad (7)$$

$$\bar{n} = \frac{k_p[BD]_0 C}{k_{ü}2.3\lg(1/(1-C)) + k_p[Ni]}$$

$$= \frac{[BD]_0 C}{[Ni] + k_{ü}/k_p[2.3\lg(1/(1-C))]} \qquad (8)$$

According to Eq. (8) $\bar{n}$ can be calculated in terms of the dependence of the initial butadiene concentration $[BD]_0$, the nickel concentration $[Ni] = [Ni]_{tot}$, and the conversion C.

The validity of Eq. (7) follows from Fig. 5, where the relation between the parameter $\nu(\bar{n}^{-1}) - 1$, which gives the number of free chains per nickel, and the conversion per nickel $2.3 [\lg(1/(1-C))][Ni]^{-1}$ is shown.

From the reciprocal slope of the regression line the ratio of the rate constants $k_p/k_{ü} \approx 635$ l mol^{-1} can be obtained. The experimental error amounts to about 100 l mol^{-1}.

Thus, it has been established for the first time that in the case of the 1,4-cis polymerization of butadiene, catalyzed by the C_{12}-allylnickel(II) complex 1, the polymerization degree or chain length $\bar{n}$ can be exactly described by a simple chain propagation–transfer reaction model with the β-hydride elimination as the rate determining step for the transfer reaction of the catalyst to the butadiene, which starts the generation of a new chain.

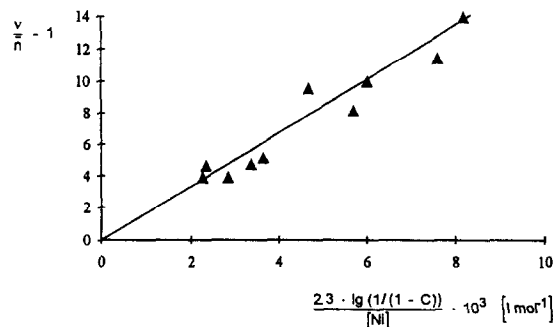With the given ratio $k_p/k_{ü}$ as a specific parameter of the catalyst and in the frame of the usable

Fig. 5. Relation between the number of free chains per nickel $\nu(\bar{n}^{-1}) - 1$ and the conversion per nickel $2,3 [\lg(1/(1-C))][Ni]^{-1}$ according to Eq. (7) for 10 runs of polymerization in the range of temperature between 0 and 50°C.

experimental conditions the polymerization degree could be varied in a theoretically predictable way between $\bar{n} \approx 400$ till $\bar{n} \approx 2500$ in agreement with the reaction model. Thus, it can be concluded that the whole amount of the catalyst **1** is indeed catalytically active. Furthermore the deactivation of the catalyst, which has been observed at a longer time of reaction[15], can be neglected to a very good approximation under the experimental conditions used in this work.

As we have found the polymerization degree can be increased until $\bar{n} \approx 3000$, which is the range of technical interest, by mass polymerization in liquid butadiene at 0°C. Under these conditions the concentration of butadiene has reached the maximal value of 12 M, but the ratio $k_p/k_{\ddot{u}}$ decreases to $280 \pm 20 \, 1 \, mol^{-1}$. Very probably this is a medium effect [15].

Furthermore, in the solution polymerization, the ratio of the constants $k_p/k_{\ddot{u}}$ shows an interesting dependence on the concentration of the catalyst. If the nickel concentration is increased to $[Ni] = 10^{-3}$ M the ratio $k_p/k_{\ddot{u}}$ also increases by one order of magnitude as a result of a corresponding decrease of the transfer constant $k_{\ddot{u}}$. Under these conditions the polymerization degree $\bar{n}$ approaches the theoretical chain length ν at corresponding short reaction time. In this way the polymerization degree can also be increased to an extent as is characteristic for the technical nickel catalyst [12,16].

The decrease of the transfer constant $k_{\ddot{u}}$ with increasing catalyst concentration could indicate some influence of the anion on the rate of the β-hydride elimination, possibly by an increasing penetration ion pair formation[17].

A similar effect has been established by us in the case of the 1,4-*cis* polymerization of butadiene with the C_{12}-allylnickel(II) complex $[Ni(C_{12}H_{19})]PF_6$ as the catalyst. If the concentration of the anion is increased by adding the corresponding tetraethylammonium salt NEt_4PF_6 in a ratio Ni:X = 1:100 the ratio $k_p/k_{\ddot{u}}$ increases by the factor of 3 [18]. Obviously the interaction with the anion opens an additional possibility to regulate the mol mass very precisely and we

investigate this effect further to deepen our understanding of the catalytic structure–reactivity relationship and to design tailor-made catalysts for the 1,4-*cis* polymerization of butadiene of technical interest.

4. Conclusions

In the 1,4-*cis* polymerization of butadiene, catalyzed by the C_{12}-allylnickel(II) complex **1** the mol mass regulation can be described quantitatively to a very good approximation by a simple chain propagation and transfer reaction model with the β-hydride elimination as the rate determining reaction step for the transfer reaction of the catalyst to the monomer to start the formation of a new chain.

The validity of the kinetic reaction model is proved experimentally by the constancy of the ratio $k_p/k_{\ddot{u}}$ under the investigated variation of the different experimental parameters. This ratio of the rate constants for the chain propagation and the transfer reaction of the catalyst to the monomer is practically independent of temperature in the range of the used experimental conditions and determines – as a structure specific property of the catalyst – the polymerization degree $\bar{n}$, which is obtainable under the given experimental conditions.

According to the value of the ratio $k_p/k_{\ddot{u}} \approx 635$ mol 1^{-1} being characteristic for the catalyst **1** at concentrations $[Ni] \leq 2 \cdot 10^{-4}$ M in toluene the polymerization degree $\bar{n}$ can be regulated quantitatively in a theoretically predictable way between $\bar{n} \approx 400$–3000 ($M_n \approx 20000$–160000 g mol^{-1}) in terms of the butadiene concentration and conversion. The highest value of $\bar{n} \approx 3000$ could be obtained in liquid butadiene ($[BD]_0 \approx 12$ M) by mass polymerization and reaches the range of technical interest. From our results we can conclude that no deactivation of the catalyst takes place under the chosen experimental conditions and that the nickel complex is catalytically active in its total concentration.

By elucidating the mechanism of mol mass regulation the reaction model for the allyl nickel complex catalyzed 1,4-*cis* polymerization of butadiene becomes complete in a theoretically and practically important aspect. On this basis the control of mol mass regulation in terms of the structure of the nickel catalyst and the experimental conditions can be investigated further much more thoroughly and directly to reach our final goal, the development of 'tailor made' catalysts.

Acknowledgements

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