A Comparison of Neodymium Versatate, Neodymium Neopentanolate and Neodymium Bis(2-ethylhexyl)phosphate in Ternary Ziegler Type Catalyst Systems With Regard to their Impact on the Polymerization of 1,3-Butadiene

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A Comparison of Neodymium Versatate, Neodymium Neopentanolate and Neodymium Bis(2-ethylhexyl)phosphate in Ternary Ziegler Type Catalyst Systems With Regard to their Impact on the Polymerization of 1,3-Butadiene

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In ternary Ziegler catalyst systems comprised of a Nd-component, diisobutylaluminum hydride (DIBAH) and ethylaluminum sesquichloride (EASC), three Nd salts [neodymium versatate (NdV), neodymium neopentanolate (NdA) and neodymium bis(2-ethylhexyl)phosphate (NdP)] are compared regarding their activities in the polymerization of 1,3-butadiene (BD) and the various features of the poly(butadiene)s obtained. For these three systems, the impact of the molar ratios n_{Cl}/n_{Nd} and n_{DIBAH}/n_{Nd} on catalyst activity and polymer properties ($\bar{M}_n$, PDI and microstructure) has been studied. The highest polymerization activity is found for the catalyst system NdV/DIBAH/EASC at $n_{Cl}/n_{NdV} = 2$ and $n_{DIBAH}/n_{NdV} = 30$. The NdP based system is characterized by remarkably high activity, especially at low ratios of n_{DIBAH}/n_{NdP} (e.g. $n_{DIBAH}/n_{NdP} = 5$). The NdA containing catalyst systems are less active compared to NdV and NdP systems. In all three catalyst systems, the cis-1,4-content decreases with increasing ratios of n_{DIBAH}/n_{Nd}. The highest cis-1,4 content (97.6%) is found for the NdP-containing system at $n_{DIBAH}/n_{NdP} = 5$ and $n_{Cl}/n_{NdP} = 2$.

Keywords alcoholate, carboxylate, diene polymerization, living polymerization, neodymium, phosphate, polybutadiene, ziegler catalysis, rubber

Introduction

In large scale production of *cis*-1,4-polybutadiene (i.e., butadiene rubber = BR) various Ziegler type catalysts are used. These catalysts are based on the transition metals titanium, cobalt, nickel and the rare earth metal neodymium (Nd) (1–3). With Nd-based catalysts, higher *cis*-1,4-contents (97–99%) are obtained in poly(butadiene) (Nd-BR), as well as in poly(isoprene) (i.e., isoprene rubber = IR) than with the other

metals (1, 2). For highly active catalyst systems, the Nd component is combined with an aluminum alkyl compound and a halide donor. Due to the high *cis*-1,4-content, unvulcanized Nd-BR, as well as the respective vulcanizates, exhibit strain induced crystallization which results in superior tensile strength, good abrasion resistance and excellent dynamic performance (4–6). These properties are advantageous for the use of Nd-BR in different tire parts and various technical rubber goods such as golf ball cores.

As a consequence of problems (most notably gel formation) associated with partially or completely heterogeneous Nd catalyst systems, hydrocarbon soluble Nd systems are preferred in industrial Nd-BR-production. This solubility requirement is met by Nd salts with appropriate anions that provide high solubility in solvents such as *n*-hexane, cyclohexane and toluene. The most commonly used Nd salts which exhibit the desired high solubility in hydrocarbons are carboxylates, alcoholates, and phosphates which are based on branched or cyclic aliphatic groups that preferably contain eight or more carbon atoms.

These three types of anions and their use in Nd catalyzed diene polymerization are briefly reviewed in the following section.

The development and use of neodymium carboxylates has been promoted by Bayer since the early 1980s. The most frequently reported carboxylates in academic and patent literature are:

1. Neodymium versatate (NdV; versatate is an isomeric mixture of α,α-disubstituted decanoic carboxylates) (7–12).
2. Neodymium 2-ethylhexanoate (13–16).
3. Neodymium octanoate (17–21).
4. Neodymium naphthenate (an isomeric mixture of substituted cyclopentyl- and cyclohexyl-carboxylates) (22, 23).

Beside these "top four" carboxylates, other more sophisticated Nd carboxylates are presently under investigation in order to determine the mechanism of catalyst activation and the structure of the active Nd-species (24).

The development and industrial application of Nd alcoholates were mainly promoted by the Italian company, Anic and its succeeding organizations, Montecatini, Enichem, etc. (25). In diene polymerization, the most intensely studied Nd alcoholates are $Nd(OBu)_3$ (26–29) and $Nd(O^iPr)_3$ (30, 31).

To the best of our knowledge, only one neodymium phosphate compound is described for use in diene polymerization: Neodymium bis(2-ethylhexyl)phosphate (NdP). The potential of NdP based catalyst systems was recently demonstrated by P. Laubry in several patents (32–35). With the described NdP based catalyst systems, poly(isoprene) with a *cis*-1,4-content >98% is obtained. Other interesting features of these systems are high activity at low molar ratios $n_{Al}/n_{NdP} < 5$, the potential to selectively polymerize isoprene contained in the C5 fraction of raffinates (32) and the feasibility of preparing BD-isoprene-copolymers (35).

A vast number of studies on the characteristics of Nd mediated polymerizations have been performed and numerous aspects of the multi-parameter Nd systems have been looked at in great detail (3). Despite the large number of studies, the impact of the anion was the focus of only a few. D. J. Wilson systematically varied the structure of carboxylates and studied the influence of hydrocarbon solubility on polymerization activity (36). This study showed that neocarboxylates ($Nd(OCOCR_3)_3$) have a higher activity than isocarboxylates ($Nd(OCOCH_2R)_3$). Also, the length of the aliphatic groups

in the carboxylates has an impact on catalyst activity. Among isocarboxylates, anions with longer hydrocarbon chains exhibit higher polymerization activities. Wilson did not observe this systematic trend for the neocarboxylates.

E. Kobayashi et al. studied the electron withdrawing effect of a series of halogenated carboxylates on catalyst activity: $Nd(OCO-R)_3$, where $R= CF_3, CCl_3, CHCl_2, CH_2Cl, CH_3$ (37). In this study, the highest activity was found for $Nd(OCOCCl_3)_3$.

Comparative studies on anions, which bear different substituents, are not available for Nd alcoholates or Nd phosphates. Furthermore, there is no literature available in which Nd-carboxylates, Nd-alcoholates and Nd-phosphates are compared under the same experimental conditions. We, therefore, decided to comparatively study neodymium versatate (NdV), neodymium neopentanolate (NdA) and neodymium bis(2-ethylhexyl)phosphate (NdP) (Scheme 1) as components of ternary Nd Ziegler catalyst systems. Throughout this study, the cocatalyst diisobutylaluminum hydride (DIBAH) and the halide donor ethylaluminum sesquichloride (EASC) were used.

We investigated the following catalyst systems in detail:

1: NdV/DIBAH/EASC
2: NdA/DIBAH/EASC
3: NdP/DIBAH/EASC

From these investigations we expected to gain further insight into the effect of the anion in the Nd catalyzed polymerizations.

Experimental

Materials

n-Hexane was distilled before use and stored over molecular sieves (4 Å) resulting in a residual water content of 4 ppm (determined by Karl Fischer titration monitored by
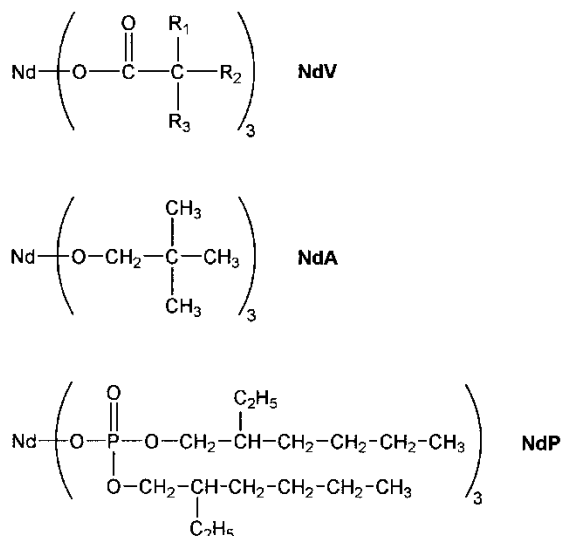
Scheme 1. Neodymium versatate (NdV), neodymium neopentanolate (NdA) and neodymium bis(2-ethylhexyl)phosphate (NdP) which were compared in the ternary catalyst systems **1**, **2** and **3**.

coulometry). Butadiene (BD) was obtained from a *Bayer AG* production plant and was freed from stabilizer by passing it through consecutive columns (basic aluminum oxide and 4 Å molecular sieves). Neodymium versatate (NdV) was purchased from *Rhône-Poulenc* as a solution in hexane containing 9 wt% Nd, 200 ppm water and 8.73 wt% versatic acid. The solvent was removed *in vacuo* at 160°C in order to eliminate versatic acid and water. The residual NdV was dissolved in *n*-hexane (0.1 M). Neodymium neopentanolate (NdA) was synthesized by A. Fischbach (Technische Universität München, Germany) according to the literature (38) and used as a 0.1 M solution in *n*-hexane. The synthesis of neodymium bis(2-ethylhexyl)phosphate (NdP) was carried out as described in literature (34). NdP was used as pure solid material. Neodymium chloride hexahydrate for NdP synthesis was obtained from Aldrich in 99.99 % purity and was used without further purification. DIBAH (1.0 M in hexane fraction) and EASC (0.91 M in toluene) were used as received from Aldrich. 2,2′-Methylene-bis-(4-methyl-6-*tert*-butylphenol) (BKF) was purchased from Aldrich and was used for the stabilization of BR during work-up procedure.

Molar Masses

The molar masses of BR were determined by size exclusion chromatography (SEC). Solutions containing 1 mg BR per mL CHCl$_3$ (dissolved for several hours at 25°C) were passed through a 0.2 μm syringe filter prior to characterization by SEC, which was calibrated by 1,4-polybutadiene standards ($\bar{M}_w/\bar{M}_n \leq 1.02$) from FLUKA. SEC was operated with a pump supplied by Waters (type: Waters 510) and Ultrastyragel® columns with pore sizes 500, 1000, 10,000, and 100,000 Å. The signals were detected by the difference of the refractive indices (Waters 410). The flow rate was 1 mL min^{-1}.

Microstructure by IR Analysis. The microstructure of BR was determined by IR spectroscopy (Fa. Bruker IFS 55, Fa. Bruker Vector 22 (ATR)). The following peaks were used for quantitative determination of the poly(butadiene) microstructure: 735 cm^{-1} (δ(cis-R–CH=CR–H), → *cis*-1,4, $\varepsilon = 0.192$), 912 cm^{-1} (δ(R–CH=CH–H), → 1, 2, $\varepsilon = 1.0$), 965 cm^{-1} (δ(trans-R–CH=CR–H), → *trans*-1,4, $\varepsilon = 0.769$). The validity of the Lambert-Beer law was assumed.

Monomer Conversion

Monomer conversion was determined gravimetrically. For this purpose, samples were taken and weighed (still containing solvent and monomer). The weight of the samples was determined again after the polymerization had been shortstopped with methanol/ BKF and after the residual BD and the solvent had been removed by vacuum drying at 65°C.

Polymerization Experiments

Polymerization experiments were carried out in a 1 L autoclave (Büchi BEP 280). In all cases, a syringe/septum technique was used which is described in detail in Reference (39). The inert gas (argon) was purified by passing it through two columns. Residual oxygen was removed by the first column loaded with copper oxide BTS-catalyst purchased from Fluka and water was eliminated in the second column containing molecular sieves (4 Å). For the polymerization experiments with NdV and NdA, the reactor was filled

with dry solvent and dry BD and heated to 60°C. The catalyst components were then quickly added in the following sequence: Neodymium component (NdV or NdA), DIBAH and EASC. For the polymerization experiments with NdP, the reactor was first charged with NdP and then the reactor was filled with dry solvent and dry BD. The heterogeneous mixture was warmed up to 60°C and was vigorously stirred for several hours in order to dissolve NdP. After the NdP was completely dissolved, the other catalyst components DIBAH and EASC were quickly added to initiate polymerization. The polymerization was shortstopped by cooling to ambient temperature and quenching with methanol. Finally, the reaction mixture was poured into 500 mL of methanol containing 0.2 wt% BKF-stabilizer. The coagulated polymer was isolated and dried at 65°C *in vacuo.*

Results and Discussions

The three catalyst systems, **1**, **2** and **3**, were compared with respect to their polymerization activity and the various properties of the polymers obtained ($\bar{M}_n$, polydispersity and microstructure). For each of the three catalyst systems the impact of the molar ratios of n_{Cl}/n_{Nd} and of n_{DIBAH}/n_{Nd} was systematically studied.

In this context, it is important to mention that the catalyst systems were neither preformed nor aged in any way. For catalyst systems **1** and **2**, the reactor was sequentially charged as follows: 1) hexane, 2) BD, 3) NdV or NdA, 4) DIBAH and 5) EASC. For system **3**, the reactor was charged in the order: 1) NdP, 2) hexane, 3) BD, 4) DIBAH and 5) EASC. For system **3**, a different addition order had to be applied as NdP dissolves very slowly and forms highly viscous solutions in hexane. Even at high dilutions, NdP solutions exhibit enormous viscosity, which causes problems during the injection process. Because of this, NdP was first charged to the reactor in solid form. In our opinion, changing the order of addition does not limit the comparability of experiments as all polymerizations are initiated by the components DIBAH and EASC, which are added at the end of the charging procedure in all three polymerization series.

The variations performed and the data obtained in the three sets of experiments are given in Table 1. The data for the catalyst system NdV/DIBAH/EASC (**1**) is taken from an earlier study (12).

Catalyst Activities

In our previous studies, on NdV catalyst systems we used the apparent rate constant k_a in order to quantify polymerization activities (12, 40). This constant k_a was obtained from a first order kinetic study. In the present study first order kinetics could only be applied to catalyst system **1** (12). For the other two catalyst systems, the consumption of monomer cannot be described by first order kinetics. In order to compare the polymerization activities of the three systems in simple terms the turnover frequency (TOF) is used. TOF was determined according to Equation (1) ([Nd]$_0$ = concentration of the Nd component at the start of polymerization).

$$\text{TOF} = \frac{1}{[\text{Nd}]_0} \cdot \left[-\frac{d[BD]}{dt} \right]_{t=0} \tag{1}$$

TOF is calculated from the tangent in the conversion-time-curve at the start of polymerization ($t = 0$). The differential coefficient $-d[BD]/dt$ is determined by fitting

Table 1

Investigation of the Nd-components NdV, NdA and NdP in the ternary Ziegler catalyst systems **1**, **2** and **3** for BD polymerization

Nd Comp.	n_{Cl}/n_{Nd}	n_{DIBAH}/n_{Nd}	Time (min)	Conv. (%)	TOF (h^{-1})	$\bar{M}_n$ ($g \cdot mol^{-1}$)	PDI	*cis* (%)	trans (%)	1, 2 (%)
NdV[a]	2	5	332	0	—	—	—	—	—	—
NdV[a]	2	10	221	65	454900	144000	1.9	97.3	1.9	0.8
NdV[a]	2	20	168	83	480100	85000	2.5	96.1	3.1	0.8
NdV[a]	2	30	108	94	808200	55000	2.4	94.5	4.3	1.2
NdV[a]	2	50	260	99	500400	44000	3.9	92.4	6.3	1.3
NdA	1	20	1215	76	53100	75900	2.5	94.2	5.3	0.5
NdA	2	20	1440	11	22800	27200	6.3	95.3	4.2	0.5
NdA	3	20	1383	23	24600	21000	8.2	96.0	3.2	0.8
NdA	1	5	1260	0	—	—	—	—	—	—
NdA	1	10	1350	21	29500	24100	8.2	95.7	3.5	0.8
NdA	1	30	1135	89	86100	17100	6.8	92.3	7.2	0.5
NdA	1	50	1390	100	114200	23800	3.1	88.1	11.2	0.7
NdP	1	20	235	87	262400	58400	2.6	93.4	6.3	0.3
NdP	2	20	175	100	451900	65800	2.1	92.5	7.2	0.3
NdP	3	20	195	100	601100	Gel	—	—	—	—
NdP	2	5	142	98	722200	164400	1.7	97.6	2.2	0.2
NdP	2	10	170	99	620900	97500	2.0	95.2	4.6	0.2
NdP	2	30	250	100	378100	43000	2.1	89.6	10.0	0.4
NdP	2	50	270	100	299200	37300	1.9	88.6	10.9	0.5

[a]Data taken from (12).

Reaction conditions: **1**: NdV/DIBAH/EASC: (12). **2**: NdA/DIBAH/EASC: reactor Büchi-BEP-280 autoclave; *n*-hexane ($V_{Hex} = 0.44$ L); $[NdA]_0 = 0.38$ mmol $\cdot L^{-1}$; $[DIBAH]_0 = 1.9$, 3.8, 7.6, 11.4, 19.0 mmol L^{-1}; $[EASC]_0 = 0.13$, 0.25, 0.38 mmol L^{-1}; $[M]_0 = 1.90$ mol $\cdot L^{-1}$; T $= 60°$C; order of addition: hexane-BD-NdA-DIBAH-EASC. **3**: NdA/DIBAH/EASC: reactor Büchi-BEP-280 autoclave; *n*-hexane ($V_{Hex} = 0.44$ L); $[NdA]_0 = 0.38$ mmol $\cdot L^{-1}$; $[DIBAH]_0 = 1.9$, 3.8, 7.6, 11.4, 19.0 mmol L^{-1}; $[EASC]_0 = 0.13$, 0.25, 0.38 mmol$\cdot L^{-1}$; $[M]_0 = 1.90$ mol $\cdot L^{-1}$; T $= 60°$C; order of addition: NdP-hexane-BD-NdA-DIBAH-EASC.
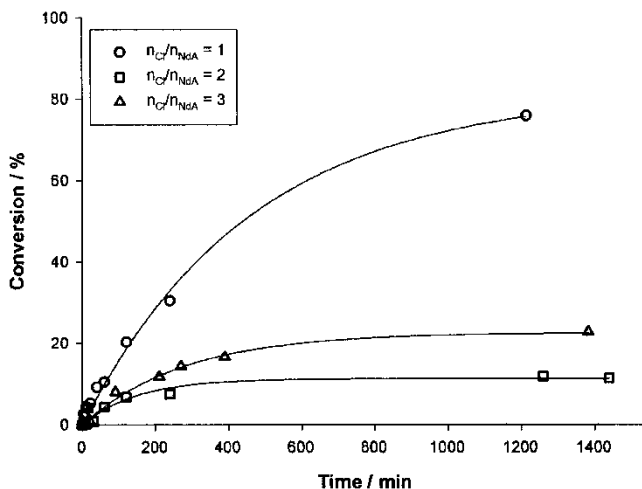
Figure 1. Impact of molar ratios n_{Cl}/n_{NdA} on conversion-time evolution for the polymerization of BD with the catalyst system NdA/DIBAH/EASC (**2**). Reaction conditions: see Table 1.

the conversion-time-curve with an exponential function (applied function: conversion $=$ a $(1 - e^{-b \cdot t})$; a, b $=$ coefficients). From the resulting fitting functions, the slope of the tangent at $t = 0$ was obtained by calculation of the first derivative.

Variations of n_{Cl}/n_{Nd} and its Impact on Catalyst Activities

For the three catalyst systems, **1**, **2** and **3**, the molar ratios of n_{Cl}/n_{Nd} were investigated at $n_{Cl}/n_{Nd} = 1$, 2 and 3. The respective conversion-time-plots are given for **2** in Figure 1 and for **3** in Figure 2. The optimum n_{Cl}/n_{NdV}-ratio for system **1** was determined in a previous study to be $n_{Cl}/n_{NdV} = 2$ (12).
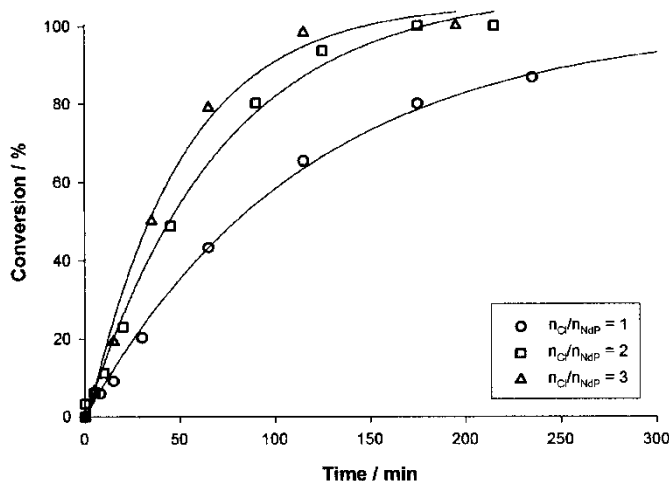

Figure 2. Impact of molar ratios n_{Cl}/n_{NdP} on conversion-time evolution for the polymerization of BD with the catalyst system NdP /DIBAH /EASC (**3**). Reaction conditions: see Table 1.

Thus, the maximum catalyst activities for the three catalyst systems were determined to be at the following n_{Cl}/n_{Nd}-ratios:

1: NdV/DIBAH/EASC: $n_{Cl}/n_{NdV} = 2$ (see Ref. (12))
2: NdA/DIBAH/EASC: $n_{Cl}/n_{NdA} = 1$
3: NdP/DIBAH/EASC: $n_{Cl}/n_{NdP} = 3$

As the NdP containing catalyst system **3** yields insoluble (gelled) polymer at a molar ratio $n_{Cl}/n_{NdP} = 3$, further studies with system **3** were performed at $n_{Cl}/n_{NdP} = 2$.

Variations of n_{DIBAH}/n_{Nd} and its Impact on Catalyst Activities

For the three catalyst systems the amount of cocatalyst DIBAH (n_{DIBAH}/n_{Nd}) was varied at constant n_{Cl}/n_{Nd} ratios as discussed in the previous chapter. For **1**, the respective conversion-time-plots have been previously reported (12). Plots for **2** can be found in Figure 3 and for **3** in Figure 4.

In Figure 5, the dependencies of catalyst activities (TOF) on n_{DIBAH}/n_{Nd} are shown for the three catalyst systems NdV/DIBAH/EASC (**1**), NdA/DIBAH/EASC (**2**) and NdP/DIBAH/EASC (**3**). For **1**, TOF reaches a maximum at $n_{DIBAH}/n_{NdV} = 30$. For the NdA based system **2**, TOF increases with an increasing ratio of n_{DIBAH}/n_{NdA} and for the NdP-based catalyst **3** TOF decreases with an increasing ratio of n_{DIBAH}/n_{NdP}.

The highest catalyst activity (TOF $= 808200 \, h^{-1}$) is observed for NdV/DIBAH/EASC (**1**) at $n_{DIBAH}/n_{NdV} = 30$. It is interesting to note that the NdP based catalyst system **3** exhibits the highest activity (TOF $= 722200 \, h^{-1}$) at a n_{DIBAH}/n_{NdP}-ratio as low as 5. This is unique in this study as **1** and **2** are completely inactive at this
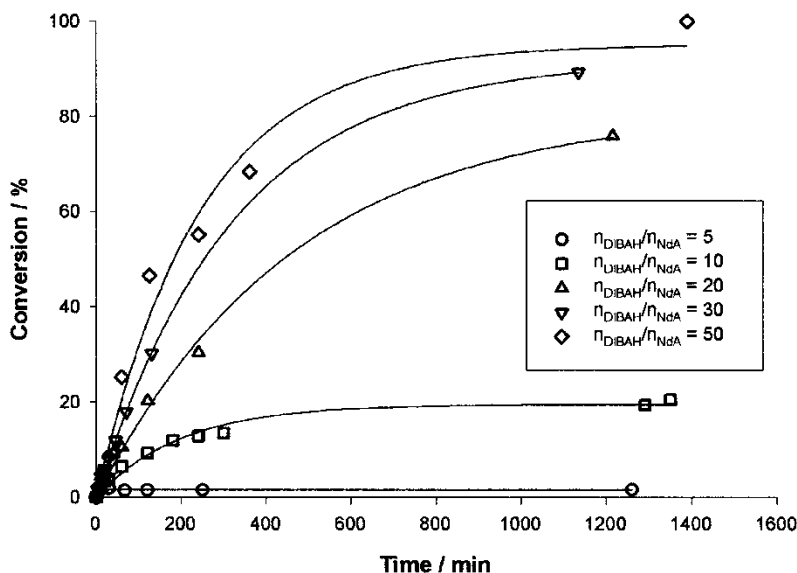
Figure 3. Impact of molar ratios n_{DIBAH}/n_{NdA} on conversion-time evolution for the polymerization of BD with the catalyst system NdA/DIBAH/EASC (**2**). Reaction conditions: see Table 1.
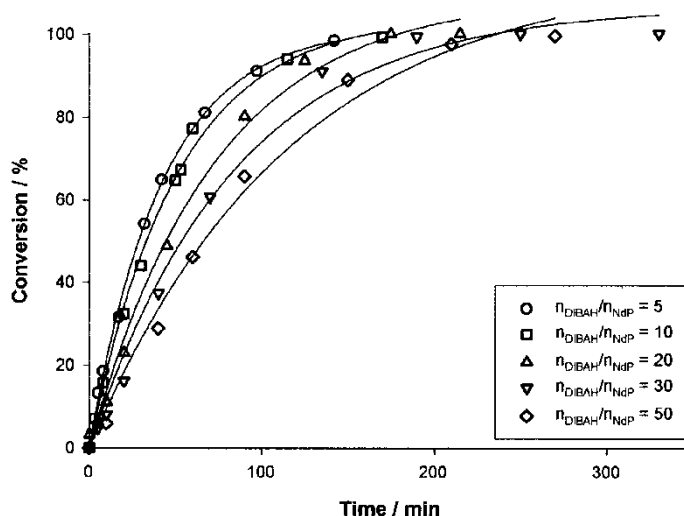
Figure 4. Impact of molar ratios n_{DIBAH}/n_{NdP} on conversion-time evolution for the polymerization of BD with the catalyst system NdP/DIBAH/EASC (**3**). Reaction conditions: see Table 1.

n_{DIBAH}/n_{Nd}-ratio. Since the aluminum alkyl cocatalyst is a major factor in total catalyst cost the high activity of **3** at $n_{DIBAH}/n_{NdP} = 5$ has to be particularly emphasized from an economic point of view. NdA is inferior to NdP and NdV as the NdA-based system exhibits a significantly lower peak activity (TOF = 114200 h^{-1} at $n_{DIBAH}/n_{NdA} = 50$).
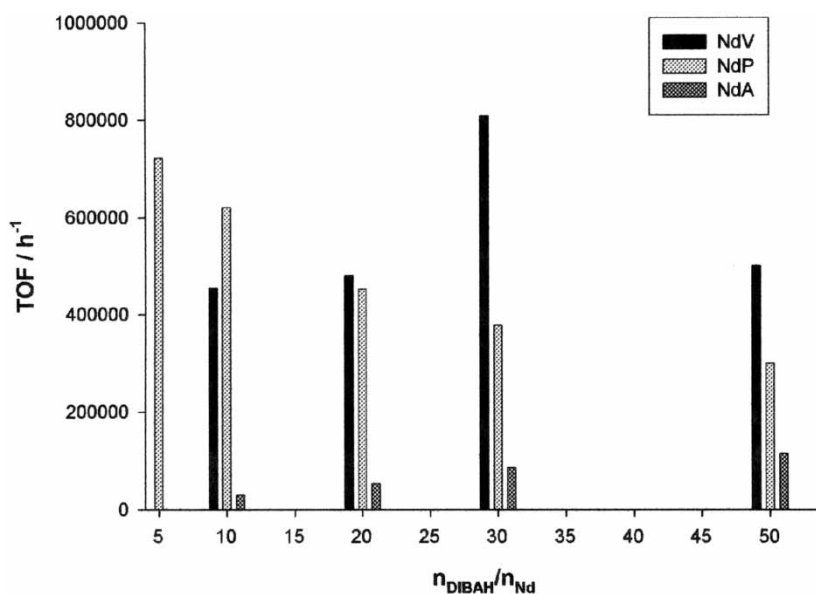
Figure 5. Comparison of the turnover frequencies (TOF) of the catalyst systems NdV/DIBAH/EASC (**1**), NdA/DIBAH/EASC (**2**) and NdP/DIBAH/EASC (**3**) at various molar ratios n_{DIBAH}/n_{Nd}.

It should be mentioned that for the polymerization of isoprene P. Laubry previously tested similar NdP based catalyst systems. Laubry also observed high catalyst activities at very low molar ratios of $n_{DIBAH}/n_{NdP} < 5$ (34).

Microstructure

Data on the microstructure (*cis*-1,4-content, *trans*-1,4-content and *vinyl*-1,2-content) of the BR samples obtained with the three catalyst systems **1**, **2** and **3** is given in Table 1. As the *vinyl*-1,2-content almost remains unchanged (0.2–1.3%) for the three catalyst systems the further discussion on microstructure is confined to *cis*-1,4-content.

The dependence of *cis*-1,4-content on the molar ratio n_{DIBAH}/n_{Nd} is depicted for the three catalyst systems (Figure 6). For **1**, **2** and **3**, the *cis*-1,4-content decreases with increasing amounts of DIBAH. The performance of NdP is particular since it allows polymerization at a molar ratio as low as $n_{DIBAH}/n_{Nd} = 5$ and yields a polymer with the highest *cis*-1,4-content observed within in the whole study (97.6%). At the higher molar ratios of $n_{DIBAH}/n_{Nd} = 10$, 20, 30, and 50 NdV based catalyst systems yield higher *cis*-1,4-contents than NdP or NdA based systems. At molar ratios of $n_{DIBAH}/n_{Nd} = 20$ and 30 NdA yields *cis*-1,4-contents which are distinctly higher than those of NdP. At molar ratios of $n_{DIBAH}/n_{Nd} = 10$ and 50, the *cis*-1,4-contents of NdA and NdP are identical within experimental error.

The decrease in *cis*-1,4-content with increasing amounts of DIBAH can be explained by a model put forward in a previous paper (12). According to this model DIBAH can act as a ligand coordinating to vacant sites of Nd. As the number of available coordination sites influences the mode of BD coordination to the Nd center, the amount of DIBAH affects the *cis*-1,4-content.
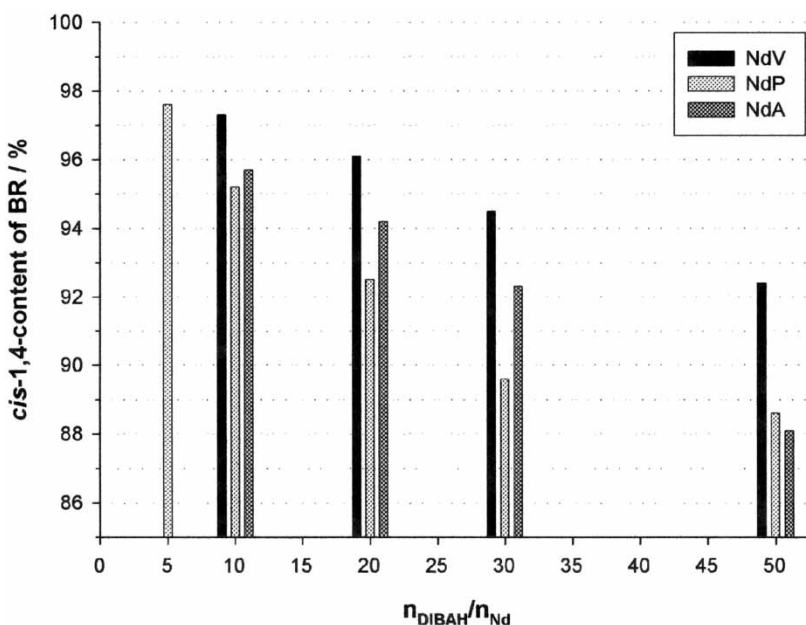
Figure 6. Dependence of *cis*-1,4-contents on molar ratios of n_{DIBAH}/n_{Nd} for the catalyst systems NdV/DIBAH/EASC (**1**), NdA/DIBAH/EASC (**2**) and NdP/DIBAH/EASC (**3**).

According to numerous publications on Nd-BR the highest *cis*-1,4-contents observed for Nd-mediated polymerizations are in the range 97–99%. The highest *cis*-1,4-contents found in this paper are slightly lower than these values. In this context, it is important to note that the *cis*-1,4-content depends on the analytical method, as well as the applied calibration (41). For this reason, the lower level of *cis*-1,4-contents reported in this work can be easily accounted for. Even though the absolute level of *cis*-1,4-contents might be too low in this study, the relative trends allow for the interpretations given.

Conclusions

The three ternary neodymium catalyst systems NdV/DIBAH/EASC (**1**), NdA/DIBAH/EASC (**2**) and NdP/DIBAH/EASC (**3**) are compared with regard to catalytic activity and BR microstructure. The NdP based catalyst system is remarkable concerning two points: First, it exhibits a very high polymerization activity at a molar ratio n_{DIBAH}/n_{NdV} as low as 5 and second at this low molar ratio the NdP based catalyst yields the highest *cis*-1,4-content of the three catalyst systems studied. Even though for the NdV based catalyst system **1** a higher peak activity is found than for **3**, the catalyst system **1** is inferior to **3** as it requires a significantly higher molar ratio of $n_{DIBAH}/n_{NdV} = 30$ in order to achieve in this high polymerization activity. In addition the *cis*-1,4-content of BR obtained by system **1** at $n_{DIBAH}/n_{NdV} = 30$ is lower than for **3** at $n_{DIBAH}/n_{NdV} = 5$. If catalyst costs are taken into consideration NdP based systems exhibit the best overall performance of the three catalyst systems studied. NdA based catalyst systems (**2**) are inferior in every respect.

Acknowledgements

References

1. *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Ed.; VCH: Weinheim, Germany, 1993; Vol. A4, 221, 261.
2. Taube, R. and Sylvester, G. (1996) Stereospecific polymerization of butadiene or isoprene. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 1st Ed.; Cornils, B. and Herrmann, W.A., eds.; Wiley-VCH: Weinheim, Germany; Vol. 280.
3. Osakada, K. and Takeuchi, D. (2004) Coordination Polymerization of Dienes, Allenes, and Methylenecycloalkanes. *Adv. Polym. Sci.*, 171: (Polymer Synthesis), 137–194.
4. Bruzzone, M. and Gordini, S. (1991) Lanthanide catalysts for diene polymerization: some peculiarities and unresolved questions, Meeting of the ACS Rubber Division, October 8–11, Detroit, Michigan.
5. Sylvester, G. and Stollfuß, B. (1988) Meeting of the ACS Rubber Division, April 19–22, Dallas, Texas Paper No. 32.
6. Wu, X., Wu, Z., Liu, H., Yin, J., Mo, K., and Qiao, S. (2002) The performance of cis-polybutadiene with Nd coordinate polymerization catalyst. *J. Polym. Mater.*, 19 (3): 329–333.

7. Jenkins, D.K. (1985) Butadiene polymerization with a rare earth compound using a magnesium alkyl cocatalyst. *Polymer*, 26 (1): 152–158.

8. Wilson, D.J. and Jenkins, D.K. (1992) Butadiene polymerization using ternary neodymium-based catalyst systems. The effect of catalyst component addition order. *Polym. Bull.*, 27 (4): 407–411.

9. Pross, A., Marquardt, P., Reichert, K.H., Nentwig, W., and Knauf, T. (1993) Modelling the polymerization of 1,3-butadiene in solution with a neodymium catalyst. *Angew. Makromol. Chem.*, 211: 89–111.

10. Quirk, R.P. and Kells, A.M. (2000) Polymerization of butadiene using neodymium versatate-based catalyst systems: preformed catalysts with $SiCl_4$ as halide source. *Polym. Int.*, 49 (7): 751–756.

11. Kwag, G., Lee, H., and Kim, S. (2001) First *in situ* observation of pseudo-living character and active site of Nd-based catalyst for 1,3-butadiene polymerization using synchrotron X-ray absorption and UV-visible spectroscopies. *Macromolecules*, 34 (16): 5367–5369.

12. Friebe, L., Nuyken, O., Windisch, H., and Obrecht, W. (2002) Polymerization of 1,3-butadiene initiated by neodymium versatate/diisobutylaluminum hydride/ethylaluminum sesquichloride: Kinetics and conclusions about the reaction mechanism. *Macromol. Chem. Phys.*, 203 (8): 1055–1064.

13. Sylvester, G.; Witte, J.; Marwede, G.. Catalyst for solution polymerization of butadiene. Ger. Patent 2830080, Jan 17, 1980.

14. Throckmorton, M.C. Molecular weight modifier for use with lanthanide and actinide catalysts. US Patent 4663405, May 05, 1987.

15. Gehrke, K., Kohlheim, J., and Gebauer, U. (1994) Butadiene polymerization with the $Nd(oct)_3$/$AlBr_3$/$AlEt_3$ catalyst system. *Plaste Kautsch.*, 41 (5): 213–216.

16. Gehrke, K., Krueger, G., Gebauer, U., and Lechner, M.D. (1996) Polymerization of butadiene with the catalyst system neodymium tris(2-ethylhexanoate)/diisobutylaluminum chloride/triisobutylaluminum. *Kautsch. Gummi Kunstst.*, 49 (11): 760–765.

17. Ricci, G., Boffa, G., and Porri, L. (1986) Polymerization of 1,3-dialkenes with neodymium catalysts. Some remarks on the influence of the solvent. *Makromol. Chem., Rapid Commun.*, 7 (6): 355–359.

18. Ricci, G., Italia, S., Cabassi, F., and Porri, L. (1987) Neodymium catalysts for 1,3-diene polymerization: influence of the preparation conditions on activity. *Polym. Commun.*, 28 (8): 223–226.

19. Oehme, A., Gebauer, U., Gehrke, K., Beyer, P., Hartmann, B., and Lechner, M.D. (1994) The influence of the catalyst preparation on the homo- and copolymerization of butadiene and isoprene. *Macromol. Chem. Phys.*, 195 (12): 3773–3781.

20. Nickaf, J.B., Burford, R.P., and Chaplin, R.P. (1995) Kinetics and molecular weights distribution study of neodymium-catalyzed polymerization of 1,3-butadiene. *J. Polym. Sci., Part A: Polym. Chem.*, 33 (7): 1125–1132.

21. Oehme, A., Gebauer, U., Gehrke, K., and Lechner, M.D. (1996) The influence of ageing and polymerization conditions on the polymerization of butadiene using a neodymium catalyst system. *Angew. Makromol. Chem.*, 235: 121–130.

22. Shen, Z., Ouyang, J., Wang, F., Hu, Z., Fu, Y., and Qian, B. (1980) The characteristics of lanthanide coordination catalysts and the cis-polydienes prepared therewith. *J. Polym. Sci.: Polym. Chem. Ed.*, 18 (12): 3345–3357.

23. Wilson, D.J. and Jenkins, D.K. (1995) Butadiene polymerization using ternary neodymium-based catalyst systems: the effect of Nd:halide ratio and halide type. *Polym. Bull.*, 34 (3): 257–264.

24. Fischbach, A., Perdih, F., Sirsch, P., Scherer, W., and Anwander, R. (2002) Rare-earth Ziegler-Natta catalysts: Carboxylate-alkyl interchange. *Organometallics*, 21 (22): 4569–4571.

25. Andreussi, P., Lauretti, E., and Miani, B. (1994) Europrene Neocis: Improved cis-1,4-Polybutadiene by Neodymium Catalyst, June 6–10, Stepol, Milano, Italy.

26. Pedretti, U., Lugli, G., Poggio, S., and Mazzei, A. Catalyst and method for the polymerization and copolymerization of diolefins. Ger. Patent 2833721, Feb 08, 1979.

27. Carbonaro, A., Ferraro, D., and Bruzzone, M. (1993) Polymerizing conjugate diolefins. Eur. Patent 76535, Apr 13.

28. Carbonaro, A., and Ferraro, D. Polymerization of conjugate diolefins. Eur. Patent 92270, Oct 26, 1983.

29. Biagini, P., Lugli, G., Garbassi, F., and Andreussi, P. (1998) Catalytic system and process for the production of polydiolefins. Eur. Patent 667357, Aug 16.

30. Dong, W. and Masuda, T. (2003) Homogeneous neodymium iso-propoxide/modified methylaluminoxane catalyst for isoprene polymerization. *Polymer*, 44 (5): 1561–1567.

31. Dong, W., Endo, K., and Masuda, T. (2003) Effect of tert-butyl chloride on the isoprene polymerization with neodymium isopropoxide/diisobutylaluminum hydride and neodymium isopropoxide/methylaluminoxane catalysts. *Macromol. Chem. Phys.*, 204 (1): 104–110.

32. Laubry, P. (2002) Method for obtaining a polyisoprene with high cis-1,4 configuration. PCT Int. Appl. 2002048218, June 20.

33. Laubry, P. (2002) Synthetic polyisoprene and their preparation method. PCT Int. Appl. 2002038635, May 16.

34. Laubry, P. (2002) Catalytic system and method for preparing elastomers using same. PCT Int. Appl. 2002038636, May 16.

35. Laubry, P. (2003) Method for preparing butadiene-isoprene copolymers and resulting copolymers. PCT Int. Appl. 2003048221, June 12.

36. Wilson, D.J. (1993) A rare earth catalyst system for the polymerization of 1,3-butadiene: the effect of different carboxylates. *Polymer*, 34 (16): 3504–3508.

37. Kobayashi, E., Hayashi, N., Aoshima, S., and Furukawa, J. (1998) Homo- and copolymerization of butadiene and styrene with neodymium tricarboxylate catalysts. *J. Polym. Sci., Part A: Chem. Ed.*, 36 (2): 241–247.

38. Barnhart, D.M., Clark, D.L., Gorden, J.C., Huffman, J.C., Watkin, J.G., and Zwick, B.D. (1993) Tetrameric lanthanide neopentoxide complexes with agostic Ln H-C interactions: X-ray crystal structures of $Ln_4(OCH_2Bu-terts_{12}$ (Ln = La, Nd). *J. Am. Chem. Soc.*, 115 (18): 8461–8462.

39. Herzog, S. and Dehnert, J. (1964) A systematic anaerobic working method. *Z. Chem.*, 4 (1): 1–11.

40. Friebe, L., Nuyken, O., Windisch, H., and Obrecht, W. (2004) Polymerization of 1,3-butadiene initiated by neodymium versatate/triisobutylaluminum/ethylaluminum sesquichloride: Impact of the alkylaluminum cocatalyst component. *J. Macromol. Sci., Pure Appl. Chem.*, A41 (3): 245–256.

41. Thorn-Csanyi, E. and Luginsland, H.D. (1997) Quantitative determination of the microstructure and composition of crosslinked rubber blends. *Rubber Chem. Technol.*, 70 (2): 222–230.