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Molar Mass Control by Diethyl Zinc in the Polymerization of Butadiene Initiated by the Ternary Catalyst System Neodymium

Versatate/Diisobutylaluminum Hydride/Ethylaluminum Sesquichloride

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Molar Mass Control by Diethyl Zinc in the Polymerization of Butadiene Initiated by the Ternary Catalyst System Neodymium Versatate/ Diisobutylaluminum Hydride/Ethylaluminum Sesquichloride

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The polymerization of 1,3-butadiene (BD) catalyzed by the ternary Ziegler/Natta catalyst system neodymium versatate (NdV)/diisobutylaluminum hydride (DIBAH)/ethylaluminum sesquichloride (EASC) is investigated in regard to molar mass control by diethyl zinc (ZnEt₂). Within the investigated range of ratios of ZnEt₂ to NdV, the features of a living polymerization with a reversible exchange of the living polybutadienyl chains between neodymium and zinc are observed. In summary, ZnEt₂ can be considered as an efficient molar mass control agent, which has a negligible impact on polymerization rates. In addition to the reduction of molar masses, ZnEt₂ also reduces the polydispersity (PDI) and leads to a decrease of the cis-1,4-content.

Keywords diene polymerization, living polymerization, molar mass control, neodymium, rubber, Ziegler-Natta-catalysis, zinc alkyls

Introduction

Neodymium Ziegler Catalysis for Diene Polymerization

Since the fundamental patent on lanthanide based diene polymerization filed by Union Carbide Corporation in 1964 (1), large scale production of poly(*cis*-1,4-butadiene) (butadiene rubber = BR) catalyzed by neodymium (Nd) has become an industrially established process. Nd catalysts yield poly(butadiene) (*i.e.*, butadiene rubber = BR) and poly(isoprene) (*i.e.*, isoprene rubber = IR) with a very high *cis*-1,4-content ($\geq 98\%$) (2, 3).

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In contrast to BR prepared by using different catalysts (e.g. Li-BR: *cis*-content = 40%, Ti-BR: 93%, Co-BR: 96% and Ni-BR: 97%) (3, 4), rubber articles made from high-*cis*-Nd-BR (*cis*-1,4-content \geq 98%) exhibit remarkably low glass transition temperatures and perform extremely well at low operating temperatures. In addition, these articles show high resilience, good abrasion resistance and a low heat build-up in dynamic applications. Due to the high *cis*-1,4-content, the unvulcanized (raw) Nd-BR rubbers, as well as their respective vulcanizates, exhibit strain induced crystallization which results in superior tensile strength and excellent dynamic performance (5–7). These properties render Nd-BR based vulcanizates very useful for special tire parts such as silica loaded treads, sidewalls, sub-treads and carcasses, as well as for various rubber articles such as conveyor belts and golf ball cores.

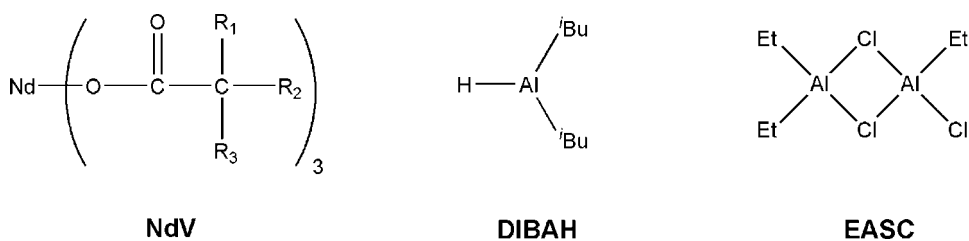
The Nd-component of the catalyst system is commonly comprised of a Nd salt with anion bearing long-chain aliphatic groups, which provide solubility in hydrocarbon solvents. The Nd components most commonly used in commercial applications are carboxylates (8, 9), alcoholates (10, 11) and phosphates (12). Nd allyls (13), Nd cyclopentadienyl complexes (14) and Nd amides (15) have also been reported in the scientific literature. In order to obtain highly active catalyst systems, an aluminum alkyl compound and a halide donor are added to the Nd salts. Thus, binary and ternary catalyst systems are obtained.

One of the catalyst systems, which is used in large scale production, comprises the three components neodymium versatate (NdV), diisobutylaluminum hydride (DIBAH), and ethylaluminum sesquichloride (EASC) (Scheme 1).

In the literature, a great variety of Nd catalyst systems are published. These catalysts are used for the polymerization of dienes (16), the copolymerization of butadiene/ethylene (14) and the copolymerization of butadiene/styrene (17, 18). In addition to the polymerization of double bond containing monomers, Nd catalysts are also applied for the polymerization of cyclic monomers such as lactones and lactides (19). Recently, we reported the use of a Nd catalyst for the preparation of a compatibilized poly(ϵ -caprolactone)/*cis*-1,4-poly(butadiene) (PCL/BR) blend (20). Despite the vast number of papers published on Nd polymerization catalysis, neither the catalyst activation, the polymerization mechanism, nor the impact of the various catalyst components on the polymerization kinetics, are understood in full detail.

Molar Mass Control in Neodymium Catalyzed Butadiene Polymerization

For the large scale production of BR with a high *cis*-1,4 content, Ziegler/Natta-catalysts based on Ni, Co, Ti and Nd are used. In large-scale processes, control of molar mass is an



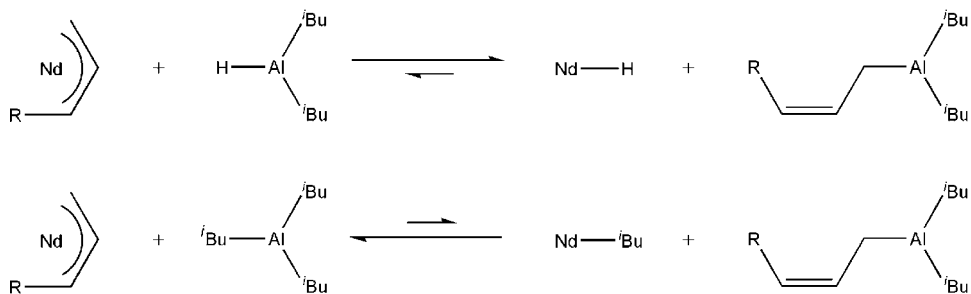
Scheme 1. Ternary catalyst system neodymium(III) versatate (NdV)/diisobutylaluminum hydride (DIBAH)/ethylaluminum sesquichloride (EASC), used in industrial Nd-BR production.

important aspect, since the molar mass strongly influences the compounding performance of the raw rubbers, the processing characteristics of the rubber compounds, as well as the physical properties of the vulcanizates. For catalyst systems based on Ti, Ni and Co, the molar mass is controlled by additives such as hydrogen, 1,2-butadiene or cyclooctadiene. In Nd initiated butadiene polymerizations these molar mass control agents are not effective (2, 21). Various additives such as ethanol, dihydronaphthalene, chloroform, diethyl aniline, triphenylmethane, octanoic acid, allyl iodide and diallylether have been tested without success (22). In addition, propene, oxygen, 1,5-hexadiene, ethyl-trichloroacetate and *n*-butanol resulted in the deactivation of the catalyst system without the decrease of molar mass (23).

To date, no appropriate molar mass control agent has been found for Nd-catalyzed butadiene polymerization. Therefore, in Nd-catalysis, molar mass has to be controlled differently. Polymerization temperature, the monomer/catalyst-ratio (n_M/n_{Nd}) and the n_{Nd}/n_{Al} -ratio are appropriate means for adjusting the molar mass. According to Witte and Taube *et al.*, an increase in the polymerization temperature leads to the reduction of molar mass (3, 24). The option of reducing the molar mass by decreasing the n_M/n_{Nd} -ratio is directly based on the living nature of the butadiene polymerization, which to the best of our knowledge was first observed by Shen *et al.* (25) and quite recently by Taube *et al.* (26). The most important option to reduce molar mass in the butadiene polymerization is by an increase of the n_{Al}/n_{Nd} -ratio (3, 27). The impact of the n_{Al}/n_{Nd} -ratio on molar mass reduction was reported by Nickaf *et al.*, who used the ternary catalyst system based on neodymium octanoate/triisobutyl aluminum (TIBA)/diethylaluminum chloride (28). According to the suggested mechanism put forward by these authors, isobutyl groups and poly(butadienyl) chains are exchanged irreversibly between TIBA and Nd. The authors consider the formed "TIBA-poly(butadienyl)-species" as a dead species. An analogous type of exchange of allyl groups between an allyl lanthanide complex and TIBA has recently been confirmed by Woodman *et al.* (29). In contrast to these observations, the increase of the n_{Al}/n_{Nd} -ratio did not have any effect on the reduction of molar masses in the two allyl Nd systems $Nd(\eta^3-C_3H_5)_2Cl \cdot 1.5 THF$ and $Nd(\eta^3-C_3H_5)Cl_2 \cdot 2 THF$, which Taube *et al.* studied (30).

Recently, we reported the results of a comparative study on the impact of the two aluminum compounds TIBA and DIBAH in the ternary Nd-Ziegler-catalyst systems NdV/TIBA/EASC and NdV/DIBAH/EASC regarding polymerization kinetics of 1,3-butadiene (BD) polymerization and molar mass control (27, 31). We found that DIBAH is much more effective in molar mass control than TIBA. This higher activity was assigned to DIBAH's hydride group. A quantitative analysis of the data revealed that only 5% of TIBA and 41% of DIBAH are involved in molar mass control. Further analysis showed that the activity of DIBAH's hydride group is 20 times higher than the activity of one isobutyl group. These observations and conclusions are summarized in Scheme 2. In this scheme the relative activities of the hydride and the isobutyl groups as well as the respective equilibrium positions are described in a qualitative way (31).

One major shortcoming of molar mass control by varying the n_{Al}/n_{Nd} -ratio is that a variation of this parameter simultaneously influences the rate of polymerization. As shown for the system NdV/DIBAH/EASC, the rate of polymerization is doubled if the molar ratio of n_{DIBAH}/n_{NdV} is increased from 10 to 30 (31). If the same variation is performed in the system NdV/TIBA/EASC (*i.e.*, from $n_{TIBA}/n_{NdV} = 10$ to $n_{TIBA}/n_{NdV} = 30$) the rate increases twenty seven-fold (31). Therefore, the variation of the n_{Al}/n_{Nd} -ratio effective for molar mass control, however leads to an undesired side effect. Particularly, in the continuous production of Nd-BR, a variation of the



Scheme 2. Reversible transfer of living polymer chains from Nd to Al in the catalyst systems NdV/DIBAH/EASC (top) and NdV/TIBA/EASC (bottom) (31). The equilibrium arrows label the different molar mass control activities of DIBAH and TIBA. The charge and the ligands at the neodymium centers are omitted for clarity.

$n_{\text{DIBAH}}/n_{\text{NdV}}$ -ratio leads to changes in the residence time, which results in changes of the final conversion at the end of the reactor line. Due to these interdependencies, in the large scale continuous production of Nd-BR, an adjustment of the $n_{\text{DIBAH}}/n_{\text{NdV}}$ -ratio has to be accompanied by adaptations of the residence time in order to keep the final conversion at the end of the reactor line and the level of residual monomers constant. From these considerations, it becomes evident that an important requirement for an appropriate molar mass control agent is its ability to regulate molar masses *without* influencing the respective rates of polymerization.

Since organometallic compounds like aluminum (hydrido) alkyls are capable of exchanging their substituents with the poly(butadien)yl chains attached to Nd, it is apparent that other metal alkyls should allow for the same mechanism of molar mass control. In this respect, diethyl zinc (ZnEt_2) should be a promising candidate. Strong evidence in favor of diethyl zinc comes from the observation that organo zinc compounds decrease the viscosity of polymer solutions if applied in NdV/ MgR_2 systems (32). Based on this evidence, we decided to perform a detailed study of molar mass control by diethyl zinc in the polymerization of butadiene initiated by the ternary catalyst system NdV/DIBAH/EASC. Herein, we report the results obtained in this study.

Experimental

Materials

n-Hexane was distilled before use and stored over molecular sieves (4 \AA), resulting in a residual water content of 4 ppm (determined by Karl Fischer titration monitored by coulometry). Butadiene (BD) was obtained from a production plant of Bayer AG and was freed from stabilizer by consecutively passing it through two columns (basic aluminum oxide and 4 \AA molecular sieves). Neodymium versatate (NdV) was obtained in hexane solution from Rhodia and was used as received. DIBAH (1.0 M in hexane fraction), EASC (0.91 M in toluene) and ZnEt_2 (1.0 M in hexane fraction) 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.

Molar Masses

The molar masses of BR were determined by size exclusion chromatography (SEC). The polymer solution was precipitated into methanol (containing BKF-stabilizer), the coagulated polymer was then isolated and dried at 65°C in vacuum. Solutions containing 1 mg BR per mL CHCl₃ (dissolved for several hours at 25°C) were passed through a 0.2 μm syringe filter prior to the characterization by SEC, which was calibrated by 1,4-polybutadiene standards ($\overline{M}_w/\overline{M}_n \leq 1.02$) from Fluka. SEC was operated with a pump supplied by Waters (type: Waters 510) and Ultrastyrigel[®]-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.

BR-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 the quantitative determination of the poly(butadiene) microstructure: 735 cm⁻¹ ($\delta(\text{cis-R-CH=CR-H})$, → *cis*-1,4, $\epsilon = 0.192$), 912 cm⁻¹ ($\delta(\text{R-CH=CH-H})$, → 1,2, $\epsilon = 1.0$), 965 cm⁻¹ ($\delta(\text{trans-R-CH=CR-H})$, → *trans*-1,4, $\epsilon = 0.769$). The validity of the Lambert-Beer law was assumed.

Monomer Conversion

The 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 (33). The inert gas (argon) was purified by passing it through two columns. Residual oxygen was removed by the first column filled with copper oxide BTS-catalyst purchased from Fluka and water was eliminated in the second column containing molecular sieves (4 Å).

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: NdV (0.25 M hexane solution), DIBAH (1.0 M hexane fraction solution), EASC (0.91 M toluene solution) and ZnEt₂ (1.0 M hexane fraction solution). For the determination of the monomer conversion, samples were taken at appropriate intervals. In order to terminate the polymerization, it was shortstopped by cooling the reaction mixture to ambient temperature and by quenching with methanol. Finally, the reaction mixture was poured into 500 mL methanol containing 0.2 wt-% BKF-stabilizer, the coagulated polymer was isolated and dried at 65°C in vacuum.

Results and Discussions

In order to screen the potential of ZnEt₂ as a cocatalyst, as well as a molar mass control agent, a first experiment was performed in which DIBAH was replaced by ZnEt₂ in the

standard catalyst system NdV/DIBAH/EASC. As the system comprising NdV/ZnEt₂/EASC is inactive towards butadiene polymerization, the conclusion from this observation is unambiguous. It can be clearly stated that ZnEt₂ does not act as a cocatalyst.

In subsequent experiments, the potential of ZnEt₂ as a molar mass control agent was evaluated. For this purpose, ZnEt₂ was added to the catalyst system NdV/DIBAH/EASC. Thus, the quaternary system NdV/DIBAH/EASC/ZnEt₂ was obtained. A series of polymerizations were performed in which the ratio of $n_{\text{ZnEt}_2}/n_{\text{NdV}}$ was varied. In these experiments, the molar ratio of $n_{\text{Cl}}/n_{\text{NdV}} = 3$ was kept constant. The results of three runs with different amounts of ZnEt₂ added were compared with a reference performed at $n_{\text{ZnEt}_2}/n_{\text{NdV}} = 0$. As the ZnEt₂-containing catalyst system comprises four different components, the order of addition of these components to the monomer solution is not trivial. In this context it is important to mention that the order in which the reactor was loaded was kept constant for all experiments: hexane–BD–NdV–DIBAH–EASC–ZnEt₂. The catalyst system was neither preformed nor aged in any way prior to the addition to the monomer solution.

The conversion-time-curves of the polymerizations performed with the quaternary catalyst system NdV/DIBAH/EASC/ZnEt₂ revealed that the addition of ZnEt₂ has negligible influence on the rate of polymerization, even at the highest level applied ($n_{\text{ZnEt}_2}/n_{\text{NdV}} = 30$) (Figure 1). Only a marginal increase of the polymerization rate can be attributed to ZnEt₂ (see also apparent rate constants k_a in Table 1).

The first order plots of $-\ln(1 - x)$ over polymerization time exhibit straight lines for all four polymerizations (Figure 2). Therefore, it can be concluded, that the polymerization characteristics (and the living character as shown later) of the polymerization catalyzed by NdV/DIBAH/EASC (27) is not affected by the presence of ZnEt₂.

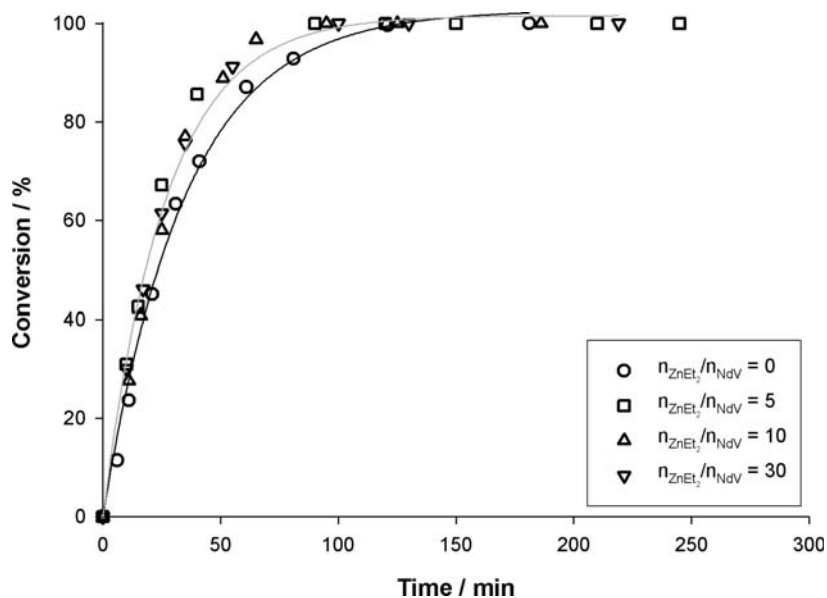


Figure 1. Conversion-time-plots of the BD polymerization with the quaternary catalyst system NdV/DIBAH/EASC/ZnEt₂ at various molar ratios of $n_{\text{ZnEt}_2}/n_{\text{NdV}}$. The gray curve gives an average of the three runs with ZnEt₂, the black curve represents the experiment without ZnEt₂. Reaction conditions: see caption of Table 1.

Table 1

Polymerization of BD initiated by NdV/DIBAH/EASC/ZnEt₂. Reaction: Büchi-BEP-280 autoclave; *n*-hexane ($V_{\text{Hex}} = 0.44$ L); $n_{\text{Cl}}/n_{\text{NdV}} = 3$; $n_{\text{DIBAH}}/n_{\text{NdV}} = 20$; $[\text{NdV}]_0 = 0.39$ mmol L⁻¹; $[\text{DIBAH}]_0 = 7.8$ mmol L⁻¹; $[\text{EASC}]_0 = 0.39$ mmol L⁻¹; $[\text{ZnEt}_2]_0 = 0, 1.95, 3.90, 11.7$ mmol L⁻¹, $[\text{M}]_0 = 1.93$ mol L⁻¹, $T = 60^\circ\text{C}$. Order of charging the reactor: hexane-BD-NdV-DIBAH-EASC-ZnEt₂. The calculation of the apparent first order rate constant k_a is based on the kinetic law $-d[\text{M}]/dt = k_a [\text{NdV}] \cdot [\text{M}]$

$n_{\text{ZnEt}_2}/n_{\text{NdV}}$	Time min	Conversion %	\bar{M}_n g · mol ⁻¹	PDI	$p_{\text{exp.}}$	<i>cis</i> -1,4- content	Apparent first order rate constant k_a L mol ⁻¹ min ⁻¹
0	181	100	35450	2.63	7.6	94.5	84
5	245	100	31530	2.43	8.6	90.2	119
10	186	100	29780	2.15	9.3	88.6	120
30	219	100	26500	1.82	10.2	84.3	109

A quantitative analysis of the influence of the ratio of $n_{\text{ZnEt}_2}/n_{\text{NdV}}$ on the rate of polymerization is given in Table 1. The apparent first order rate constants k_a increase from $k_a = 84$ L · mol⁻¹ min⁻¹ to an average of 116 L · mol⁻¹ min⁻¹ upon addition of ZnEt₂. This increase of 38% is small in comparison to the increase of 116% caused by DIBAH and 2600% caused by TIBA upon molar variations of the amount of the aluminum alkyl cocatalyst in the same range (from $n_{\text{Al-Alkyl}}/n_{\text{NdV}} = 10$ to 30) (31).

The respective \bar{M}_n -conversion-plots are linear and show that the molar masses of BR decrease with increasing amounts of ZnEt₂. The linearity of these plots is not influenced by

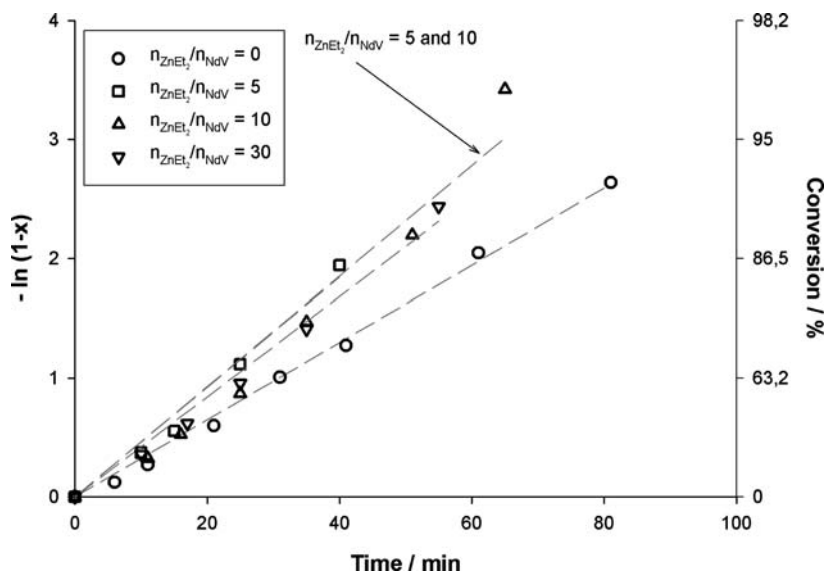


Figure 2. Plot of $-\ln(1-x)$ vs. polymerization time for the BD polymerization with the catalyst system NdV/DIBAH/EASC/ZnEt₂ at various molar ratios of $n_{\text{ZnEt}_2}/n_{\text{NdV}}$.

the amount of ZnEt_2 . It therefore can be concluded that ZnEt_2 has no negative impact on the living character of the polymerization (Figure 3). Thus, ZnEt_2 meets the requirements of an ideal molar mass control agent: on the one hand ZnEt_2 barely influences the speed of polymerization, and on the other hand, defined amounts of ZnEt_2 allow for the desired reduction of molar masses.

In order to quantify the molar mass control efficiency of ZnEt_2 , the data are further analyzed. For classical living polymerizations such as anionic polymerizations initiated by an initiator (I), the theoretical average degree of polymerization ($\text{DP}_{n,\text{theo.}}$) is calculated on the basis of Equation (1). In this equation, the molar ratio of monomer (M) and initiator (I) is given by n_M/n_I and x describes the degree of monomer conversion ($X = 0 \dots 1$).

$$\text{DP}_{n,\text{theo.}} = (n_M/n_I) \cdot X \quad (1)$$

In order to calculate $\text{DP}_{n,\text{theo.}}$ for polymerizations in which the number (p) of polymer chains generated per catalyst species (e.g. Nd) is different from 1, Equation (2) is applicable. In this consideration the full activity of every Nd species is assumed.

$$\text{DP}_{n,\text{theo.}} = p^{-1}(n_M/n_{\text{Nd}}) \cdot X \quad (2)$$

For complex catalyst systems, p usually is not known a priori. If the average degree of polymerization DP_n is determined experimentally ($\text{DP}_{n,\text{exp.}}$), p_{exp} can be calculated by Equation (3):

$$p_{\text{exp.}} = \text{DP}_{n,\text{theo.}}/\text{DP}_{n,\text{exp.}} \quad (3)$$

In this way, the formal number of BR chains ($p_{\text{exp.}}$) formed per Nd atom is calculated for complete monomer conversion. As depicted in Figure 4, $p_{\text{exp.}}$ increases with an increase of the $n_{\text{ZnEt}_2}/n_{\text{NdV}}$ -ratio. The application of 30 eq. of ZnEt_2 results in a 34% increase of $p_{\text{exp.}}$ compared to the reference experiment without ZnEt_2 . With the

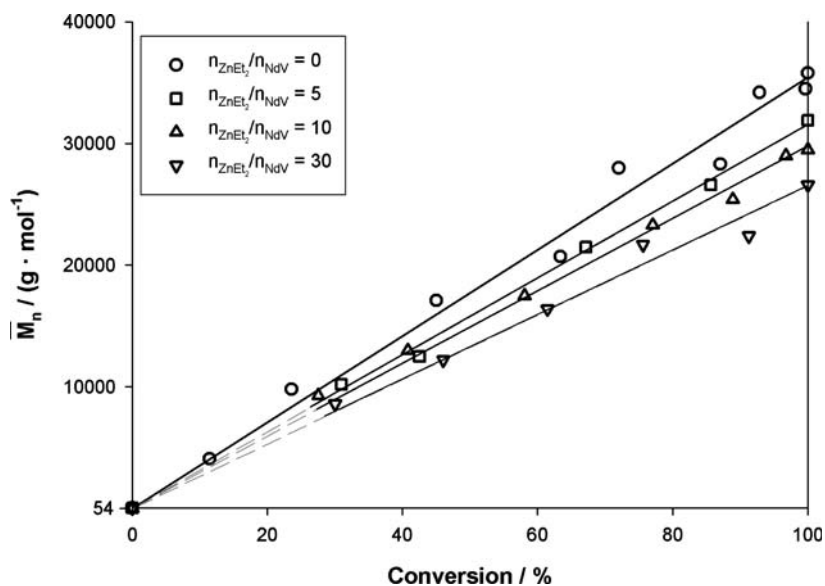


Figure 3. Plot of the number average molar mass \bar{M}_n vs. conversion for the BD polymerization with the system NdV/DIBAH/EASC/ ZnEt_2 at various molar ratios $n_{\text{ZnEt}_2}/n_{\text{NdV}}$.

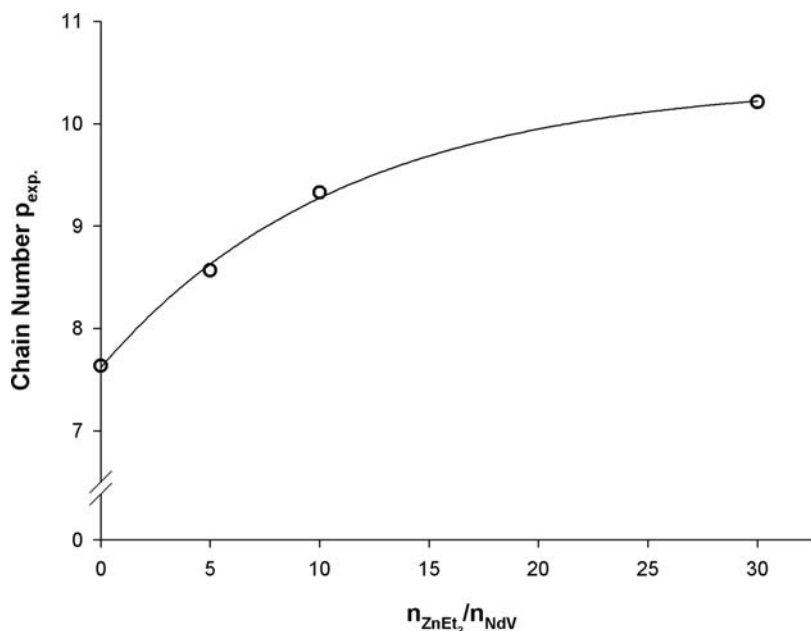


Figure 4. Plot of the formal chain number $p_{\text{exp.}}$ per Nd atom vs. the molar ratio $n_{\text{ZnEt}_2}/n_{\text{NdV}}$ for the BD polymerization with the catalyst system NdV/DIBAH/EASC/ZnEt₂.

addition of only 5 eq. of ZnEt₂, the chain number increases significantly from 7.6 (without ZnEt₂) to 8.6 (5 eq. ZnEt₂).

A comparison of the molar mass control efficiencies of ZnEt₂, and DIBAH and TIBA, which were reported elsewhere (31), allows for the establishment of the following ranking: DIBAH > ZnEt₂ > TIBA.

For the set of experiments in which $n_{\text{ZnEt}_2}/n_{\text{NdV}}$ was varied between 0, 5, 10 and 30, the molar mass distributions (MMD) obtained at complete monomer conversion are depicted in Figure 5. These four GPC-traces reveal that the molar mass control by ZnEt₂ can be attributed to two effects. On one hand, even small amounts of ZnEt₂ significantly reduce the high molar mass BR-fraction, which is usually formed at the very start of the polymerization (27) and on the other hand, the molar mass of the BR-fraction, which is attributed to the living species, is also reduced by ZnEt₂. Thus, the control of molar masses by ZnEt₂ has a fundamental impact on the whole distribution of molar masses. By the addition of ZnEt₂ the polydispersity index (PDI) decreases and the whole distribution is shifted towards lower molar masses. The elimination of the high-molar mass BR fraction results in a remarkable decrease of the PDI from 2.63 (without ZnEt₂) to 1.82 for the experiment in which 30 eq. of ZnEt₂ had been applied (Table 1).

A major disadvantage for the commercial use of molar mass control by ZnEt₂ is the reduction of the *cis*-1,4-content, which is accompanied by an increase of the *trans*-1,4-content. When no ZnEt₂ is applied, the *cis*-1,4-content is 94.5%. If 30 eq. of ZnEt₂ are used, the *cis*-1,4-content is lowered to 84.3%. ZnEt₂ has no impact on the *vinyl*-1,2-content, which remains constant at 0.5% for the entire range of $n_{\text{ZnEt}_2}/n_{\text{NdV}}$ -ratios studied.

In an earlier paper, we suggested a rapid and reversible exchange of the living poly (butadienyl) chains attached to Nd with the hydride or alkyl groups attached to Al. By

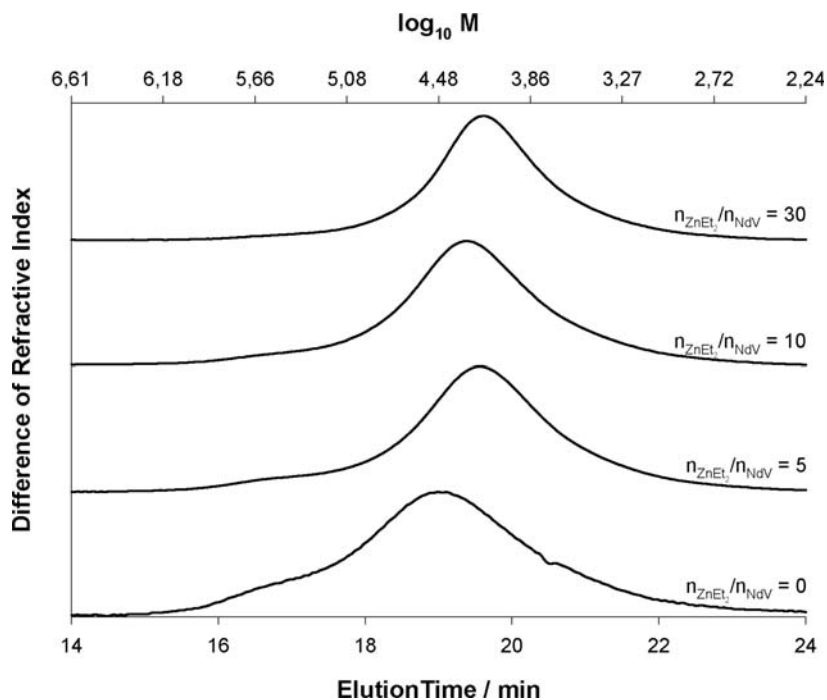
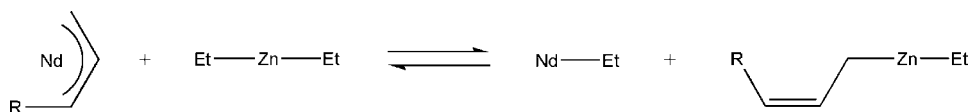


Figure 5. MMD of BR (monomer conversion = 100%) obtained by polymerization with the catalyst system NdV/DIBAH/EASC/ZnEt₂ at the molar ratios $n_{\text{ZnEt}_2}/n_{\text{NdV}} = 0, 5, 10, 30$. SEC with RI-detection.

means of this exchange reaction, we explained the reduction of the molar mass of the polymer fraction, which can be attributed to the living species (31). As the addition of ZnEt₂ to the catalyst system NdV/DIBAH/EASC has a comparable impact on the decrease of molar masses, a similar transfer reaction between Nd and Zn seems to be applicable. This transfer-reaction is outlined in Scheme 3.

Conclusions

In the ternary catalyst system NdV/DIBAH/EASC, the addition of ZnEt₂ allows for molar mass control. ZnEt₂ does not change the living nature of the polymerization and has limited impact on the rate of polymerization. The reduction in molar mass by ZnEt₂ is accomplished in two ways: by eliminating (or reducing to a large extent) the high molar mass fraction of BR, which is formed at an early stage of the polymerization,



Scheme 3. Molar mass control by ZnEt₂: Reversible transfer of poly(butadien)yl chains from neodymium to zinc by poly(butadien)yl-ethyl interchange. Ligand sphere and charge of neodymium are omitted for clarity.

and by reducing the molar mass of BR which is formed by the living species. Thus, the addition of ZnEt_2 not only reduces the molar masses but also leads to a reduction of the PDI. The only detrimental effect which can be attributed to ZnEt_2 is a reduction of the *cis*-1,4-content.

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