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Polymerization of 1,3-Butadiene Initiated by Neodymium Versatate/Triisobutylaluminum/Ethylaluminum Sesquichloride: Impact of the Alkylaluminum Cocatalyst Component

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ABSTRACT

The polymerization of 1,3-butadiene (BD) by the ternary Ziegler/Natta (Z/N) catalyst system neodymium versatate (NdV)/ethylaluminum sesquichloride (EASC)/aluminum alkyl is investigated. Special attention is paid to the impact of the aluminum alkyl on the polymerization kinetics and on the control of molar masses. In this respect diisobutyl aluminumhydride (DIBAH) and triisobutylaluminum (TIBA) are compared. Within a broad range of $n_{\text{Al-Alkyl}}/n_{\text{NdV}}$-ratios for both aluminum compounds the features of a living polymerization with a reversible exchange of the living polybutadienyl chains between neodymium (Nd) and aluminum are observed. The equilibrium position of this reaction is different for TIBA and DIBAH. At the same molar loadings DIBAH results in polybutadienes with molar masses which are 1/8 of those obtained in the presence of the cocatalyst TIBA. This difference is explained by a

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significantly more facile substitution of a hydride moiety from DIBAH than an isobutyl group from either DIBAH or TIBA by a living polybutadienyl chain.

Key Words: Aluminium alkyls; Butadiene polymerization; Living polymerization; Kinetics; Mechanism; Ziegler–Natta-polymerization.

INTRODUCTION

Among the different catalysts used for the industrial polymerization of conjugated dienes, neodymium (Nd) catalysts yield the highest *cis*-1,4-content.[1,2] By means of these catalysts polybutadiene [butadiene rubber (BR)] with a *cis*-1,4-content up to 98%[2] and polyisoprene [isoprene rubber (IR)] with a *cis*-1,4-content of 98.5%[3] are obtained. The high *cis*-1,4-content is important for the mechanical and dynamic properties of BR based vulcanizates which are used for the production of a variety of technical rubber goods and different tire parts. Various papers discuss the use of Nd-catalysts for the homopolymerization of dienes,[4,5] the copolymerization of dienes,[6] the copolymerization of dienes with olefins such as butadiene/styrene,[7,8] and butadiene/ethylene.[9] In these papers, the high activity of Nd catalysts is demonstrated. On the other hand, various Nd catalysts are able to homopolymerize butadiene in the presence of styrene monomer.[10] In addition supported Nd catalysts are reported in the scientific as well as in the patent literature.[11–14] These catalysts are used for the gas phase polymerization of dienes.[13,14] Furthermore, Nd based catalysts are used for the homopolymerization of cyclic monomers such as caprolactone.[15] We recently used a Nd catalyst for the preparation of a poly(ε-caprolactone)/*cis*-1,4-poly(butadiene) (PCL/BR) block copolymer.[16]

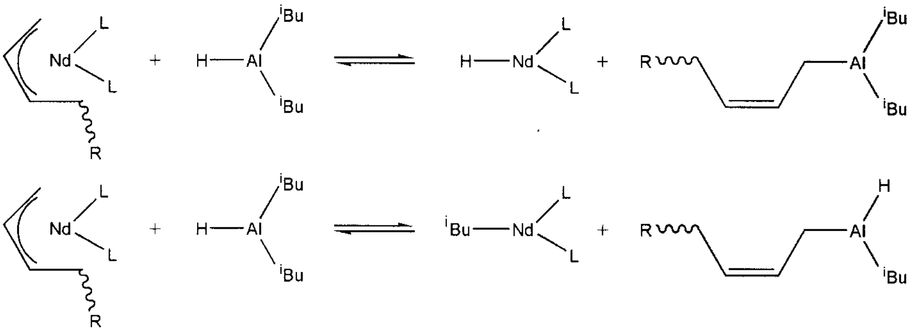
Apart from the above mentioned beneficial features of Nd-catalysis only very little is known about the chemical role of the different catalyst components involved[4] and about the nature of the active catalyst species.[17,18] Recently, we reported on the impact of the aluminum compound DIBAH in the ternary Ziegler/Natta (Z/N)-catalyst system neodymium versatate (NdV)/diisobutylaluminum hydride (DIBAH)/ethylaluminum sesquichloride (EASC) on the polymerization of 1,3-butadiene (BD).[5] Our investigations led to the proposal of a reaction mechanism which accounts for the control of molar masses by the reversible transfer of living polydienyl chains from Nd on to the alkylaluminum component DIBAH (Sch. 1).

We found that only one third of DIBAH is involved in the control of molar masses. A possible explanation for this surprising result is the aggregation of DIBAH which reportedly forms trimers.[19] In order to clarify which of the two proposed chain transfer reactions is relevant (Sch. 1) it was of interest to comparatively study the impact of triisobutylaluminum (TIBA) and DIBAH on the regulation of molar masses. From this study, information about the influence of the substitution pattern of the aluminum alkyl component is expected.

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. Reversible transfer of living polymer chains from Nd to Al. L = ligand.

coulometry). Butadiene was obtained from a production plant of Bayer AG, Leverkusen, Germany, and was freed from stabilizer by consecutively passing it through two columns. The first column contained basic aluminum oxide and the second column contained molecular sieves (4 Å). Neodymium versatate was obtained in hexane solution from Rhodia and was used as received. The TIBA, DIBAH (both 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*-butylphenole) (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 in methanol (containing BKF-stabilizer), the coagulated polymer was isolated and dried at 65°C in vacuum. 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 the characterization by SEC, which was calibrated by 1,4-polybutadiene standards ($\bar{M}_w/\bar{M}_n \leq 1.02$) from Fluka. The 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}.

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 Ref.[20]. 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. Then, the different catalyst components were quickly added in the following sequence: NdV (0.25 M hexane solution), TIBA or DIBAH (1.0 M in hexane fraction), and finally the polymerization was started by the addition of EASC (0.91 M toluene solution). For the determination of the monomer conversion samples were taken at appropriate intervals. At the end of the reaction the polymerization was shortstopped by cooling the reaction mixture down 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 DISCUSSION

In the ternary Z/N-catalyst system comprising NdV/EASC and either DIBAH or TIBA the amount of the aluminum compound TIBA or DIBAH was varied at molar ratios ranging from $n_{\text{Al-Alkyl}}/n_{\text{NdV}} = 10$ to 50. In these variations the molar ratio of $n_{\text{Cl}}/n_{\text{NdV}} = 3/1$ was kept constant. The variations performed and the most relevant results are listed in Table 1.

Time–conversion plots for the set of polymerizations in which the molar ratio of $n_{\text{TIBA}}/n_{\text{NdV}}$ is varied between 10 and 50 are given in Fig. 1. These plots show that the polymerization of BD goes to full conversion for $n_{\text{TIBA}}/n_{\text{NdV}} = 20$–50 and that the conversion of BD is not complete for the lowest amount of TIBA applied ($n_{\text{TIBA}}/n_{\text{NdV}} = 10$). There is an increase in the polymerization rate with increasing amounts of TIBA as can be seen in Fig. 1, as well as in the respective rate constants given in Table 1 and Fig. 3.

Table 1. Polymerization of BD initiated by NdV/DIBAH/EASC and NdV/TIBA/EASC in *n*-hexane at 60°C.

Alum. alkyl	$n_{\text{Al-Alkyl}}/n_{\text{NdV}}$	$[\text{Al-Alkyl}]_0$ (mmol L^{-1})	t (min)	Conversion (%)	$\bar{M}_n$ (g mol^{-1})	App. first-order rate const. k_a (calc. from conv.-t-curves) (L mol^{-1} min^{-1})
DIBAH	10	3.8	123	100	93,700	98
DIBAH	30	11.4	115	100	21,800	212
DIBAH	50	19.0	90	100	15,100	141
TIBA	10	3.8	160	32	254,000	7
TIBA	20	7.6	120	100	209,900	58
TIBA	30	11.4	120	100	174,200	189
TIBA	50	19.0	120	100	116,800	311

Note: (Vessel: 1 L Büchi-BEP-280 autoclave, $V_{\text{Hex}} = 0.44$ L; $[\text{NdV}]_0 = 0.38$ mmol L^{-1}; $[\text{M}]_0 = 1.90$ mol L^{-1}; $[\text{EASC}]_0 = 0.38$ mmol L^{-1}; $n_{\text{Cl}}/n_{\text{NdV}} = 3$; $T = 60$°C). The calculation of the apparent first-order rate constant k_a is based on the kinetic law $-d[\text{M}]/dt = k_a \cdot [\text{NdV}] \cdot [\text{M}]$ and on the corresponding plots $\ln(1 - x) = f(t)$ (x = degree of monomer conversion).

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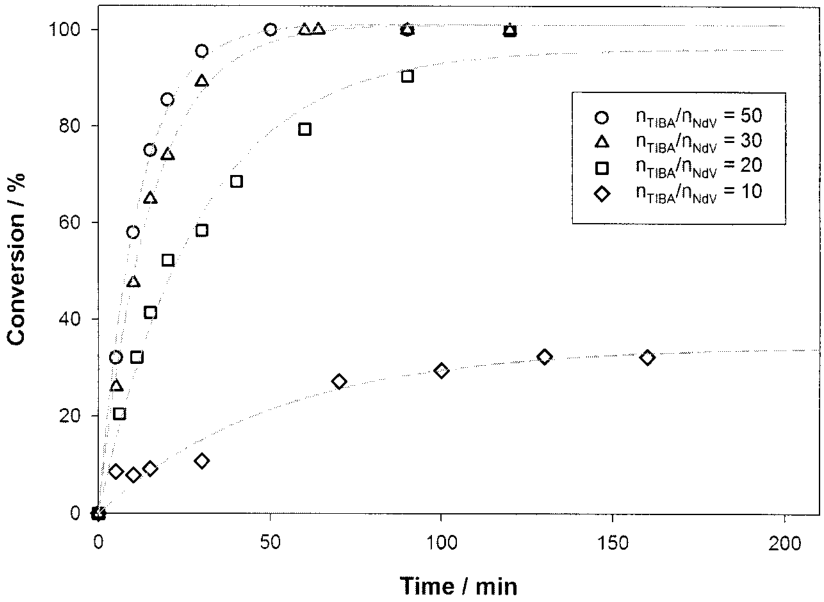


Figure 1. Monomer conversion as a function of time for different ratios of $n_{TIBA}/n_{NdV} = 10$, 20, 30, and 50. Reaction: see Table 1.

The decrease of the monomer concentration during the course of the polymerization can be described by first order kinetics (Fig. 2). These plots reveal, that there is no induction period if TIBA is used as a cocatalyst.

For the experiments, in which the aluminum compound DIBAH was applied the time–conversion curves and the first order plots are not given. For these polymerizations some of the respective first order plots do not pass through the origin. Results which confirm these observations with the cocatalyst DIBAH were reported earlier.[5] Contrary to the TIBA mediated polymerizations the polymerizations performed in the presence of DIBAH go to full BD conversion for the whole range of $n_{DIBAH}/n_{NdV} = 10–50$.

The dependence of the apparent first order rate constants k_a on the ratio of n_{DIBAH}/n_{NdV} exhibits an optimum as shown in Fig. 3. A remarkable difference between TIBA and DIBAH is observed at low ratios of $n_{Al\text{-}Alkyl}/n_{NdV} = 10$. For this ratio, the DIBAH mediated polymerization goes to complete monomer conversion, whereas TIBA activation results in a low final monomer conversion of 32%. Another significant difference between the cocatalysts DIBAH and TIBA is demonstrated by the dependence of the apparent first order rate constants k_a on the ratio $n_{Al\text{-}Alkyl}/n_{NdV}$ as depicted in Fig. 3. As can be seen in this figure, TIBA activation results in a S-shaped curve with a k_a maximum of 311 L mol^{-1} min^{-1} at $n_{Al\text{-}Alkyl}/n_{NdV} = 50$. Contrary to this dependence, the use of DIBAH activation results in a curve with an optimum of $k_a \approx 220$ L mol^{-1}min^{-1} at $n_{Al\text{-}Alkyl}/n_{NdV} = 35$. For these different dependencies of k_a on the amount of the aluminum alkyl applied no straightforward explanation can be given.

On the other hand, Fig. 3 indicates that the number of active sites present during the polymerization depends on the nature of the aluminum alkyl, as well as on the ratio of $n_{Al\text{-}Alkyl}/n_{NdV}$. This plot can also be interpreted in terms of an activating effect of the

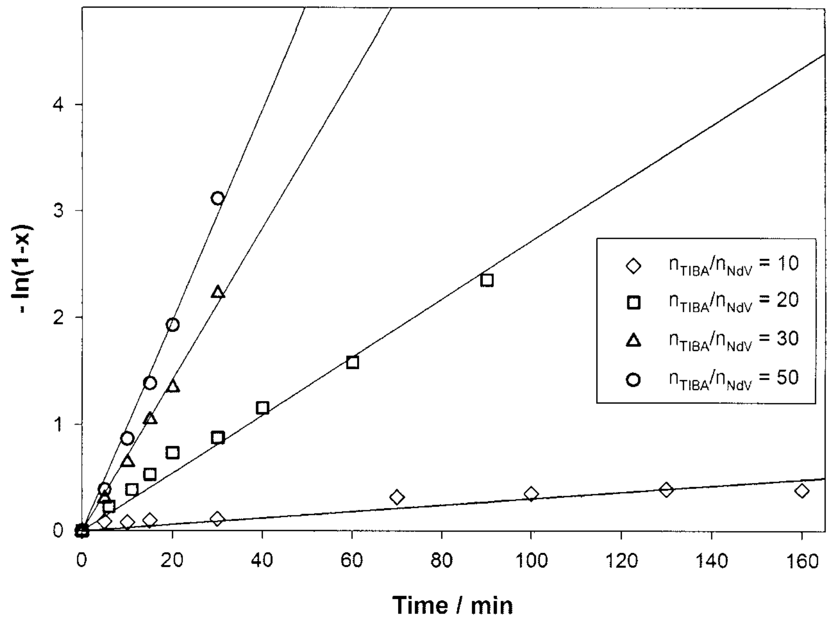


Figure 2. Dependence of $-\ln(1-x)$ on polymerization time for different ratios of $n_{\mathrm{TIBA}}/n_{\mathrm{NdV}} = 20$, 30, and 50. $x =$ Degree of conversion. Reaction: see Table 1.

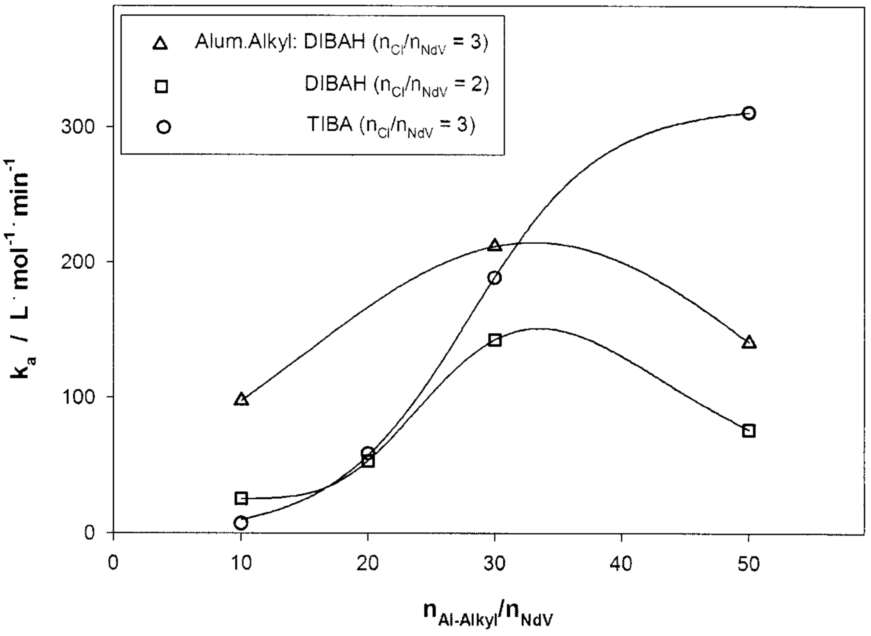


Figure 3. Dependence of the apparent rate constant k_a on the ratio $n_{\mathrm{Al\text{-}Alkyl}}/n_{\mathrm{NdV}}$. Reaction: see Table 1 and Ref.[5].

aluminum alkyl on Nd. It might be speculated that the aluminum cocatalyst has an activating effect by either increasing the concentration of active Nd or by increasing the number of active sites per Nd.

In Fig. 3, results from an earlier study are included.[5] This study was performed at a ratio of $n_{\mathrm{Cl}}/n_{\mathrm{NdV}} = 2$ and the cocatalyst DIBAH was used. Water and an excess of versatic acid were removed from NdV by drying the commercial hexane solution of NdV in hexane in vacuum at 160°C prior to use.[5] As shown in Fig. 3, the experimental conditions applied in the earlier study result in a lower activity of the catalyst system. This lower activity might be caused by either the lower chlorine content ($n_{\mathrm{Cl}}/n_{\mathrm{NdV}} = 2$) or by the lower level of water and free versatic acid. It is interesting to note that these variables just affect the magnitude of k_a but not the shape of the curve.

In Fig. 4, the dependence of $\bar{M}_n$ on conversion is given for the experiments with the cocatalyst TIBA. For the three molar ratios of $n_{\mathrm{TIBA}}/n_{\mathrm{NdV}} = 20, 30, 50$ straight lines are obtained. Together with the linear plots of $-\ln(1 - x)$ vs. time (Fig. 4) this is a strong indication for the living character of the polymerization.[21] A straight line, however, was not obtained for the lowest molar ratio of $n_{\mathrm{TIBA}}/n_{\mathrm{NdV}} = 10$. Therefore, these data were not used in the further consideration.

In Fig. 4, intercepts on the y-axis are found, which increase with decreasing ratios of $n_{\mathrm{TIBA}}/n_{\mathrm{NdV}}$. These intercepts can be explained by the occurrence of an initial polymerization at the very start of the reaction, prior to the first sample being taken from the polymerization reactor (<5 min). This initial polymerization results in a BR fraction with a very high molecular weight, which does not further increase during the course of the polymerization. As the relative amount of this polymer fraction decreases with

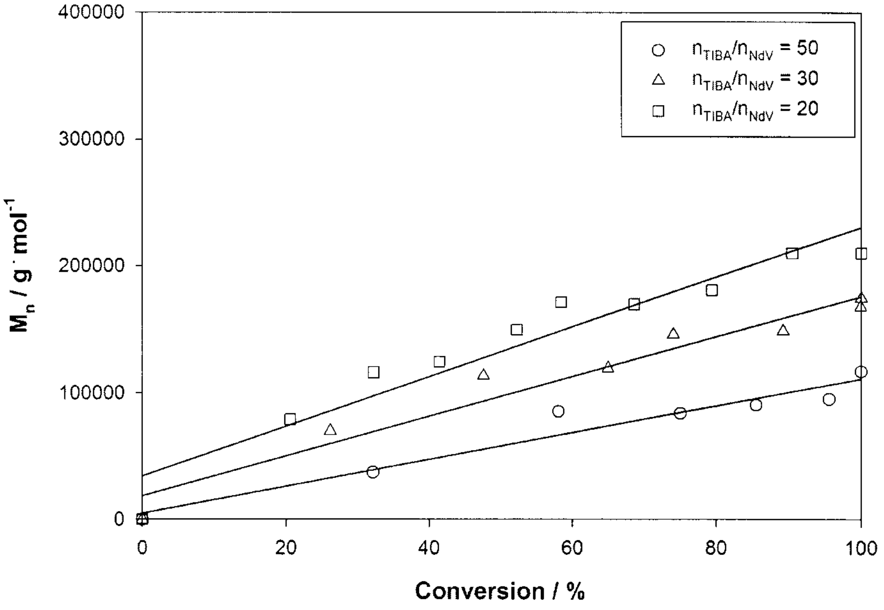


Figure 4. Evolution of the molar masses of BR with conversion for $n_{\mathrm{TIBA}}/n_{\mathrm{NdV}} = 20$, 30, and 50. Reaction: see caption of Fig. 1.

increasing monomer conversion, the molar mass distribution narrows during the course of the polymerization. At full monomer conversion the high molar mass fraction is still detectable. As shown in Fig. 5, the relative proportions of the high molecular weight fractions at 100% monomer conversion decrease with an increasing ratio of $n_{\mathrm{TIBA}}/n_{\mathrm{NdV}}$.

The formal number (p) of BR chains formed per Nd atom is calculated by the application of Eq. (1). The $\bar{M}_{\mathrm{n}}$ at 100% monomer conversion are listed in Table 1.

$$p = \frac{[\mathrm{BD}]_0/[\mathrm{NdV}]_0 M_{\mathrm{BD}}}{\bar{M}_{\mathrm{n}}} \tag{1}$$

where M_{BD} is the molar mass of BD and $\bar{M}_{\mathrm{n}}$ is the experimental $\bar{M}_{\mathrm{n}}$ at 100% conversion.

In Fig. 6, the formal number of chains formed per Nd atom are plotted over the molar ratio of $n_{\text{Al-Alkyl}}/n_{\mathrm{NdV}}$. In this plot, it is assumed that the total amount of Nd used is active.

From Fig. 6, it is apparent that the formal number of polymer chains formed per Nd atom is significantly lower for TIBA than for DIBAH. Therefore, TIBA is less efficient in the control of molar masses than DIBAH. By the ratio of the two slopes, the relative efficiencies of DIBAH and TIBA in the control of molar masses can be quantified and an eight-fold efficiency of DIBAH over TIBA is obtained.

If we consider the slope = 0.05 as molar mass regulation efficiency for the three isobutyl groups, present in TIBA, we can calculate the formal efficiency for one isobutyl group of TIBA ($0.05/3 = 0.017$). Assuming that this value can be applied on each of DIBAHs two isobutyl groups the molar mass regulation efficiency of the hydride group of

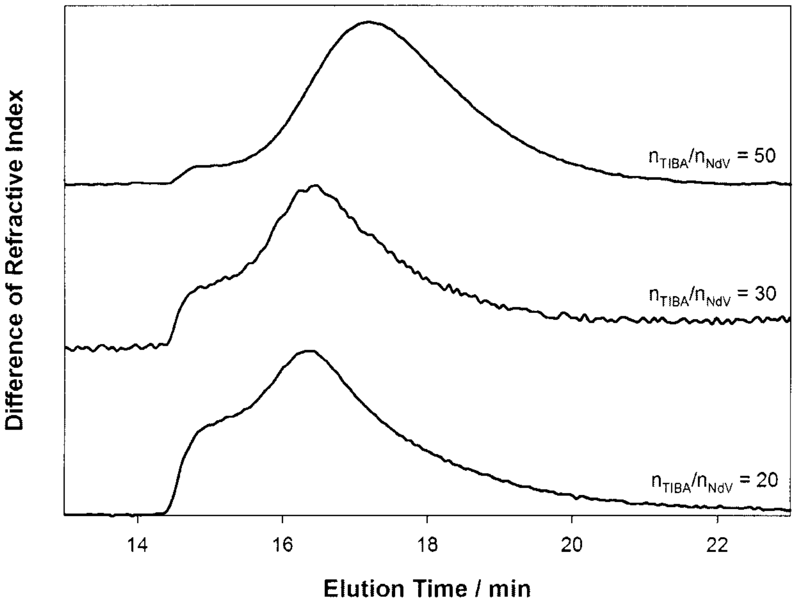


Figure 5. Molar mass distributions of BR (100% monomer conversion) obtained at different $n_{\mathrm{TIBA}}/n_{\mathrm{NdV}}$ with the catalyst NdV/TIBA/EASC. Elugrams obtained by SEC (RI detection). Reaction: see Table 1.

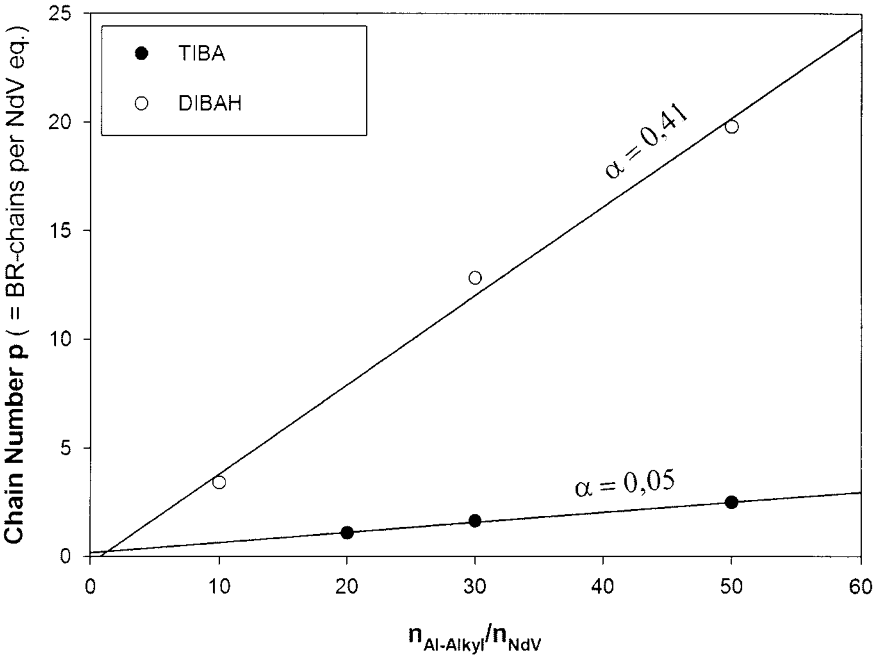
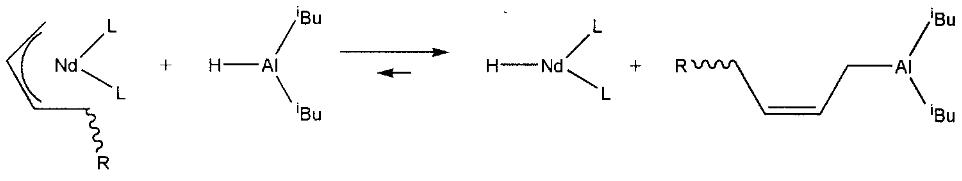


Figure 6. Dependence of the number (p) of chains per Nd on the molar ratio $n_{\text{Al-Alkyl}}/n_{\text{NdV}}$ for the aluminum alkyls TIBA and DIBAH. Reactions: see Table 1.

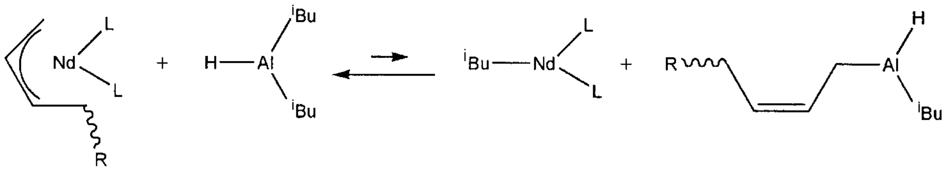
DIBAH can be calculated. It is 0.38 (0.41 − 0.017 − 0.017 = 0.38). If this consideration holds true even for the chemically different isobutyl groups of DIBAH and TIBA this calculation gives the probability for one hydride group to be substituted by a living polybutadienyl chain. The substitution probability is about twenty two-fold greater for a hydride moiety than for one single isobutyl group (0.38/0.017 = 22).

For the regulation of molar masses by the aluminum compounds TIBA and DIBAH a reversible exchange of polybutadienyl ↔ isobutyl/hydride is proposed as depicted in Sch. 1. The differences between TIBA and DIBAH in the respective reaction rates and in the equilibrium positions are schematically given in the Schs. 2 and 3.

As described in the schemes depicted below, the hydride group in DIBAH and the isobutyl group in TIBA have substantially different activities in the substitution of the living polybutadienyl chains. It is not yet clarified if the substitution of the isobutyl groups occurs in a direct way as depicted in the above schemes, or whether this substitution occurs



Scheme 2. Molar mass control with DIBAH.



Scheme 3. Molar mass control with TIBA.

in an indirect way, in which an Al–H species is formed by the β-elimination of isobutylene prior to the substitution by a living polybutadienyl chain.

CONCLUSION

The difference between TIBA and DIBAH as molar mass control agents is significant. The DIBAH is eight times more effective in molar mass control than TIBA and one hydride moiety exhibits an approximately twenty two-fold higher activity than one isobutyl group. This huge difference reflects the great importance of the Al–H moiety in the molar mass regulation process. From this result, it may be concluded that AlH_3 or $LiAlH_4$ are more efficient in molar mass regulation than DIBAH or TIBA. The Nd catalyzed polymerizations of butadiene are usually carried out in nonpolar hydrocarbons such as hexane or cyclohexane. The solubility of the different catalyst components, as well as of the molar mass regulators in these solvents is an important issue especially as inhomogeneities in the reaction mixture are often considered to be the primary cause of gel formation and of reactor fouling. As $LiAlH_4$ has poor solubility in these non polar solvents it is not suitable in this respect. AlH_3 is expected to have increased solubility in nonpolar solvents over the ionic compound $LiAlH_4$. Unfortunately, AlH_3 is only soluble in hexane if small amounts of ethers are present.[22] As polar additives, such as ethers are expected to have a detrimental effect on the Nd catalyzed polymerization, AlH_3 is not considered to be a useful molar mass control agent, either. Therefore, the technical use of either AlH_3 or $LiAlH_4$ as control agents in the Nd catalyzed polymerization of dienes is questionable.

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