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Comparison of the Solvents *n*-Hexane, *tert*-Butyl Benzene and Toluene in the Polymerization of 1,3-Butadiene with the Ziegler Catalyst System Neodymium Versatate/Diisobutylaluminum Hydride/Ethylaluminum Sesquichloride

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The influence of the solvents n-hexane, tert-butyl benzene (TBB) and toluene on the Nd-catalyzed polymerization of butadiene was studied. Special emphasis was placed on polymerization kinetics and on the evolution of molar masses and molar mass distributions with monomer conversion. Distinct differences were found between the three solvents. From the polymerization kinetics there is evidence which supports Porri's view on the competitive coordination between aromatic solvents and butadiene to active Nd-sites. In addition, there are indications for the irreversible transfer of benzyl-H-atoms from toluene to active allyl-anionic polymer chains. The evolution of molar mass distributions with monomer conversion provides evidence for the existence of two active catalyst species which are present in all three solvents. One of these two species is highly reactive ("hot") and short-lived. This species generates BR with high molar mass. The second species has a low reactivity and lives throughout the entire course of the polymerization. In n-hexane the "hot", short-lived species is present only at the start of the polymerization, whereas in TBB and toluene, the short-lived species becomes evident at monomer conversion $>10\%$ and is constantly (re)generated. Cis-1,4-contents determined at final monomer conversion are not in line with other available studies in this field.

Keywords neodymium, diene polymerization, ziegler catalysis, polybutadiene, rubber, solvents

Introduction

Since the fundamental patent on the polymerization of dienes by lanthanide based catalyst systems was filed by Union Carbide Corporation in 1964 (1) the large scale production of

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poly(*cis*-1,4-butadiene) (butadiene rubber = BR) by neodymium (Nd) Ziegler catalysis has become an industrially established technology. In the basic patent, UCC describes the use of a binary catalyst system. Presently, highly active ternary catalyst systems are used. These catalyst systems are based on a Nd precursor, an aluminum alkyl compound and a halide donor. Commonly used Nd-components are neodymium alcoholates (2–4), neodymium carboxylates such as Nd versatate (NdV) (5) and neodymium phosphates (6–8). Well established aluminum alkyls comprise triethyl aluminium (TEA), triisobutyl aluminium (TIBA) and diisobutylaluminum hydride (DIBAH). Commonly used halide donors are ^{t}butyl chloride, (^{t}BuCl), diethyl aluminium chloride (DEAC) and ethylaluminum sesquichloride (EASC). Nd-based catalyst systems yield poly(butadiene) (i.e., butadiene rubber = BR) and poly(isoprene) (i.e., isoprene rubber = IR) with a very high *cis*-1,4-content (*cis*-1,4-content $\geq$98%) (9, 10). As opposed to BR with a lower *cis*-1,4-content (*e.g.* Li-BR: *cis*-content = 40%, Ti-BR 93%, Co-BR 96% and Ni-BR 97%) (10, 11) rubber articles made from high-*cis*-Nd-BR exhibit remarkably low glass transition temperatures (T_g) and perform extremely well at low service temperatures, as well as at high frequencies. In addition, these articles show high resilience, good abrasion resistance and a low heat-build-up upon dynamic stress. Due to the high *cis*-1,4-content the unvulcanized (raw) Nd-BR rubbers, as well as the respective vulcanizates, exhibit strain induced crystallization which results in superior tensile strength properties and excellent dynamic performance (12–14). These properties render Nd-BR vulcanizates very attractive for special tire parts such as treads, side walls, sub treads and carcasses, as well as for various rubber articles such as conveyor belts and golf ball cores.

The solution polymerization of dienes mediated by Nd Ziegler catalyst systems is usually carried out in hydrocarbon solvents. Hexane, cyclohexane and pentane are the most commonly used solvents. The advantages of aliphatic solvents over aromatic solvents are in lower price and lower toxicity. Aliphatic solvents are also superior in the final steps of the industrial process. These process steps comprise the removal of the solvent from the polymer (solvent-stripping and polymer separation), as well as the recycling of solvents (purification and drying prior to reuse) (15). In contrast to aromatic solvents, aliphatic and cycloaliphatic solvents are considered to be inert (9). The use of aromatic solvents results in reduced catalyst activities as already reported in 1969 by Throckmorton (16). Another common finding of various studies on the influence of solvents is the decrease of *cis*-1,4-contents by the use of aromatic solvents, e.g. (17, 18). In addition to aliphatic and aromatic hydrocarbons, chlorinated aliphatic hydrocarbons and ethers were also tested in Nd catalyzed diene polymerizations. Chlorinated aliphatic hydrocarbons strongly decrease catalyst activity and often yield insoluble polymer gel (19). Ethers such as THF are catalyst poisons.

A series of comparative studies are available in which Nd based catalyst systems were tested in various solvents. Hsieh et al. studied the influence of cyclohexane, *n*-hexane, *n*-pentane, chlorinated arenes, toluene, 1-hexane, tetrachloroethylene and styrene in diene polymerization with the binary system $NdX_3 \cdot n\,D/AlR_3$ (20). Duvakina et al. investigated the influence of chlorobenzene, toluene and cyclohexane on the *trans*-1,4-content. In this study, the binary *trans*-1,4-specific catalyst system $NdCl_3$ TBP/$Mg(^nC_4H_9)(^iC_8H_{17})$ was used (21). For binary $Nd(O^iPr)_3$ containing catalyst systems, the influence of the solvents heptane, cyclohexane, toluene, dichloromethane was investigated by Dong et al. (22, 23). Information about the influence of solvents on ternary Nd systems are available for $Nd(N(SiMe_3)_2)_3$/TIBA/DEAC (17, 18), NdV/DIBAH/^{t}BuCl (24), $Nd(O^iPr)_3/[HNMe_2Ph]^+[B(C_6F_5)_4]^-$/TIBA (25) and NdV/methyl alumoxane (MAO)/^{t}BuCl (19).

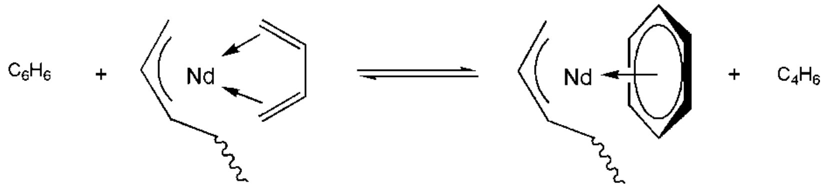
One of the most detailed studies on the influence of solvents is available from Porri et al. (26, 27). In these studies, the Nd carboxylate based system Nd(isooctanoate)$_3$/TIBA/DEAC was used. Regarding catalyst activities, Porri et al. gives the following ranking of the solvents studied: *cis*-butene > 1-pentene > heptane > heptane (+3% toluene) > toluene > mesitylene > toluene (+7% hexamethylbenzene). The reduction of polymerization rates by aromatic solvents or by the presence of small amounts of aromatic compounds is explained by competitive coordination of monomer and arenes to vacant Nd-sites. This view is supported by the fact that η^6-toluene complexes of Nd could be isolated and characterized. In addition, η^6-toluene complexes were successfully used for the initiation of diene polymerizations (28). Porri et al. put forward a scheme for the coordination equilibrium of arenes and dienes to active Nd–centers (Scheme 1) (26, 27).

In Scheme 1, the Nd-center to which a diene is coordinated is active in polymerization, whereas the Nd-center to which an arene is coordinated is inactive. According to the authors, the decrease of catalyst activities from toluene > mesitylene > toluene (+7% hexamethylbenzene) correlates with the electron richness (i.e., Lewis basicity) of the aromatic compounds. With increasing Lewis basicity of the aromatic compounds, the equilibrium is shifted to the Nd-benzyl-species and the concentration of active catalyst species is decreased. As a consequence of this equilibrium, reaction rates decrease and molar masses increase with increasing Lewis basicity of the aromatic compound. According to Scheme 1 complete poisoning of the active catalyst will only occur with highly electron rich arenes.

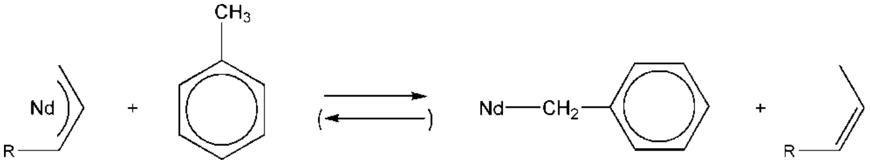
The conceivable transfer reaction of benzyl-H-protons from toluene, mesitylene and hexamethylbenzene by allyl-anionic polybutadienyl chains was not considered by Porri et al. (Scheme 2).

If the transfer reaction given in Scheme 2 is fully reversible and if Nd-benzyl is an active species the result to be observed would be molar mass reduction with a negative impact on catalyst activity. Irreversible transfer, according to Scheme 2 would result in the termination of the living poly(butadienyl) chains. The Nd benzyl derivative which is formed according to Scheme 2 most probably rapidly decomposes at polymerization temperatures ~60°C as Nd(benzyl)$_3$ is reported to be stable only below −15°C (29). As a consequence of the low thermal stability of the Nd benzyl species proton transfer from solvents such as toluene is most likely irreversible. Therefore, this transfer reaction will result in the reduction of active catalyst sites, the reduction of reaction rates and a considerable increase of molar mass.

In order to elucidate the issue of chain termination by benzyl-H-protons we designed a study in which the influence of the three solvents *n*-hexane, *tert*-butyl benzene (TBB) and toluene on polymerization kinetics and on the evolution of molar mass as well as on molar mass distributions are compared. As inert reference solvent *n*-hexane was chosen. TBB



Scheme 1. Competitive coordination of dienes and arenes to active Nd-centers according to Porri et al. (26, 27).



Scheme 2. Transfer of a benzyl-H-atom from toluene (solvent) to the allyl-end of the poly(butadien)yl chain (R = poly(butadien)yl) resulting in chain termination (ligands and charge of Nd are omitted for clarity).

was selected as highly nucleophilic aromatic π-donor. Toluene was selected as an aromatic solvent which comprises π-donating properties as well as benzyl-H-protons.

Experimental

Materials

Toluene, *n*-hexane and *tert*-butyl benzene (TBB) were distilled and stored over molecular sieves (4 Å). Prior to use, the residual water content of the solvents was determined by Karl Fischer titration monitored by coulometry: *n*-hexane: 4 ppm, toluene: 15 ppm, TBB: 35 ppm. Butadiene (BD) was obtained from a Bayer AG production plant. BD was freed from the stabilizer and residual water by passing it through two columns filled with basic aluminum oxide and 4 Å molecular sieves. Neodymium versatate (NdV) was obtained in hexane solution from Rhodia and was used as received. Toluene and TBB were purchased from Aldrich. 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.

Molar Masses

Molar mass determinations were performed 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 the characterization by SEC. SEC was calibrated by 1,4-polybutadiene standards ($M_w/M_n \leq 1.02$) from *FLUKA*. SEC was operated with pumps supplied by Waters (type: Waters 510) and Ultra styragel®-columns with pore sizes 500, 1000, 10000 and 100000 Å. The signals were monitored by a refractive index detector (Waters 410). The flow rate was $1\,mL \cdot min^{-1}$.

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 short stopped with methanol/BKF and after residual BD and solvent had been removed by vacuum drying at 65°C.

Polymerization Experiments

Polymerizations were carried out in a 1 L autoclave (*Büchi BEP 280*). In all cases, a syringe/septum technique was used which was described in detail in the references (30). The inert gas (argon) was purified by passing it through two columns. Residual oxygen was removed by the first column loaded with a copper oxide BTS-catalyst purchased from Fluka. Water was eliminated in the second column which contained molecular sieves (4 Å). For the polymerization experiments, 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 order: NdV, DIBAH and EASC. Polymerizations were short stopped by cooling to ambient temperature and quenching with methanol. Finally, the reaction mixture was poured into 500 mL of methanol containing a 0.2 wt% BKF-stabilizer. The coagulated polymer was isolated and dried at 65°C *in vacuo*.

Results and Discussions

For the evaluation of the influence of the three solvents on the polymerization of butadiene the Nd-based catalyst system NdV/DIBAH/EASC was used. This catalyst system was previously used in a series of studies in which various aspects of the Nd-catalyzed polymerization of butadiene were investigated (31–35). It is worth mentioning that in the present study the sequence of addition of the catalyst components was: 1) NdV, 2) DIBAH and 3) EASC. As in the previous studies, catalyst components were directly added to the solution of butadiene without prior catalyst preformation or catalyst aging.

Three sets of experiments were performed in order to study comparatively the influence of the solvents *n*-hexane, *tert*-butyl benzene (TBB) and toluene. The major results of the three experimental series performed are summarized in Table 1.

Catalyst Activities

The conversion-time plots for the polymerizations reveal that polymerization rates decrease in the order: *n*-hexane > TBB > toluene (Figure 1). In *n*-hexane monomer conversion is quantitative after 2 h, whereas in TBB and in toluene, monomer conversion is not complete even after 21 h (TBB: 95%, toluene: 69%).

The conversion time-plots of Figure 1 are transferred into first-order plots (-ln(1-x) vs. time) which are given in Figure 2. A linear dependence is only obtained for the polymerization in *n*-hexane. The respective first-order plots for the polymerizations of butadiene in TBB and in toluene are curved. The deviation from the respective straight lines is more pronounced for toluene than for TBB. On the basis of this evidence only the polymerization in *n*-hexane is in compliance with the first order requirement for a living polymerization (36, 37). Due to the deviations from the first order dependencies the polymerizations in TBB and in toluene do not comply with this requirement. On the basis of the arguments given by Penczek et al. it can be concluded that irreversible

Table 1

Polymerization of BD with the catalyst system NdV/DIBAH/EASC in the solvents *n*-hexane, *tert*-butyl benzene (TBB) and toluene. Reaction conditions: Büchi-BEP-280-autoklave; $V_{solvent} = 0.43$ L; $n_{Cl}/n_{NdV} = 3$; $n_{DIBAH}/n_{NdV} = 20$; $[NdV]_0 = 0.39$ mmol L^{-1}; $[DIBAH]_0 = 7.8$ mmol $^{-1}$; $[EASC]_0 = 0.39$ mmol $\cdot$ L^{-1}; $[M]_0 = 1.94$ mol L^{-1}, T = 60°C

Solvent	Time (min)	Conversion (%)	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	*cis*-1,4-content	TOF (h^{-1})
n-hexane	120	100	32220	93000	3.1	94.0	937000
TBB	1255	95	48900	147000	3.0	98.0	265800
Toluene	1255	69	30700	131100	4.3	96.0	175000

chain termination reactions occur in toluene and in TBB. These transfer reactions are more pronounced in toluene than in TBB.

In order to quantitatively compare catalyst activities in *n*-hexane, TBB and toluene catalyst turnover frequencies (TOF) (see Table 1) were calculated from the time-conversion plots given in Figure 1 (34). The following order of TOF values was determined: 937000 h^{-1} (*n*-hexane) > 265800 h^{-1} (TBB) > 175000 h^{-1} (toluene). From the ratios of TOF-values the relative apparent concentrations of active species can be estimated: 1 (*n*-hexane) > 0.28 (TBB) > 0.19 (toluene). The reduction of active Nd-sites in TBB and in toluene can be qualitatively explained on the basis of competitive coordination between butadiene and aromatic solvents to active Nd-centers (Scheme 1). As TBB and toluene have a similar Lewis basicity, the lower polymerization activity in toluene is a hint to an additional reduction of active sites by irreversible chain termination.

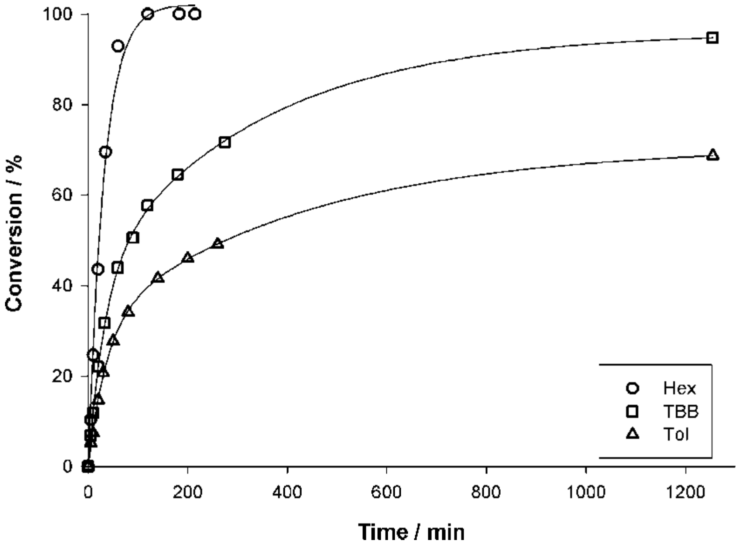


Figure 1. Time-conversion plots for the BD polymerization with the catalyst system NdV/DIBAH/EASC in the solvents *n*-hexane (Hex), *tert*-butyl benzene (TBB) and toluene (Tol).

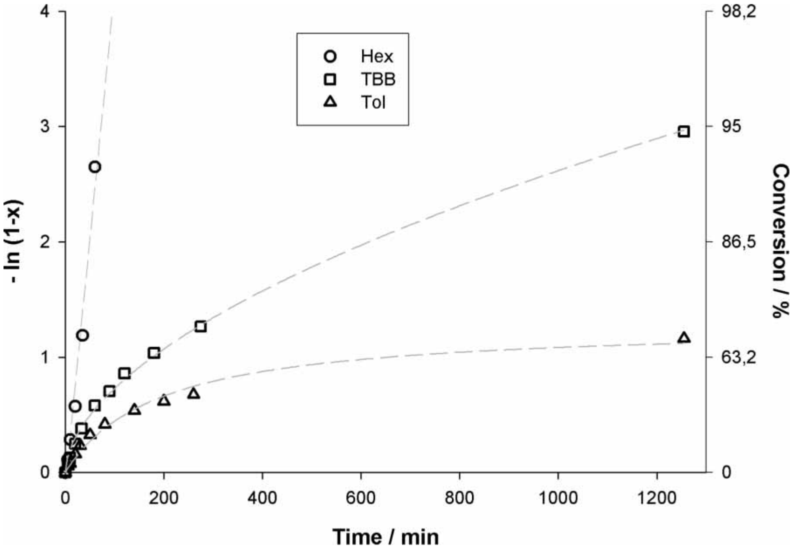


Figure 2. Plot of −ln(1-x) vs. polymerization time (based on conversion time curves in Figure 1) for BD polymerization with the catalyst system NdV/DIBAH/EASC in different solvents.

As benzyl-H-atoms are present in toluene and not in TBB the transfer of benzyl-H-atoms from toluene to living poly(butadienyl) chains is a plausible mechanism (Scheme 2).

Evolution of Molar Mass with Monomer Conversion

The evolution of M_n on monomer conversion was monitored by SEC. The results obtained for the polymerizations in the three solvents are given in Figure 3.

In Figure 3, the following aspects are remarkable:

1. From the start of the polymerization M_n values are significantly higher for the solvents TBB and toluene than for *n*-hexane. The M_n values at 100% conversion (extrapolated for the polymerization in toluene and TBB) are: TBB: 52000 g mol^{-1} > toluene: 38000 g mol^{-1} > *n*-hexane: 30000 g mol^{-1}. From the TOF-values and the respective relative concentrations of active catalyst species a much higher molar mass is expected for toluene than for TBB. As M_n-values are lower for toluene than for TBB there is an additional factor which contributes to the reduction of M_n. A possible explanation is the reduction of molar mass by the transfer of benzyl-H-atoms from toluene.
2. The M_n-conversion plots are highly linear for the polymerization in *n*-hexane and only slightly curved for the polymerization in TBB. The respective plot for the polymerization in toluene is significantly curved. According to Penczek et al. linear M_n/conversion plots are a characteristic feature for living polymerizations in which no chain termination reactions occur. Curved plots are characteristic for the presence of irreversible chain transfer reactions (36, 37). On the basis of the interpretation given by Penczek et al. the scope of transfer reactions is higher in toluene than in TBB. This argument also is in line with the transfer of benzyl-H-atoms from toluene to living poly(butadienyl) chains.

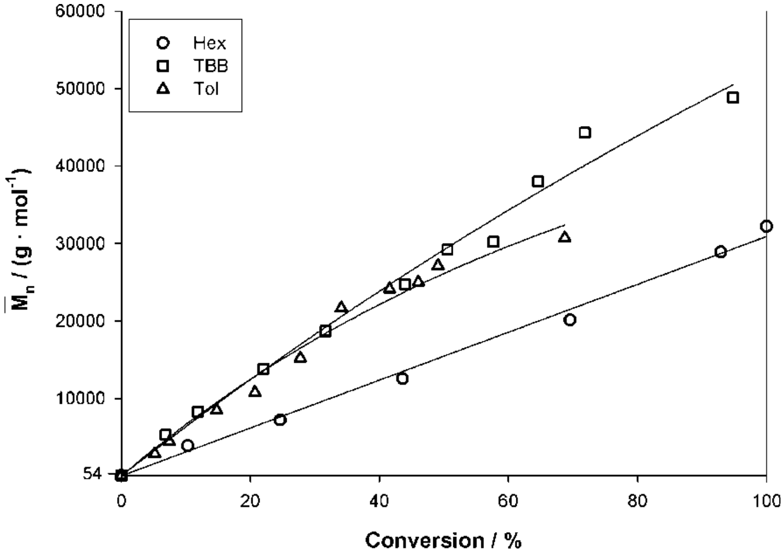


Figure 3. Molar mass evolution with conversion for BD polymerization with the catalyst system NdV/DIBAH/EASC in different solvents.

Evolution of Molar Mass Distributions with Monomer Conversion

The evolution of molar mass distributions (MMD) was monitored by SEC. For the polymerizations in *n*-hexane, TBB and toluene the respective SEC-traces are given in Figures 4, 5, and 6.

As can be seen in Figure 4 the polymerization in *n*-hexane results in a set of molar mass distributions which are (at least) bimodal from low (<10.3%) to high monomer conversion (100%).

A high molar mass peak (retention time ~16 min) is already present at a low monomer conversion (10.3%). Neither the position nor the intensity of this peak changes during the course of the polymerization. It therefore, can be concluded that the catalyst species which generates this peak is very reactive ("hot") and short-lived. Contrary to the high molar mass peak the position and the relative intensity of the low molar mass peak changes with increasing monomer conversion. At 10.3% monomer conversion this peak appears at a retention time of ~23 min. At 100% monomer conversion the retention time is reduced to 20 min. As the originally low molar mass fraction grows during the whole course of the polymerization, the catalyst species which generates this polymer fraction lives throughout the whole course of the polymerization. From these observations, it can be concluded that the respective active Nd-species has a lower reactivity and is long-lived (or "living").

The sequence of SEC-traces for the polymerization in TBB are given in Figure 5. Contrary to the polymerization in *n*-hexane, at low monomer conversion (<6.9%) the polymerization in TBB results in a monomodal MMD. The distribution becomes distinctly bimodal at monomer conversions >11.8%. The low molar mass peak originally exhibits a retention time of 22 min. With increasing monomer conversion, this peak shifts in retention time and grows in intensity. At almost complete monomer conversion, the retention time of this peak is at 16.5 min.

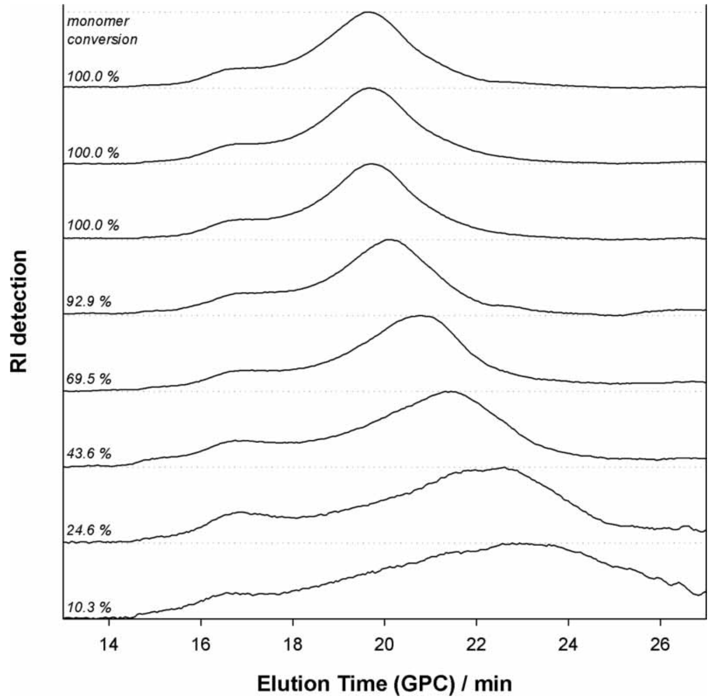


Figure 4. Evolution of the molar mass distribution with conversion for BD polymerization in *n*-hexane.

Due to these observations, it can be concluded that the catalyst species, which generates the originally low molar mass peak, has a low reactivity and is long-lived. This catalyst species exhibits the features of a living species. The high molar mass peak (retention time 16–17 min) becomes visible only at monomer conversions $> 11.8\%$. Over the whole course of the polymerization, this peak increases in intensity, but not in molar mass. On the basis of these two observations it can be concluded that the catalyst species, which generates the high molar mass BR, is non-living and is constantly generated (or regenerated) during the course of the polymerization. This catalyst species is short-lived and highly reactive "hot" as it forms high molar mass BR within short periods of time. The sequence of SEC-traces obtained for the polymerization in toluene is given in Figure 6.

The evolution of MMD in toluene is quite similar to the polymerization in TBB. Also in toluene, a high molar mass peak is not visible at the start of the polymerization. A small high molar mass peak becomes visible at monomer conversions $> 10\%$. As for the polymerization in TBB, the retention time of the high molar mass peak does not change with increasing monomer conversion. Only the peak intensity increases with monomer conversion. The evolution of the low molar mass peak with monomer conversion is comparable with the polymerizations in TBB and *n*-hexane. On the basis of these observations it can be summarized that the polymerization in toluene is also propagated by two active catalyst species. One of these catalyst species has a low reactivity and is "living" whereas the other species has a high reactivity, is short-lived and is constantly (re)generated. In toluene the influence of the short-lived species on MMD is less pronounced than in TBB.

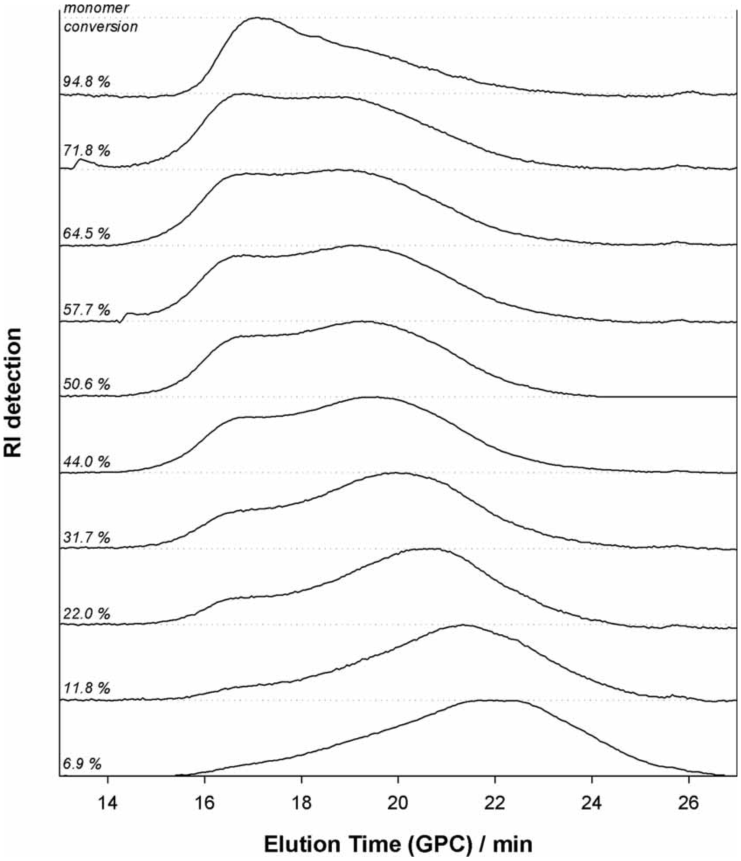


Figure 5. Evolution of the molar mass distribution with conversion for BD polymerization in *tert*-butyl benzene.

In Figure 7, the evolution of PDIs (M_w/M_n) with monomer conversion are given for the polymerizations in *n*-hexane, TBB and toluene. In *n*-hexane PDI considerably decreases from 14 to 3 during the course of the polymerization. This dependence reflects the dilution of the high molar mass peak by the increasing polymer portion which is generated by the living catalyst species. In the aromatic solvents TBB and toluene PDIs decrease to a much lower extent than in *n*-hexane. This dependence is caused by the lack of a high molar mass fraction at the start of the reaction and by the fact that the short-lived highly active species becomes active only at higher monomer conversions.

Microstructure

The *cis*-1,4-contents of the three BR-samples, which were recovered at the end of the polymerization, are given in Table 1. The following 1,4-*cis*-contents were determined: 94.0% (*n*-hexane), 96.0% (toluene) and 98.0% (TBB). The 1,2-contents are not influenced by the choice of the solvent (constant at 0.4%). The observation that *cis*-1,4-contents are higher in aromatic solvents than in *n*-hexane is in contradiction with most studies which

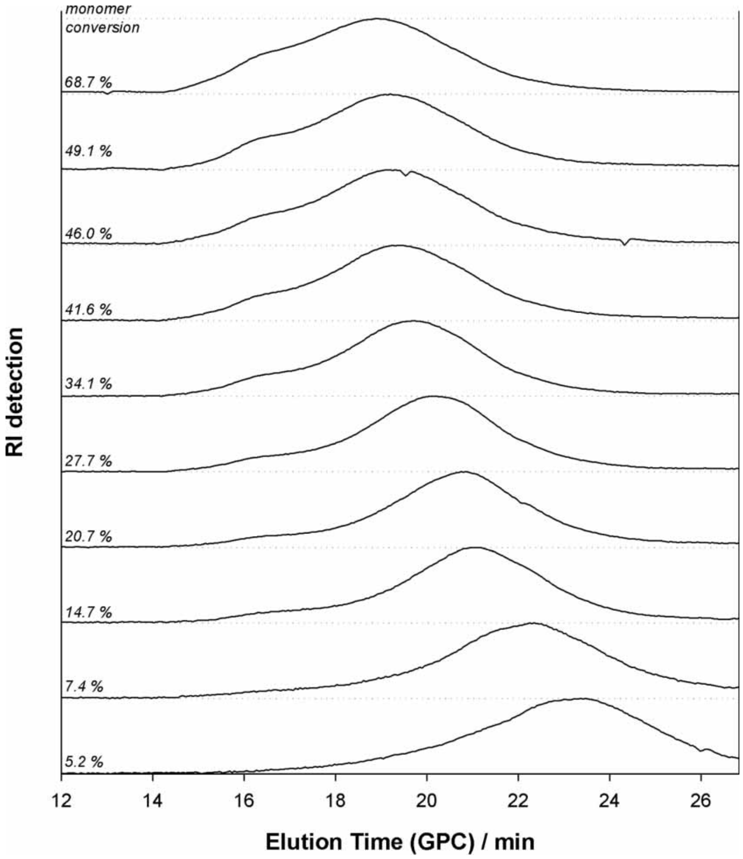


Figure 6. Evolution of the molar mass distribution with conversion for BD polymerization in toluene.

deal with the influence of solvents on microstructure. According to the available studies in the field, a higher *cis*-1,4-content is expected for aliphatic than for aromatic solvents. For the discrepancy between the results of this study with published data, no straightforward explanation can be given, at the present.

Mechanistic Interpretations

Reaction rates in TBB and in toluene are lower than in *n*-hexane (Figures 1 and 2). This reduction of reaction rates by the aromatic solvents provides evidence for the interaction of the aromatic solvents with active Nd-sites. By the concept of competitive coordination put forward by Porri et al., the reduction of the concentration of active Nd-species can be accounted for on the basis of Scheme 1 (26, 27). As the Lewis basicities of TBB and toluene should not differ very much, the large differences of reaction rates and TOF-numbers between TBB and toluene can not be accounted for on the basis of Scheme 1. The large difference of TOF-numbers between TBB and toluene point to an additional reaction by means of which the concentration of active sites is decreased. The irreversible

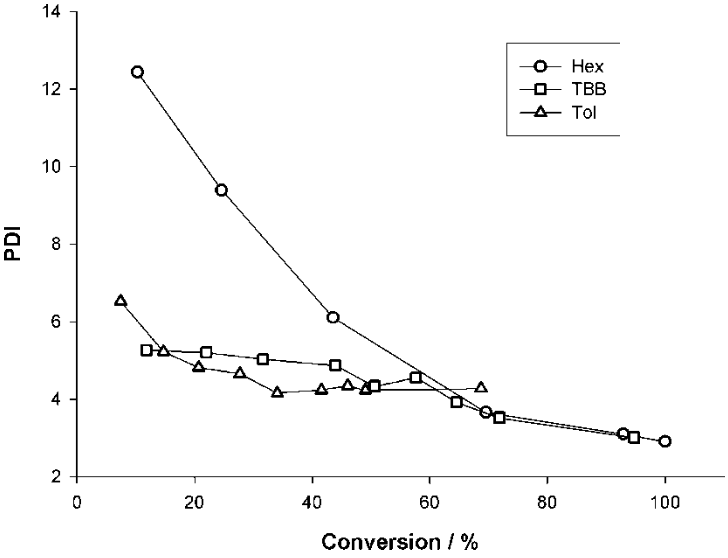


Figure 7. PDI evolution with conversion for BD polymerization with the catalyst system NdV/DIBAH/EASC in different solvents.

transfer of benzyl-H-atoms from toluene to anionic poly(butadienyl) chains provides a potential explanation.

Additional evidence in favor of transfer reactions which occur in toluene to a much larger extent than in TBB comes from the following observations:

1. On the basis of TOF-values, it can be concluded that the concentration of active catalyst sites decreases in the order: *n*-hexane > TBB > toluene. As a direct consequence, M_n-values should increase in the reverse order. Experimental evidence, however, clearly shows that M_n-values are higher for TBB than for toluene.
2. M_n/-conversion–plots exhibit a higher curvature for toluene than for TBB. According to the definition of a living polymerization put forward by Penczek, this observation provides another piece of evidence in favor of irreversible transfer reactions which occur in toluene.

As benzyl protons are only present in toluene and not in TBB, only toluene is prone to both types of reactions depicted in Schemes 1 and 2. TBB can only act as a π-donor (Scheme 1), and accordingly inhibits the polymerization to a much lower extent than toluene does. This view is in agreement with the experimental findings on polymerization kinetics (Figures 1 and 2).

Conclusions

We studied the influence of the solvents *n*-hexane, *tert*-butyl benzene (TBB) and toluene in the Nd-catalyzed polymerization of butadiene with the catalyst system neodymium versatate/diisobutylaluminum hydride/ethylaluminum sesquichloride. As the two aromatic solvents compete with monomer for active Nd-sites, the catalytic activity in these solvents is reduced. From the polymerization kinetics, as well as from the evolution of molar masses, we obtained indications for the irreversible transfer of benzyl-H-atoms from toluene to active allyl-anionic polymer chains. For all three solvents, the evolution of molar mass distributions with monomer conversion provides evidence for the existence of two active catalyst species. One of these species is highly active and short-lived, the other species is long-lived, less active but "living". The living species is present in all solvents. The appearance of the short-lived species, however, significantly differs between the aliphatic solvent *n*-hexane and the two aromatic solvents.

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