Cationic η³-allyl sulfide complexes of nickel(II) for the polymerization of butadiene in aqueous emulsion

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ABSTRACT

Reaction of the dimeric allyl-nickel(II) chloro complex [Ni(η³-C₃H₅)(μ-Cl)]₂ (5) with sulfur donor ligands (L = L₁₀–L₁₃) in the presence of NaBAr$_4^F$ (Ar$_4^F$ = 3,5-(CF₃)₂C₆H₃) gives the corresponding cationic mononuclear complexes of the type [Ni(η³-C₃H₅)(L)₂]⁺ (1–4) [L = L₁₀ = diphenyl sulfide (1); L = L₁₁ = 4,4′-thiodiphenol (2); L = L₁₂ = 4,4′-thio-bis(6-*tert*-butyl-*o*-cresol) (3); L = L₁₃ = 4,4′-thio-bis (6-*tert*-butyl-*m*-cresol) (4)]. All of these complexes were characterized by elemental analysis and NMR spectroscopy, as well as the representative complex 3 additionally by single-crystal X-ray analysis. In comparison to the known complex [Ni(η³-C₃H₅)(η⁶-BHT)][BAr$_4^F$] (BHT = 3,5-di-*tert*-butyl-4-hydroxytoluene), the herein described cationic complexes show an increased stability towards water. The activity of the complexes for butadiene polymerization in aqueous emulsions was studied.

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1. Introduction

Over the past decades there has been considerable interest in the development of nickel based polymerization catalysts [1], and in particular in the ability of certain allyl-nickel(II) complexes to act as efficient catalysts for the polymerization of dienes [2,3]. Wilke et al. showed that the catalytic activity of η³-allyl-nickel chlorides can be increased dramatically by adding aluminium halides or organoaluminium halides [4]. Generally, the addition of Lewis acids promotes the polymerization of 1,3-dienes such as butadiene and isoprene [5] as a result of an increase in the cationic character of the metal center due to halide abstraction. Cationic allyl-nickel(II) complexes are capable of acting as catalysts for the polymerization of dienes without the use of additional Lewis acids. The use of cationic allyl-nickel complexes with labile ancillary ligands favors the formation of highly stereoregular 1,4-*cis*-polybutadiene [6]. In fact, work of Taube and recently Brookhart showed that "ligand-free" allyl complexes, being only coordinated by the growing polymer chain are the truly active catalysts for 1,4-*cis*-polymerization of butadiene [7].

Aqueous emulsion polymerization is a widely used industrial technology for the preparation of polybutadiene dispersions. Water is a readily available, cheap, non-toxic and non-flammable solvent with a high heat capacity. It is suitable for the preparation of polymer latices and is therefore very attractive as a reaction medium. In today′s industrial applications the emulsion polymerization is largely centered on radical-initiated reactions. Long cycle times are a big drawback of this polymerization process. Furthermore, tuning of the polymer microstructure and thus the product properties is very limited. On the other hand, highly stereoregular polybutadiene is prepared industrially by catalytic polymerization in organic solution [8]. Besides the ability to control the polymer microstructure, short reaction times as well as an enhanced process control could be significant advantages of generating the polymers by an insertion-type approach.

Recently, Mecking reported about the aqueous emulsion polymerization of butadiene in the presence of cationic allyl-nickel triphenylstibine complexes. Due to the hydrolytic lability found with these complexes, special precautions are necessary during polymerization to prevent the pre-catalyst from decomposing prematurely. Despite the potential of industrial application, this work is to our knowledge the only published work so far on aqueous

emulsion polymerization of butadiene with cationic nickel complexes [9].

Herein we report our independent studies [10] on the serendipitous finding, characterization and syntheses of novel, robust thioether-based mononuclear $Ni^{(II)}$ cationic complexes of the type $[Ni(\eta^3-C_3H_5)(L)_2][BAr_4^F]$ and their ability to catalyze the selective 1,4-polymerization of butadiene in aqueous emulsion.

2. Results and discussion

2.1. Initial screening

The objective of our work was to identify a catalyst capable of 1,4-polymerization of butadiene in an aqueous environment, which would yield a polymer suitable for impact modification of thermoplastics. Guided by the findings of Taube and others, we focused on cationic allyl-nickel complexes with easily replaceable ancillary ligands to favor 1,4-cis-polymerization of butadiene [3b]. Thus, based on Campora's report on the use of simple arene-coordinated, cationic allyl-nickel complexes as precursors of Taube's "ligandless" nickel catalysts [6], we started an extensive screening of potential arene-type ligands of the general formula $[Ni(\eta^3-C_3H_5)(L)_n]^+$ with L being such an arene (Scheme 1).

With this screening, we hoped to identify suitable ligands that would merge two properties (Scheme 2). First, the ligand should provide a sufficient stabilization of the complex against hydrolysis until the anticipated "ligandless" nickel catalyst, coiled into the growing polymer chain, would be formed. Second, the ligand should be easily replaceable by the olefinic moieties of the growing polymer chain to allow smooth polymerization, retaining as much cis-selectivity as possible (Scheme 2).

In this regard, our ideal ligand would not take part in catalysis, but would stabilize the (pre-)catalyst until the catalytic reaction commences. Once the polymerization proceeds, we speculated that
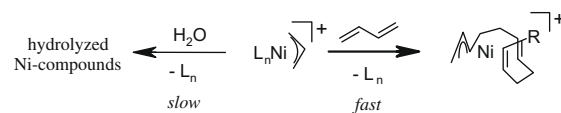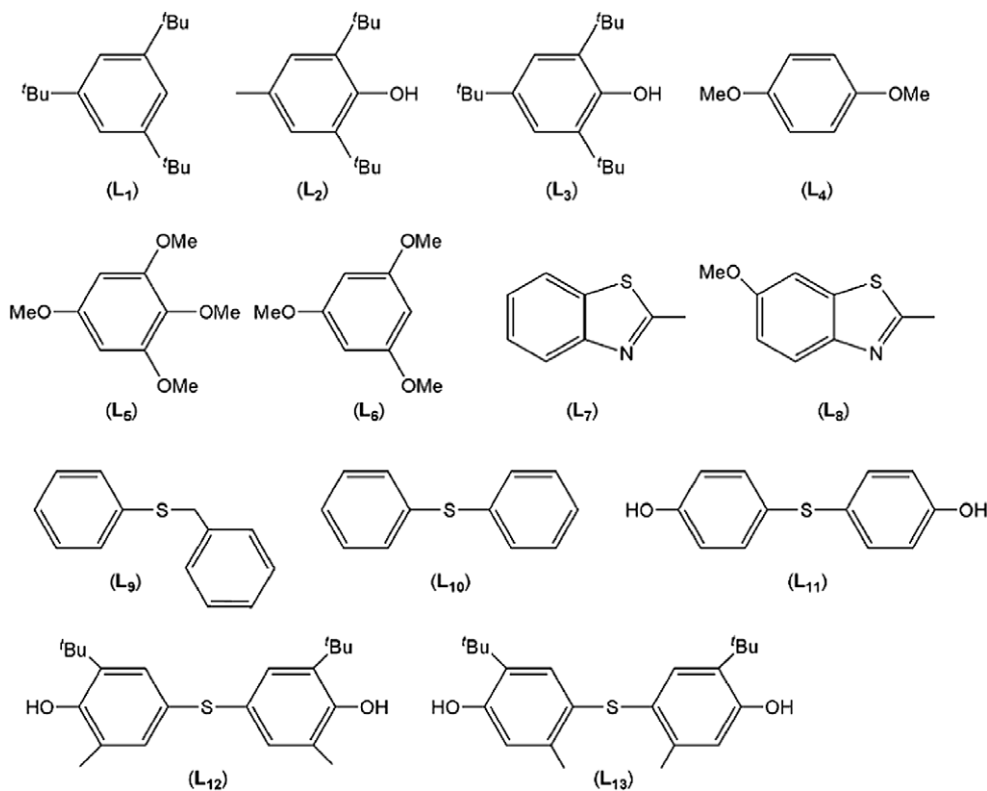

Scheme 2. Ligand tasks for aqueous emulsion polymerization of butadiene.

the growing polymer chain wrapped around the nickel center would protect the catalyst from decomposing via hydrolysis.

We studied the catalytic activity with in situ generated catalysts as emulsions in the presence of water. Interestingly, good polymerization activities were observed with sulfur-substituted arenes like 4,4'-thiodiphenol (L_{11}) or 4,4'-thio-bis(6-tert-butyl-o-cresol) (L_{12}), respectively (Scheme 1). To clarify the true coordination mode of these ligands, we decided to investigate these complexes more closely. Therefore, selected η^3-allyl-nickel(II) catalysts have been synthesized, isolated, characterized and subsequently tested for catalytic activity in the mini-emulsion polymerization of 1,3-butadiene [10].

2.2. Synthesis and characterization

The η^3-allyl-nickel(II) bridged-chloro complex $[Ni(\eta^3-C_3H_5)(\mu-Cl)]_2$ **5** reacts with four equivalents of sulfur donor ligands (L_{10}–L_{13}) in diethyl ether in the presence of $NaBAr_4^F$ ($Ar_4^F = 3,5-(CF_3)_2C_6H_3$) at $-60\,°C$ to give the mononuclear cationic complexes of the type $[Ni(\eta^3-C_3H_5)(L)_2][BAr_4^F]$ (**1–4**) in satisfactory yields of 52–60% (L = diphenyl sulfide (L_{10}), 4,4'-thiodiphenol (L_{11}), 4,4'-thio-bis (6-tert-butyl-o-cresol) (L_{12}), 4,4'-thio-bis (6-tert-butyl-m-cresol) (L_{13}) (Scheme 3). The cationic complexes **1–4** are orange-brown in color, and are isolated as bench-stable crystalline solids, only slightly sensitive against air and moisture. They are soluble in dichloromethane, acetone, chloroform, diethyl ether and insoluble in n-hexane and n-pentane.

Scheme 1. Arene-type ligands used in the initial screening for aqueous emulsion polymerization of butadiene.
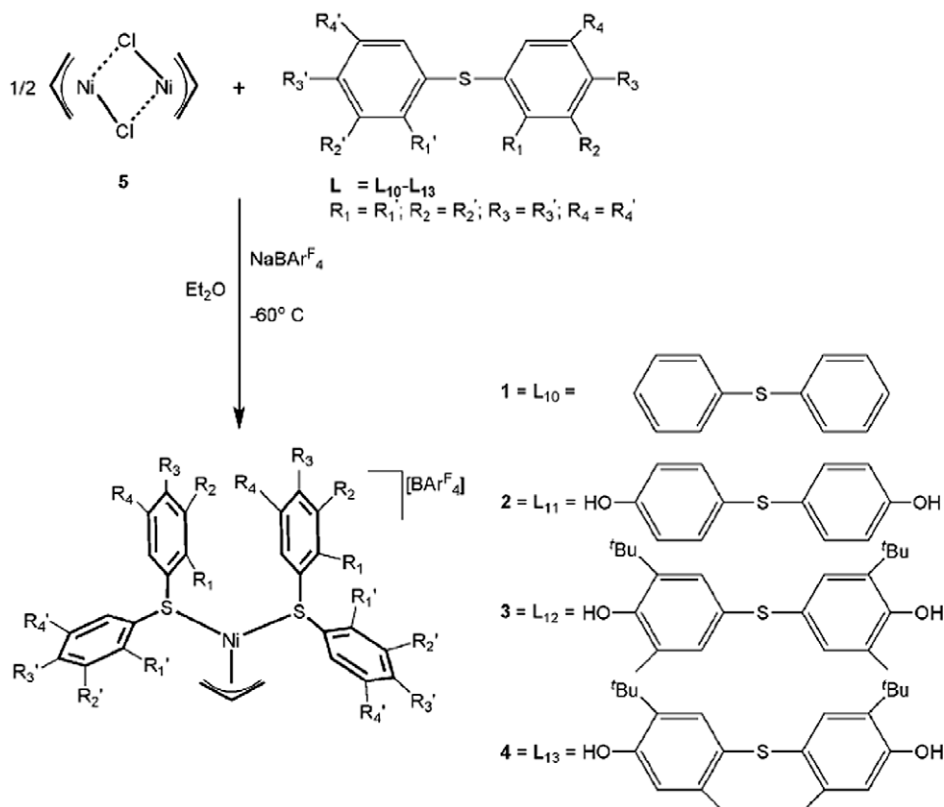
Scheme 3. Synthesis of [Ni(η^3-C$_3$H$_5$)(L)$_2$][BAr$_4^F$] complexes (**1–4**).

All the compounds are diamagnetic, and display appropriate signals in their proton NMR spectra. The ^{1}H NMR spectra of complexes **1–4** exhibit two doublets at around 2.8 and 3.4 ppm which correspond to the allyl protons of H$_{syn}$ and H$_{anti}$ and the typical multiplet for the central CH proton appears in the range 5.77–5.92 ppm. The hydroxyl (–OH) protons of complexes **2–4** appear as singlets at 5.64, 5.16 and 5.22 ppm, respectively. The methyl (–CH$_3$) protons of complexes **3** and **4** appear as singlets at 2.12 and 2.05 ppm, respectively. The tert-butyl group (t-CMe$_3$) protons of complexes **3** and **4** appear as singlets at 1.38 and 1.34 ppm. The aromatic protons of complexes **1–4** appear in the range of 6.49–7.50 ppm and the [BAr$_4^F$]$^-$ protons appear in the range 7.52–7.82 ppm.

The ^{13}C{1H} NMR spectrum of complexes **1–4** contain resonances for the allyl CH$_2$ and CH group carbons at around 70 and 117 ppm, respectively. The resonances for the aromatic carbons of complexes **1–4** appear in the range of 120–160 ppm. ^{1}H NMR studies in the presence of water were carried out in order to survey the reactivity of the complexes relative to Campora's catalyst [Ni(η^3-C$_3$H$_5$)(η^6-BHT)][BAr$_4^F$] (BHT = 3,5-Di-tert-butyl-4-hydroxytoluene) [6] towards water. Exposure of 1 to 5 equivalents of water in CD$_2$Cl$_2$ solution at room temperature resulted in decomposition of Campora's complex within a few minutes, to form a black solid and the free arene. During the decomposition, signals of a new allylic system were observed, which might indicate the formation of an intermediate aqua complex (Fig. 1) as has been reported also
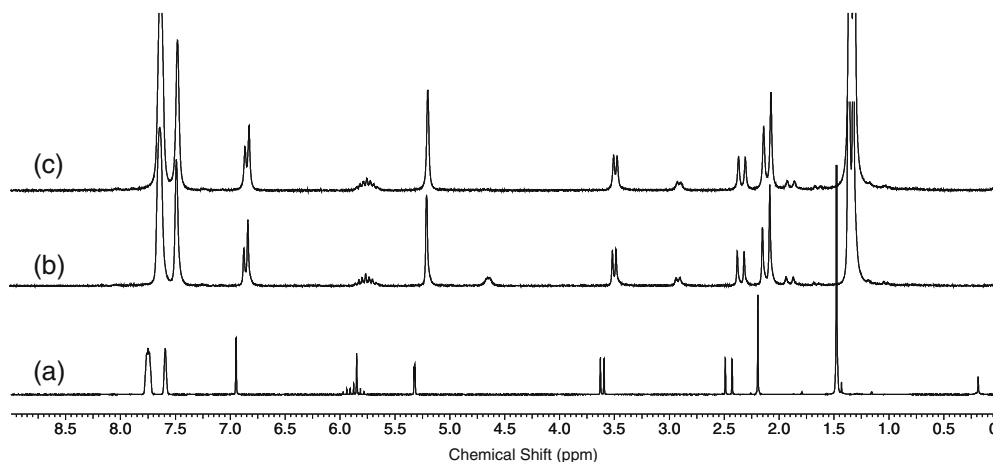

Fig. 1. ^{1}H NMR spectra (200 MHz, CD$_2$Cl$_2$) of complex [Ni(η^3-C$_3$H$_5$)(η^6-BHT)]$^+$ with (a) no water-d$_2$, (b) water-d$_2$ in 5 min and (c) water-d$_2$ in 10 min.
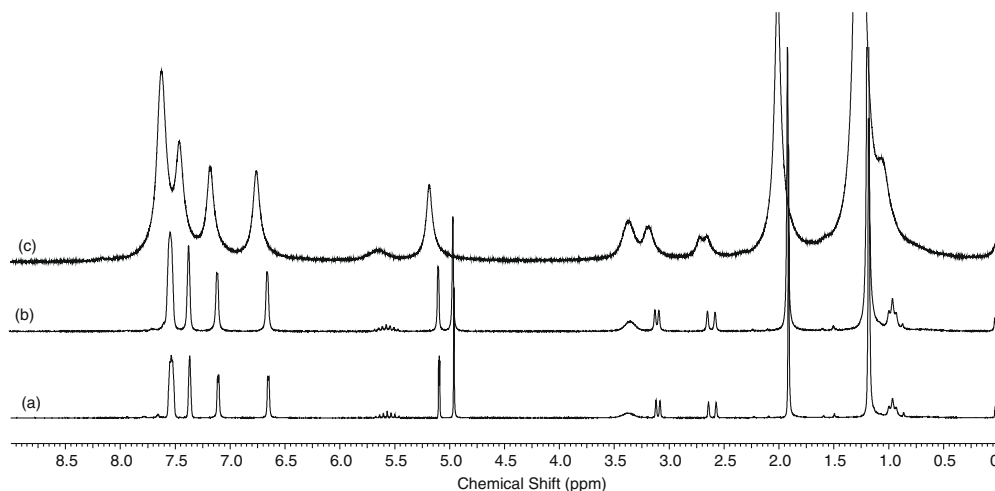
Fig. 2. ^{1}H NMR spectra (200 MHz, CD$_2$Cl$_2$) of complex **3** with (a) no water-d$_2$, (b) water-d$_2$ in 20 min and (c) water-d$_2$ in 40 min.

by Mecking in related work [9] When complexes **1**–**4** were tested under identical conditions with water they showed no immediate sign of decomposition, indicating that these complexes are much more resistant to water hydrolysis (representative spectra of complex **3** shown in Fig. 2).

2.3. Molecular structure of [Ni(η^3-C$_3$H$_5$)(4,4'-thio-bis(6-tert-butyl-o-cresol)$_2$]$^+$

The molecular structure of the mononuclear allyl-nickel-sulfide complex **3** has been established by single-crystal X-ray structure analysis (Fig. 3). A summary of the single-crystal X-ray structure analysis is shown in Table 1. The ORTEP drawing of compound **3** is shown in Fig. 3 with selected bond lengths and angles given in the caption.

Compound **3** consists of a cationic Ni$^{(II)}$ allyl complex and an associated non-coordinating [BAr$^F_4$]$^-$ anion. The complex crystallizes in the triclinic space group $P\bar{1}$. The Ni$^{(II)}$ center exists in a pseudo square-planar coordination geometry with the terminal carbons of the allyl group in a *cis* relationship [C(45)–Ni(1)–C(47) = 71.5(2)°, C(45)–Ni(1)–S(1) = 97.27(16)°, C(45)–Ni(1)–S(2) = 161.20(17)°, S(1)–Ni(1)–S(2) = 100.50(4)°]. The allyl group is almost evenly coordinated as would be expected since both sulfur ligands are identical [Ni(1)–C(45) = 2.008(5) Å, Ni(1)–C(46) = 2.006(5) Å, Ni(1)–C(47) = 2.049(5) Å, C(45)–C(46) = 1.374(7) Å, C(46)–C(47) = 1.392(7) Å]. The Ni–S bond distances are comparable to other allyl Ni$^{(II)}$ complexes with sulfur based ligands [Ni(1)–S(1) = 2.195(1) Å and Ni(1)–S(2) = 2.214(1) Å] [11]. There appears to be a π–π stacking interaction between two neighbouring phenyl rings of the sulfur ligands which are in close proximity to one another [C(1)–C(23) = 3.172(5) Å, C(2)–C(23) = 3.455(5) Å, C(3)–C(25) = 3.522(5) Å, C(3)–C(26) = 3.700(5) Å]. The dihedral angle formed by the plane containing the atoms S(1)–Ni(1)–S(2) and that containing C(45)–C(46)–C(47) is 62°.

Fig. 3. ORTEP diagram of cation **3** at 50% probability level. The anion and the non-allyl H atoms are omitted for clarity. Selected bond lengths (Å) angles (°): Ni1–C45 = 2.008(5), Ni1–C46 = 2.006(5), Ni1–C47 = 2.049(5), Ni1–S1 = 2.1951(11), Ni1–S2 = 2.214(1), S1–C1 = 1.782(4), S1–C12 = 1.789(4), S2–C34 = 1.787(4), S2–C23 = 1.793(4), S1–Ni1–S2 = 100.50(4), C45–Ni1–C47 = 71.5(2), C45–Ni1–S1 = 97.27(16), C45–Ni1–S2 = 161.84(17), C47–Ni1–S1 = 167.84(16), C47–Ni1–S2 = 90.27(15).

Table 1
Crystal data and structure refinement for complex **3**.

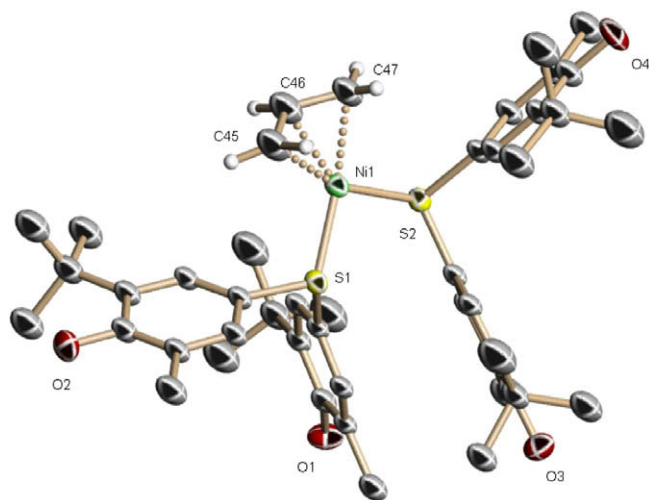|	
Empirical formula	C$_{79}$H$_{77}$BF$_{24}$NiO$_4$S$_2$
Formula weight	1680.05
T (K)	200(2)
Wavelength (Å)	0.7107
Crystal system	Triclinic
Space group	P$\bar{1}$
Crystal size (mm^3)	0.39 × 0.32 × 0.09
a (Å)	13.1424(2)
b (Å)	18.1998(1)
c (Å)	19.3080(2)
α (°)	116.371(1)
β (°)	94.478(1)
γ (°)	95.413(1)
V (Å^3)	4081.78(8)
Z	2
D_c (g cm^{-3})	1.367
$F(0\,0\,0)$	1728
Absorption coefficient (mm^{-1})	0.390
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9657 and 0.8627
θ Range for data collection (°)	1.57–24.71
Limiting indices	$-15 \leq h \leq 15$, $-21 \leq k \leq 21$, $-22 \leq l \leq 22$
Reflections collected/unique	33 734/13 902 [R_{int} = 0.0759]
Data/restraints/parameters	13 902/468/1192
Goodness-of-fit (GOF)	1.007
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0596, wR_2 = 0.1252
R indices (all data)	R_1 = 0.1237, wR_2 = 0.1530
Max., min. $\Delta\rho$ (e Å^3)	0.534, −0.341

Table 2
Polymerization of 1,3-butadiene with Ni catalysts.

Entry	Catalyst	Ratio Bu/Ni-catalyst	Solids content (%)	Yield (%)	PSD (d50) (nm)	Vinyl/cis/trans (%)[a]	M_w	M_n	M_w/M_n
1	**2**	2000	10.2	50.8	221	2/48/50	2.0×104	7.0×10^3	2.9
2	In situ **2**	2000	12.2	43.0	221	1/42/57	2.8×10^4	8.5×10^3	3.3
3	**3**	2000	10.4	39.7	212	2/32/65	2.0×10^4	7.1×10^3	2.8
4	In situ **3**	2000	10.9	41.3	185	2/19/79	1.5×10^4	5.3×10^3	2.9
5[b]	Cat. Ref. [9][c]	12 200	n.d.[d]	5	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]

Polymerization conditions entries 1–4: 40 °C, 4 h, 0.37 mmol Ni complex. *Polymerization conditions entry 5*: 20 °C, 4 h, 20 μmol complex, see Ref. [9].
  [a] Determined from IR spectra.
  [b] According to Ref. [9] only polymer from pre-polymerization obtained, no catalytic activity after mini-emulsification.
  [c] [(allyl)Ni(SbPh$_3$)$_2$]BAr$_4^F$.
  [d] n.d. "not determined".

2.4. Mini-emulsion polymerization of 1,3-butadiene with [Ni(η^3-C$_3$H$_5$)(L)$_2$]$^+$

Initial experiments showed that pre-polymerization of butadiene is helpful in protecting the active cationic Ni center against hydrolysis during emulsion polymerization. Therefore, a solution of complex **2** or **3** in toluene was treated with small amounts of 1,3-butadiene before emulsification with sodium dodecyl sulfate (SDS), hexadecane and water. For comparison, a pre-polymerized catalyst emulsion has been synthesized by *in situ* methods. Here, [Ni(η^3-C$_3$H$_5$)Cl]$_2$ was combined with two equivalents of Na[BAr$_4^F$] and the appropriate aryl sulfide and stirred for 1 h at −60 °C in toluene, followed by addition of 1,3-butadiene and finally emulsification (*vide supra*).

The polymerization of 1,3-butadiene with **2** and **3** was performed at 40 °C for 4 h. The results of the emulsion polymerizations are presented in Table 2. The polymer latices have been studied with GPC, HDF and IR spectroscopy.

The catalysts show moderate activities with polymer yields of 30–50% and solid contents of 8–12%. Interestingly, no further polymerization after emulsification is observed, when [(allyl)Ni(SbPh$_3$)$_2$]BAr$_4^F$ is used as a catalyst. Here, fine-tuning of the catalyst solubility is necessary to prevent premature decomposition of the catalyst and only a partially insoluble catalyst survives the vigorous mixing conditions of mini-emulsification [9].

No difference in activities was observed between the polymerization of 1,3-butadiene with the isolated Ni$^{(II)}$ catalysts (**2** and **3**) or the *in situ* prepared catalysts. The polymer particles have an average size (d50) of 210–260 nm. In contrast, the conventional radical-initiated polymerization yields particles with a d50 of about 100 nm. The latices have a number average molecular weight of ca. 7×10^3 g/mol. This value is lower by an order of magnitude to catalytic polymerizations with Ni(II) systems in organic solvent and still to low for applications [6,7]. It appears that chain terminations can occur with our complexes in the aqueous emulsion more readily than in organic phase, which is also reflected in the rather high polydispersity of the obtained polymers. In addition to catalyst decomposition in the presence of water, mass transfer limitation may serve as an additional source for the relatively low average molecular weight of the polymer formed in aqueous emulsion. Once the butadiene of a certain droplet is consumed, additional butadiene has to be transported to the catalyst by diffusion through the aqueous phase. This would result in a reduced effective concentration of butadiene at the catalyst and with this, the relative rate of insertion will be retarded relatively to chain termination and chain transfer [12,13]. The general catalyst efficiencies as measured in turn over numbers (ton) are in a satisfying range of 800–1000. The microstructure has been studied by IR spectroscopy [14]. The emulsion polymers exhibit a relatively high fraction of *trans*-1,4-polybutadiene; the *cis:trans* ratio varies between 50:50 and 20:80. Particularly, **3** yields polybutadiene latices with a high 1,4-*trans* content (65–79%) (Table 2). Interestingly, when using the *in situ* generated catalyst an even higher 1,4-*trans* content is observed [15]. In contrast, polymerization with the same catalysts in organic solution gives high *cis*-1,4-PBu selectivity [10,16]. Radical polymerization of 1,3-butadiene *via* mini-emulsion yields an almost unselective microstructure containing 14% *cis*-1,4-PBu, 69% *trans*-1,4-PBu and 17% 1,2-PBu units [17]. The difference in the microstructure between emulsion and solution polymerization results most likely from the presence of water, acting as a *trans*-regulating ligand for the cationic nickel complexes. The *trans*-regulating influence of coordinating ligands on the cationic nickel complexes has been described by Taube in detail [15]. In the report of Mecking et al. a similar polybutadiene microstructure (70–80% of 1,4-*trans* content) by using [Ni(η^3-C$_3$H$_5$)(SbPh$_3$)$_2$][BAr$_4^F$] and [Ni(η^3-C$_3$H$_5$)(SbPh$_3$)$_2$] [Al(OC(CF$_3$)$_3$)$_4$] is described [9]. The high 1,4-*trans* content in this work was ascribed to the coordination of water as a ligand in the active species.

3. Conclusions

We have screened several ligands for the emulsion polymerization of 1,3-butadiene using [Ni(η^3-C$_3$H$_5$)Cl]$_2$ as a precursor for the *in situ* generation of the catalyst in the presence of a ligand and Na-BAr$^F_4$. Based on our ligand screening we have isolated a series of new η^3-allyl-nickel(II) complexes containing sulfur donor ligands. Taking advantage of their good stability towards hydrolysis, these complexes have been found suitable for the aqueous emulsion polymerization of butadiene. The isolated complexes and *in situ* generated catalysts show similar activities in the aqueous emulsion polymerizations. The *cis/trans*-selectivity of the polymerization is affected by the reaction medium and results in aqueous emulsion in a higher 1,4-*trans*-content of the polymer. But, in comparison to typical radical-initiated emulsion polymerizations of butadiene, the here described catalysts give polymer particles with low 1,2-polybutadiene content and, for aqueous emulsion polymerization, an unprecedented high 1,4-*cis*-polybutadiene content of up to 48%.

4. Experimental

4.1. General remarks

All manipulations were performed under inert atmosphere using conventional Schlenk technique and a glove box. All reagents used were purchased from Aldrich, Acros, Fluka, Strem or MCat and were used without further purification, unless stated. Anhydrous solvents were dried using a SPS MBSPS-800 system from MBraun and degassed by the freeze-pump-thaw method. All ^{1}H NMR and ^{13}C{1H} NMR spectra were recorded as CD$_2$Cl$_2$ solutions on a Bruker DPX200 spectrometer (200 MHz). All ^{13}C NMR spectra were

referenced to CD$_2$Cl$_2$ (q, 53.42 ppm) as the internal standard, and all ^{1}H NMR spectra referenced to tetramethylsilane (TMS) as the internal standard with J values given in hertz. Glove box manipulations were carried out in a MB200G (LMF) glove box under an argon atmosphere. GPC analyses were performed with an Agilent 1100 series instrument in THF at 36 °C against a polybutadiene standard. IR spectra of the pure polymer were recorded on a BioRad FTS-175 spectrometer with a DTGS detector (resolution 2 cm^{-1}). Hydrodynamic chromatography (HDC) was performed with PL-PSDA (Polymer Laboratories-Particle Size Distribution Analyzer) using a PS cartridge (10–15 μm). By this method particles in between 10 and 1200 nm can be detected.

4.2. Synthesis of [Ni(η^3-C$_3$H$_5$)(L$_{10}$)$_2$][BAr$^F_4$] **1** (L$_{10}$ = diphenyl sulfide)

In a Schlenk flask a solution of diphenyl sulfide (L$_{10}$) (0.28 g, 1.52 mmol) and NaBAr$^F_4$ (0.67 g, 0.76 mmol) in 10 ml of diethyl ether was added to a stirred solution of [Ni(η^3-C$_3$H$_5$)(μ-Cl)]$_2$ **5** (0.1 g, 0.38 mmol) in diethyl ether (20 ml) at −60 °C. After 2 h, the cooling bath was removed and the mixture was allowed to stir at room temperature overnight. The solvent was evaporated under vacuum, and the residue extracted with dichloromethane (20 ml), and the resulting solution was filtered and concentrated. The product was crystallized twice form CH$_2$Cl$_2$–hexane. Yield 0.51 g (52%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ = 7.83 (s, 8H CH$_{o\text{-Ar}'}$), 7.61 (s, 4H, CH$_{p\text{-Ar}'}$), 7.41 (m, 20H, Ph), 5.92 (m, 1H, allyl CH$_{central}$), 3.48 (d, $^3J_{H-H}$ = 5.64 Hz, allyl CH$_{syn}$), 2.85 (d, $^3J_{H-H}$ = 10.08 Hz, 2H, allyl CH$_{anti}$); ^{13}C NMR (CD$_2$Cl$_2$, 75.5 MHz) δ = 161.7, 159.3, 138.5, 134.2, 129.6, 125.4, 122.3, 121.4, 119.9, 116.6, 70.1; Anal. Calc. for C$_{59}$H$_{37}$S$_2$F$_{24}$BNi: C, 53.06; H, 2.79. Found: C, 53.23; H, 2.91%.

4.3. Synthesis of [Ni(η^3-C$_3$H$_5$)(L$_{11}$)$_2$][BAr$^F_4$] **2** (L$_{11}$ = 4,4′-thiodiphenol)

This compound was prepared by the same procedure described above for **1** using **5** (0.6 g, 2.22 mmol), NaBAr$^F_4$ (3.93 g 4.44 mmol) and 4,4′-thiodiphenol (L$_{11}$) (1.94 g, 8.90 mmol). Yield 3.2 g (53%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ = 7.82 (s, 8H, CH$_{o\text{-Ar}'}$), 7.74 (s, 4H, CH$_{p\text{-Ar}'}$), 7.23 (d, 8H, CH$_{Ar}$), 6.79 (d, 8H, $^3J_{H-H}$ = 8.70 Hz, CH$_{Ar}$), 5.85 (m, 1H, allyl CH$_{central}$), 5.64 (s, 4H, OH), 3.37 (d, 2H, $^3J_{H-H}$ = 7.28 Hz, allyl CH$_{syn}$), 2.85 (d, 2H, $^3J_{H-H}$ = 13.92 Hz, allyl CH$_{anti}$); ^{13}C NMR (CD$_2$Cl$_2$, 75.5 MHz) δ = 162.7, 158.4, 135.3, 133.9, 129.1, 127.8, 122.4, 117.9, 117.5, 117.0, 69.9; Anal. Calc. for C$_{59}$H$_{37}$O$_4$S$_2$F$_{24}$BNi: C, 50.63; H, 2.66. Found: C, 50.80; H, 2.96%.

4.4. Synthesis of [Ni(η^3-C$_3$H$_5$)(L$_{12}$)$_2$][BAr$^F_4$] **3** (L$_{12}$ = 4,4′-thio-bis(6-tert-butyl-o-cresol)

This compound was prepared by the same procedure described above for **1** using **5** (0.6 g, 2.22 mmol), NaBAr$^F_4$ (3.93 g 4.44 mmol) and 4,4′-Thio-bis(6-tert-butyl-o-cresol) (L$_{12}$) (3.18 g, 8.90 mmol). Yield 4.1 g (55%). X-ray quality crystals of the complex **3** were grown by slow diffusion of hexane into a dichloromethane solution at −40 °C. ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ = 7.72 (s, 8H, CH$_{o\text{-Ar}'}$), 7.57 (s, 4H, CH$_{p\text{-Ar}'}$), 7.31 (d, 4H, CH$_{o\text{-Ar}}$), 6.84 (d, 4H, $^4J_{H-H}$ = 2.0 Hz, CH$_{o\text{-Ar}}$), 5.77 (m, 1H, allyl CH$_{central}$), 5.16 (s, 4H, OH), 3.30 (d, 2H, $^3J_{H-H}$ = 7.40 Hz, allyl CH$_{syn}$), 2.80 (d, 2H, $^3J_{H-H}$ = 14.0 Hz, allyl CH$_{anti}$), 2.12 (s, 12H, CH$_3$), 1.38 (s, 36H, ^{t}Bu); ^{13}C NMR (CD$_2$Cl$_2$, 75.5 MHz) δ = 162.6, 137.9, 135.0, 131.6, 129.3, 127.5, 125.2, 122.1, 121.4, 117.7, 116.9, 69.5, 34.9, 29.3, 15.8; Anal. Calc. for C$_{79}$H$_{77}$O$_4$S$_2$F$_{24}$BNi: C, 56.48; H, 4.62. Found: C, 56.23; H, 4.38%.

4.5. Synthesis of [Ni(η^3-C$_3$H$_5$)(L$_{13}$)$_2$][BAr$^F_4$] **4** (L$_{13}$ = 4,4′-thio-bis(6-tert-butyl-m-cresol)

This compound was prepared by the same procedure described above for **1** using **5** (0.1 g, 0.38 mmol), NaBAr$^F_4$ (0.67 g 0.76 mmol)

and 4,4′-thio-bis(6-tert-butyl-m-cresol) (L$_{13}$) (0.54 g, 1.52 mmol). Yield 0.75 g (60%). ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ = 7.72 (s, 8H, CH$_{o\text{-Ar}'}$), 7.56 (s, 4H, CH$_{p\text{-Ar}'}$), 7.47 (s, 4H, CH$_{m\text{-Ar}}$), 6.50 (s, 4H, CH$_{o\text{-Ar}}$), 5.82 (m, 1H, allyl CH$_{central}$), 5.22 (s, 4H, OH), 3.23 (d, 2H, $^3J_{H-H}$ = 7.40 Hz, allyl CH$_{syn}$), 2.80 (d, 2H, $^3J_{H-H}$ = 14.0 Hz, allyl CH$_{anti}$), 2.05 (s, 12H, CH$_3$), 1.34 (s, 36H, ^{t}Bu); ^{13}C NMR (CD$_2$Cl$_2$, 75.5 MHz) δ = 162.4, 156.3, 138.5, 136.3, 134.9, 129.3, 127.4, 122.0, 120.4, 119.2, 117.0, 68.8, 34.6, 29.1, 19.3; Anal. Calc. for C$_{79}$H$_{77}$O$_4$S$_2$F$_{24}$BNi: C, 56.48; H, 4.62. Found: C, 56.53; H, 4.41%.

4.6. Emulsion polymerization of butadiene with complexes **2** and **3** as catalyst

For emulsion polymerization, a solution of cationic complexes **2** or **3** (0.37 mmol) in toluene was treated with 6 ml of 1,3-butadiene at 0 °C. Afterwards 0.8 ml of hexadecane (0.0027 mmol) and a solution of sodium dodecyl sulfate (SDS) in water (1 g in 80 ml) is added and subsequently emulsified with an ultrasound sonotrode for 4 min.

The polymerizations were carried out in a 500 ml steel autoclave equipped with a mechanical stirrer (600 rpm) and with a cooling/heating jacket supplied with a thermostat controlled by a thermocouple dipping into the polymerization mixture. The reactor was charged with a solution of 1 g SDS in 70 ml water. Then the catalyst mini-emulsion was added and the reactor was warmed to 40 °C. Butadiene was added in five portions at intervals of 2 min. After 4 h the autoclave was cooled to room temperature. Residual butadiene was removed by applying vacuum for several times.

5. X-ray crystallography

A suitable crystal was selected, mounted on a thin glass fiber using paraffin oil, and cooled to the data collection temperature. Data was collected on a Bruker SMART CCD diffractometer using 0.3° ω scans at 0°, 90°, 180°, and 270° in φ. Initial unit-cell parameters were determined from data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied [18]. The diffraction data and unit-cell parameters were consistent with the reported space group $P\bar{1}$ for complex **3**. No symmetry higher than triclinic was observed, and the solution in the centrosymmetric space group yielded chemically reasonable and computationally stable results after refinement. The structure was solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. The fluorine atoms of the non-coordinating anion showed considerable rotation and thus several CF$_3$ groups were anisotropically modeled in two rotational positions with a total occupancy factor of 1. All scattering factors are contained in the shelxtl 6.12 program library [19]. A summary of the crystal data, data collection parameters and convergence results is compiled in Table 1.

Appendix A. Supplementary material

CCDC 707916 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.041.

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