Chinese Journal of
POLYMER SCIENCE 高分子科学

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Cite this article as:
He Jian-Yun, Cui Long, Qi Yan-Long, Dai Quan-Quan, Bai Chen-Xi. Neodymium Organic Sulfonate Complexes: Tunable Electronegativity/Steric Hindrance and Application in Controlled *Cis*-1,4-polymerization of Butadiene[J]. *Chinese J. Polym. Sci*, 2019, 37(3): 208-215. doi: 10.1007/s10118-019-2196-1

View online: https://doi.org/10.1007/s10118-019-2196-1

Chinese Journal of
POLYMER SCIENCE

ARTICLE

https://doi.org/10.1007/s10118-019-2196-1
Chinese J. Polym. Sci. **2019**, *37*, 208–215

Neodymium Organic Sulfonate Complexes: Tunable Electronegativity/Steric Hindrance and Application in Controlled *Cis*-1,4-polymerization of Butadiene

Jian-Yun He, Long Cui, Yan-Long Qi, Quan-Quan Dai*, and Chen-Xi Bai*

Key Laboratory of High-Performance Synthetic Rubber and its Composite Materials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

Electronic Supplementary Information

Abstract Rare earth catalysts possessing characteristics of cation-anion ion pair show advantages of adjusting electronegativity and steric hindrance of metal active sites, which can control the catalytic performance and stereoselectivity better than those of traditional metallocene and Ziegler-Natta catalysts in diene polymerization. In this work, a series of neodymium organic sulfonate complexes, $Nd(CF_3SO_3)_3{\cdot}xH_2O{\cdot}yL$ (*x*, *y*: the coordination number; L refers to an organic electron donating ligand, such as acetylacetone (acac), *iso*-octyl alcohol (IAOH), tributyl phosphate (TBP), *etc*.), have been synthesized to form the cationic active species in the presence of alkylaluminum such as $Al(i\text{-}Bu)_3$, $AlEt_3$, and $Al(i\text{-}Bu)_2H$, which display high activities and distinguishing *cis*-1,4 selectivities (up to 99.9%) for the polymerization of butadiene. The microstructures, yield, molecular weight, and molecular weight distribution of the resulting polymer are well controlled by adjusting electronegativity/steric hindrance of the complexes. In addition, the kinetics, active species, and the possible process of polymerization are also discussed in this article.

Keywords Neodymium catalysts; Organic sulfonate complexes; Tunable electronegativity and steric hindrance; *Cis*-1,4-polymerization; Butadiene

Citation: He, J. Y.; Cui, L.; Qi, Y. L.; Dai, Q. Q.; Bai, C. X. Neodymium organic sulfonate complexes: tunable electronegativity/steric hindrance and application in controlled *cis*-1,4-polymerization of butadiene. *Chinese J. Polym. Sci.* **2019**, *37*, 208–215.

INTRODUCTION

Metallocene and non-metallocene catalysts have obvious advantages in the development of novel classes of polymers due to their excellent characteristics of "single-site", wide range of monomers, structural control of polymers with facility, and high (co)polymerization activity,[1,2] which have become research focuses in polyolefin[3–7] and rubber industry.[8–12] Compared with Ziegler-Natta catalysts, metallocene and non-metallocene catalysts can form cationic active species with cocatalysts such as methylaluminoxane (MAO), borate ($[Ph_3C][B(C_6F_5)_4]$) or borane ($B(C_6F_5)_3$). As shown in Scheme 1, for olefin polymerization, cationic metal center accelerates the coordination, insertion, and propagation reactions with weak nucleophilic olefin monomers, which is more favorable to achieve higher activities than those of Ziegler-Natta catalysts. For polymerization of diene, a more stable coordination structure can be obtained at a faster rate in view of its relatively strong nucleophilicity.[13–19] However, the enhanced nucleophilicity will simultaneously slow down the insertion reaction, which plays a decisive role in rate-determining step of polymerization. Thus, metallocene and non-metallocene catalysts do not show distinct advantages in catalytic activities of diene polymerization. Furthermore, the intolerable cost of the cocatalysts MAO and borate restricts the applications of metallocene and non-metallocene catalysts in polydiene industry.

One of the prominent features of metallocene and non-metallocene catalysts is their active species possessing characteristics of cation-anion ion pair. Inspired by these facts, we envision that the metal compounds with innate feature of cation-anion ion pair could serve as catalysts directly instead of MAO or borate. In the presence of common alkylaluminum, these compounds can readily undergo alkylations to form cationic active species with essentially identical properties similar to the metallocene and non-metallocene catalysts, thus developing a novel, green, and highly efficient catalytic system for polymerization of olefin and diene.

Organic sulfonic acid rare earth compounds[20,21] have the characteristics of cation-anion ion pair, low cost, commercially available, easy to prepare, and intriguing structural diversity, which have drawn much attention and provided a

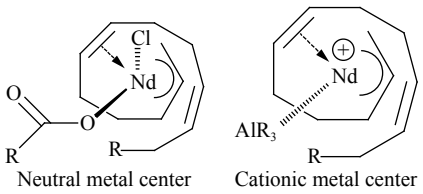
* Corresponding authors: E-mail qqdai@ciac.ac.cn (Q.Q.D.)
E-mail baicx@ciac.ac.cn (C.X.B.)

Received September 26, 2018; Accepted October 30, 2018; Published online November 21, 2018

Scheme 1 Formation of cationic active species by metallocene and non-metallocene catalysts (L: ligands)

unique scaffold for various reactions such as etherification,[22] hydrothiolation,[23] nitration,[24] and ring-opening polymerization of caprolactone.[25] In view of high coordination numbers of rare earth compounds with $4f^3$ electronic configuration, the introduction of electron-donating ligand with good aliphatic solubility will improve the compounds' solubility in organic solvents and boost the alkylated reaction in combination with alkylaluminum,[9,11,26,27] which can develop a series of novel cationic catalysts of rare earth metals.

It is noteworthy that counter ions of $[MAO]^-/[B(C_6F_5)_4]^-$ for traditional cationic metallocene and non-metallocene catalysts possess large steric hindrance and weak coordination ability, which is for the sake of keeping the charge balance. However, those novel cationic catalysts of organic sulfonic acid rare earth metals formed by alkylation introduce organic sulfonate ions (RSO_3^-) with moderate steric hindrance, which can interact with center metal, provide great changes in catalytic performance. First, the electronegativity of center metals of the novel cationic catalysts is between those of Ziegler-Natta catalysts and the metallocene catalysts. Combined with RSO_3^-, which possesses a certain donor ability, this novel catalyst can conduct the coordination faster than neutral Ziegler-Natta catalysts do and then make the insertion proceed faster than cationic metallocene and non-metallocene catalysts do in diene polymerization, respectively. Second, the double bond of propagating chain end linked with π-η^3-allyl in novel catalyst has stronger coordination ability to center metal than that of neutral Ziegler-Natta catalysts because of its relatively stronger electronegativity (Scheme 2). The back-biting coordination around cationic metal center has a broader field and much higher rigidity than that of neutral metal center, which may cause excellent copolymerization performance, larger scope of monomer, and enhanced stereoselectivity, making possible novel high-performance polydiene rubber.



Scheme 2 Structural comparison of active species with neutral metal center and cationic metal center

Recently, we reported the synthesis of a *cis*-1,4 and *trans*-1,4 polybutadiene (PB) multi-block copolymer *via* chain shuttling polymerization using a ternary neodymium sulfonate catalyst system,[28] the excellent results of which stimulated us to further investigate the effects of alkylaluminum type, steric hindrance, the nature of different electron donors, active species, possible mechanism, *etc*., on polymerization behavior of butadiene based on its unique catalytic potential, and then develop tunable neodymium organic sulfonate catalytic systems for controllable polymerization of 1,3-butadiene accordingly.

We report herein the synthesis of neodymium organic sulfonate complexes, $Nd(CF_3SO_3)_3{\cdot}xH_2O{\cdot}y$L (L is an organic electron donating ligand and x or y is the coordination number) with the characteristic of cation-anion ion pair. In the presence of alkylaluminum, such as Al(*i*-Bu)$_3$, AlEt$_3$, and Al(*i*-Bu)$_2$H, these complexes showed high activities and distinguished *cis*-1,4 selectivities for the polymerization of butadiene without halogen source as a catalyst component. Electron donors have been used to increase the solubility of neodymium sulfonate compounds and to enhance polymerization activity. The electric effect and steric hindrance of alkylaluminum and electron donors, the influence of aging time and temperature on polymerization behavior, the microstructure, molecular weight and molecular weight distribution of the resulting polymers have been examined. Meanwhile, the possible active species and the process of the polymerization are also discussed.

EXPERIMENTAL

General Considerations

All the manipulations involving air and moisture sensitive complexes were performed under a dry nitrogen atmosphere. General measurements can be found in electronic supplementary information (ESI). Butadiene (BD) was purchased from Jinzhou Petrochemical Company and purified by passing through two successive columns containing potassium hydroxide and active alumina. Hexane was purchased from Beijing Reagent Factory and dried by heating to reflux over sodium benzophenone ketyl until the solution turned blue and then distilled before use. Al(*i*-Bu)$_3$ and AlEt$_3$ were purchased from Fluka and Al(*i*-Bu)$_2$H was purchased from Akzo Nobel, which were diluted to 2.0 mol·L^{-1} solution by hexane. Antioxidant 264 (2,6-di-*tert*-butyl-*p*-methylphenol) was used as received. Tributyl phosphate (TBP) was purchased from Beijing Chemical Works. Acetylacetone (acac) was purchased from Shanghai Reagents Factory. Tetrahydrofuran (THF) and *iso*-octyl alcohol (IAOH) were purchased from Tianjin Reagents Factory. Trifluoromethanesulfonate was purchased from Shanghai Ever-thriving Trading Co., Ltd.

Synthesis of Neodymium Trifluoromethanesulfonate ($[Nd(H_2O)_9]{\cdot}(CF_3SO_3)_3$)

The compound $[Nd(H_2O)_9]{\cdot}(CF_3SO_3)_3$ was prepared from Nd_2O_3 and CF_3SO_3H in an aqueous slurry following the procedures reported by Harrowfield *et al*.[29]

Synthesis of $Nd(CF_3SO_3)_3{\cdot}H_2O{\cdot}2$acac

$[Nd(H_2O)_9]{\cdot}(CF_3SO_3)_3$ (1.0 g, 1.3 mmol) and acac (0.4 mL, 3.9 mmol) were added into a flask containing 20 mL of THF. The mixture was stirred at 90 °C for 6 h. After removing solvent under vacuum at 90 °C, the desired product (1.13 g,

https://doi.org/10.1007/s10118-019-2196-1

yield: 81.3%) was obtained. Anal. calcd. for $Nd(CF_3SO_3)_3 \cdot H_2O \cdot 2acac$: C 19.72, H 2.04, Nd 18.22; found: C 20.04, H 2.19, Nd 18.46.

Synthesis of $Nd(CF_3SO_3)_3 \cdot H_2O \cdot 2IAOH$

$[Nd(H_2O)_9] \cdot (CF_3SO_3)_3$ (1.0 g, 1.3 mmol) and IAOH (0.6 mL, 3.9 mmol) were added into a flask containing 20 mL THF. The mixture was stirred at 90 °C for 6 h. After removing solvent under vacuum at 100 °C, the desired product (1.32 g, yield: 88.0%) was obtained. Anal. calcd. for $Nd(CF_3SO_3)_3 \cdot H_2O \cdot 2IAOH$: C 26.23, H 4.40, Nd 16.58; found: C 26.58, H 4.61, Nd 16.32.

Synthesis of $Nd(CF_3SO_3)_3 \cdot H_2O \cdot 3TBP$

The compound $Nd(CF_3SO_3)_3 \cdot H_2O \cdot 3TBP$ was prepared according to the literature.[28]

Synthesis of $Nd(CF_3SO_3)_3 \cdot 0.5H_2O \cdot 3TBP$

The compound $Nd(CF_3SO_3)_3 \cdot 0.5H_2O \cdot 3TBP$ was prepared according to the literature.[28] Anal. calcd. for $Nd(CF_3SO_3)_3 \cdot 0.5H_2O \cdot 3TBP$: C 33.47, H 5.91, Nd 10.31; found: C 34.03, H 6.21, Nd 10.75.

Synthesis of $Nd(CF_3SO_3)_3 \cdot 3H_2O \cdot 3TBP$

The compound $Nd(CF_3SO_3)_3 \cdot 3H_2O \cdot 3TBP$ was prepared according to the literature.[28] Anal. calcd. for $Nd(CF_3SO_3)_3 \cdot 3H_2O \cdot 3TBP$: C 32.43, H 6.07, Nd 9.99; found: C 32.98, H 6.41, Nd 10.35.

Catalyst Preformation

Catalysts were prepared in 10 mL dried and nitrogen-purged bottles capped with rubber plugs. Neodymium trifluoromethanesulfonate complex in a hexane suspension and alkylaluminum in a hexane solution were added successively, and then the mixture ($[Nd] = 2.0 \times 10^{-2}$ mol·L^{-1}) was aged at 50 °C for 6 h.

Polymerization Procedures

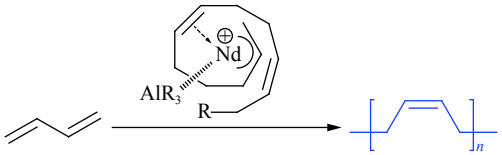
A detailed polymerization procedure is described as following as a typical example. 1,3-Butadiene was condensed into a glass vessel with volume grading, cooled at −10 °C, and transfered into a flask containing hexane. 1,3-Butadiene at a concentration of 0.1 g/mL was divided *via* a distributor into 30 mL oxygen- and moisture-free ampule bottles capped with rubber plugs, respectively, 20 mL for each. The ampule bottles were heated up to 50 °C in a water bath equipped with vibration motor and then the catalyst prepared was injected by syringe into each ampule, respectively. Polymerization was performed at 50 °C for 5 h, then terminated by adding 10 mL of ethanol containing 2,6-di-*tert*-butyl-*p*-methylphenol (1%) as a stabilizer. The polymer was coagulated, repeatedly washed with ethanol, cut into small pieces, and finally dried under vacuum at 40 °C to constant weight. The polymer yields were determined by gravimetric analysis.

RESULTS AND DISCUSSION

Polymerization Behavior with Variation of Sulfonate Ligand, Electron Donors, and Alkylaluminum

Acac, IAOH, and TBP were employed as electron donors to investigate the polymerization behavior of BD in the presence of three types of alkylaluminum ($Al(i\text{-}Bu)_2H$, $Al(i\text{-}Bu)_3$, and $AlEt_3$), which is summarized in Table 1. Configuration of sulfonate ligand imposed significant influence on the yield of polymerization by varying the electronic environment (Table 1, entries 3 and 4). $Nd(CF_3SO_3)_3 \cdot H_2O \cdot 2acac$ was found to be more active than $Nd(3\text{-}NBSO_3)_3 \cdot 2acac$ (3-$NBSO_3$: *m*-nitrobenzenesulfonate). Structurally, nitro was an electron-withdrawing group which greatly lowered the electron density of π-bond on the benzene ring. Then the electron would offset in the direction of electrophilic oxygen atom, which reduced the electronegativity of *m*-nitrobenzene ligand. Thus, the $CF_3SO_3^-$ ligand with relatively strong electronegativity had a more robust capacity to move the electron away from the neodymium ion than that of 3-$NBSO_3^-$ ligand, which increased the ability of attracting electron of the active metal center and the activity

Table 1 Butadiene polymerization results based on $Nd(CF_3SO_3)_3$ catalysts [a]



Entry	Compounds	Alkylaluminum	Yield (%)	*cis*-1,4 [b] (%)	*trans*-1,4 [b] (%)	1,2- [b] (%)	M_w [c] × 10^{-4}	PDI [c]
1	$Nd(CF_3SO_3)_3 \cdot H_2O \cdot 2acac$	$Al(i\text{-}Bu)_2H$	69.7	98.7	1.0	0.3	92.6	8.65
2		$Al(i\text{-}Bu)_3$	7.0	99.2	0.7	0.1	269.9	3.11
3		$AlEt_3$	32.1	98.1	1.2	0.7	169.1	2.36
4	$Nd(3\text{-}NBSO_3)_3 \cdot 2acac$ [d]	$AlEt_3$	17.1	70.8	26.5	2.7	131.6	5.76
5	$Nd(CF_3SO_3)_3 \cdot H_2O \cdot 2IAOH$	$Al(i\text{-}Bu)_2H$	19.8	98.8	1.0	0.2	89.1	8.38
6		$Al(i\text{-}Bu)_3$	6.3	98.3	1.5	0.2	155.9	2.60
7		$AlEt_3$	28.7	96.8	1.8	1.4	127.9	2.52
8	$Nd(CF_3SO_3)_3 \cdot H_2O \cdot 3TBP$	$Al(i\text{-}Bu)_2H$	53.9	99.9	0.1	–	85.9	9.91
9		$Al(i\text{-}Bu)_3$	31.1	99.9	0.1	–	190.0	3.99
10		$AlEt_3$	85.7	92.1	7.1	0.8	158.5	6.59
11	$Nd(CF_3SO_3)_3 \cdot 0.5H_2O \cdot 3TBP$	$Al(i\text{-}Bu)_3$	15.2	99.9	0.1	–	244.6	2.55
12	$Nd(CF_3SO_3)_3 \cdot 3H_2O \cdot 3TBP$	$Al(i\text{-}Bu)_3$	25.2	98.9	0.8	0.3	214.7	3.85

[a] Polymerization conditions: in hexane at 50 °C for 5 h, [Al]/[Nd] = 20, $[Nd] = 2 \times 10^{-5}$ mol/mL, [Nd]/[BD] = 8×10^{-5} mol/mol; [b] The microstructure was determined by FTIR; [c] Determined by GPC (THF, PSt calibration); [d] Previous research on polybutadiene in our group[30]

https://doi.org/10.1007/s10118-019-2196-1

of polymerization. Compared to other catalytic systems, $Nd(CF_3SO_3)_3·H_2O·3TBP$ catalytic system could achieve higher yield, indicating that the flexible ligand was more conducive to the catalytic activity. Besides, $Nd(CF_3SO_3)_3·H_2O·3TBP$ had good solubility in hexane by activated with alkylaluminum while the other two catalytic systems were completely insoluble in hexane and formed precipitation when activated by alkylaluminum. Thus, only a few Nd atoms located on the surface of alkylated catalytic system could take part in the reaction to form active species, which resulted in the relatively low activities.[31] It was obvious that $Nd(CF_3SO_3)_3·H_2O·3TBP$ was more facile to be alkylated, thereby possessing more active sites and exhibiting higher activity.

In addition, the nature of alkylaluminum could also have an impact on polymerization behavior, which gave rise to the difference in catalytic activity and *cis*-1,4- selectivity. As shown in Table 1, when the bulky $Al(i\text{-}Bu)_2H$ or $Al(i\text{-}Bu)_3$ was applied as an activator, all of the three alkylated catalytic systems exhibited high *cis*-1,4- selectivity (up to 99.9%) in the polymerization of BD, which was presented by ^{13}C-NMR spectroscopy in Fig. 1, while the Nd-based compound/$AlEt_3$ catalytic system showed slightly lower *cis*-1,4- selectivity (92.1%−98.1%). It is speculated that the alkyl groups in cat. equivalent alkylaluminum had moved to the ends of polymer chain by coordination and insertion reactions and no longer played an impact on the steric hindrance around the metal active sites. However, the excess alkylaluminum could continue to react with the metal center and form novel active species that coordinated with alkyl groups. Thus, the steric hindrance of metal active sites could still be tunable by the size of the alkylaluminum. Gel permeation chromatography (GPC) curves show that the molecular weight of the resulting polymers consisted with the chain transfer affinities of the alkylaluminum, decreasing in the order of $Al(i\text{-}Bu)_3$ > $AlEt_3$ > $Al(i\text{-}Bu)_2H$ (Fig. 2). The Nd-based compound/$AlEt_3$ or $Al(i\text{-}Bu)_3$ catalytic system could yield polymers with comparatively narrow molecular weight distribution. In contrast, in the presence of $Al(i\text{-}Bu)_2H$, the resulting PBD had bimodal and broader molecular weight distribution, consistent with the predominance of multiple-sites catalytic species, which indicated $Al(i\text{-}Bu)_2H$ was a much more active chain transfer agent than the hydrogen-free alkylaluminum reagents were.[31]

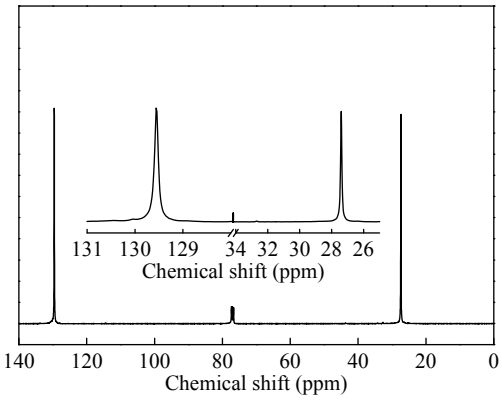


Fig. 1 The ^{13}C-NMR spectrum of polybutadiene with $Nd(CF_3SO_3)_3·H_2O·3TBP$-$Al(i\text{-}Bu)_2H$ catalyst (Table 1, entry 8)

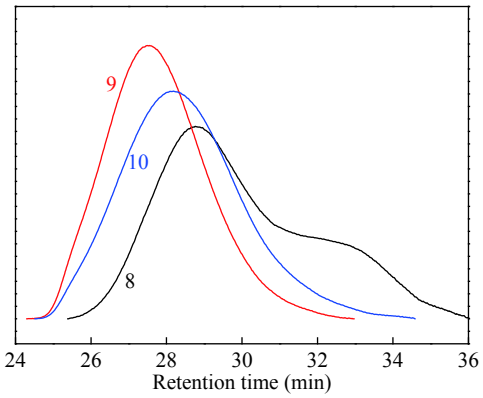


Fig. 2 GPC profiles of polybutadienes (Table 1, entries 8−10)

The impact of water content on polymerization behaviour, such as yield, *cis*-1,4- selectivity, M_w, and polydispersity was also investigated (Table 1, entries 9, 11, and 12). It was found that the addition of limited content of water produced a significant increase in yield from 15% to 31%, along with lower M_w and broader polydispersity as the molar ratio of water to Nd ($[H_2O]/[Nd]$) increased from 0.5 to 1. The *cis*-1,4-content was free from the influence of water (99.9%). However, with the further increase of water ($[H_2O]/[Nd]$ raised from 1 to 3), the yield decreased, accompanied with slightly higher M_w, narrower PDI and reduced *cis*-1,4-content (98.9%). Quirk *et al.* reported that water was necessary for the optimum NdV_3/EASC/DIBAH catalyst system in polymerization of BD and the best molar ratio of $[H_2O]/[Nd]$ equal to 0.11.[32] They speculated that water reacted with DIBAH and formed an alumoxane-type species. In addition, Carbonaro *et al.* reported that the addition of a certain amount of water was beneficial to catalytic activity in Nd-catalyzed polymerizations of butadiene.[33] According to previous reports, alumoxanes $(-^{i}Bu\text{-}Al\text{-}O-)_n$ may be generated by the interaction between limited amounts of water and $Al(i\text{-}Bu)_3$ in this work, which could increase the concentration of active center and accelerate formation of the active species to promote the polymerization. Meanwhile, it may give rise to the increase of chain transfer reactions, with lower M_w and broader PDI. However, it was speculated that excess water may result in a relatively lower $Al(i\text{-}Bu)_3$ concentration and simultaneously interact with Nd species, which may not be sufficient to promote alkylation of the Nd species to generate the active centers.

Kinetics of Polymerization

In view of the good solubility of $Nd(CF_3SO_3)_3·H_2O·3TBP$/$Al(i\text{-}Bu)_3$ in hexane and the highest *cis*-1,4- selectivity (99.9%) in the polymerization of BD with relatively narrow PDI, further investigation was carried out based on this catalytic system, which is shown in Table 2. The effects of the molar ratio of [Al]/[Nd] on BD polymerization was firstly investigated. It is shown that as [Al]/[Nd] gradually increased from 10 to 40, yield increased from 35.8% to 76% (Fig. 3 and Table 2, entries 1−4), which may be due to the accelerated formation of the active species. When [Al]/[Nd] was increased up to 20, the yield of polymerization did not grow substantially any more, and *cis*-1,4- selectivity could be maintained at 99.5%. Therefore, a molar ratio of [Al]/[Nd] at

Table 2 Butadiene polymerization based on $Nd(CF_3SO_3)_3$-Al(*i*-Bu)$_3$ catalyst [a]

Entry	[Al]/[Nd]	Aging T (°C)	Aging time (h)	Polymerization T (°C)	Yield (%)	*cis*-1,4 (%)	*trans*-1,4 (%)	1,2- (%)	$M_w \times 10^{-4}$	PDI
1	10	50	1.5	50	35.8	99.6	0.2	0.2	289.9	2.67
2	20	50	1.5	50	67.9	99.5	0.2	0.3	207.6	3.87
3	30	50	1.5	50	71.6	99.1	0.1	0.7	121.3	4.90
4	40	50	1.5	50	76.0	99.0	0.1	0.8	125.9	7.49
5	20	0	1.5	50	51.6	99.2	0.1	0.7	161.4	6.97
6	20	30	1.5	50	54.6	99.0	0.2	0.8	160.2	4.91
7	20	40	1.5	50	60.3	98.9	0.2	0.9	203.7	4.29
8	20	70	1.5	50	75.5	99.0	0.2	0.8	163.8	2.35
9	20	50	0.5	50	64.5	99.0	0.2	0.8	207.2	4.45
10	20	50	3	50	70.7	98.7	0.5	0.8	187.7	3.29
11	20	50	6	50	62.7	98.6	0.5	0.9	159.6	2.66
12	20	50	1.5	20	47.6	99.8	0.1	0.1	166.7	2.28
13	20	50	1.5	40	55.9	99.1	0.2	0.7	320.0	2.72
14	20	50	1.5	60	70.4	97.7	1.4	0.9	91.8	4.33

[a] Polymerization conditions: [Nd]/[BD] = 8×10^{-5} mol/mol, [Nd] = 2×10^{-5} mol/mL

20 was sufficient to reach a high activity in BD polymerization *via* $Nd(CF_3SO_3)_3 \cdot H_2O \cdot 3TBP/Al(i\text{-}Bu)_3$ catalytic system, which was used in further investigation. As shown in Fig. 4, [Al]/[Nd] could severely impact the molecular weight of the resulting polymer. As [Al]/[Nd] increased from 10 to 40, the M_w curve of the polymer decreased to lower molecular weight region, with a broader molecular weight distribution (2.67−7.49), and even displayed overlapping double peaks in GPC curves when [Al]/[Nd] increased to 40, which revealed that the alkyl aluminum not only played a role of an activator but also served as a chain transfer agent at excessive amounts.

In addition, the aging temperature of the $Nd(CF_3SO_3)_3 \cdot H_2O \cdot 3TBP/Al(i\text{-}Bu)_3$ catalytic systems also had significant influence on the yield and M_w of the resulting polymer (Table 2, entries 2 and 5−8). Yield raised sharply from 51.6% to 75.5% when the aging temperature increased from 0 °C to 70 °C, accompanied with high *cis*-1,4- selectivity (> 98.9%), increased M_w, and decreased PDI (Figs. 5 and 6). It was speculated that the aging temperature resulted in the

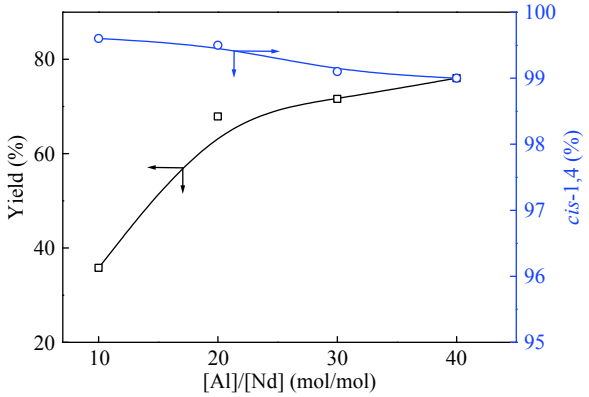


Fig. 3 Effect of [Al]/[Nd] ratio on yield and *cis*-1,4- content (Table 2, entries 1−4)

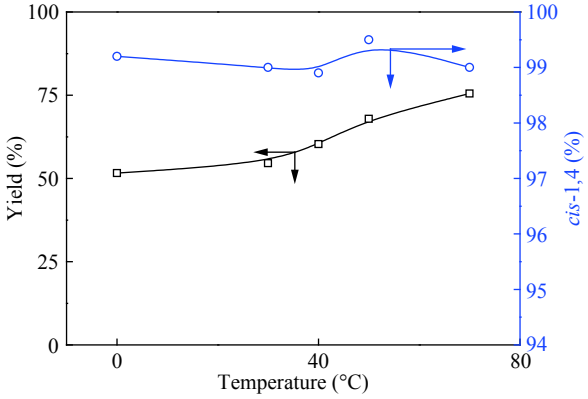


Fig. 5 Effect of aging temperature on yield and *cis*-1,4- content (Table 2, entries 2 and 5−8)

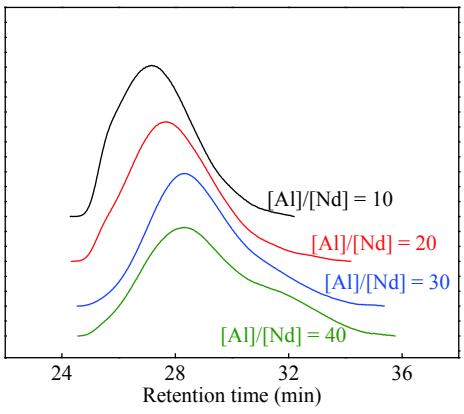


Fig. 4 GPC profiles of polybutadienes with different [Al]/[Nd] = 10, 20, 30, and 40 (Table 2, entries 1−4)

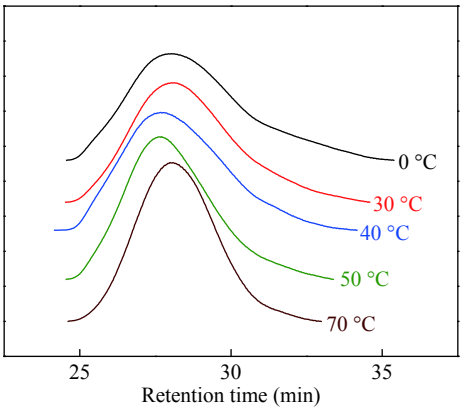


Fig. 6 GPC profiles of polybutadienes from different aging temperatures at 0, 30, 40, 50, and 70 °C (Table 2, entries 2 and 5−8)

https://doi.org/10.1007/s10118-019-2196-1

formation of a more active and homogeneous active species. In view of the highest M_w (2×10^6) and *cis*-1,4- selectivity (99.5%) when the aging temperature was 50 °C, thus this reaction condition was the optimum for further research.

Then a series of polymerization reactions were conducted to examine the effect of the aging time from 0.5 h to 6 h on BD polymerization (Table 2, entries 2 and 9−11). The highest yield of 70.7% was observed when the aging time was 3 h and then decreased to 62.7% at 6 h. In addition, a gradual decline of M_w and PDI of the polymer with the increase of aging time from 0.5 h to 6 h can be seen in Fig. 7. It is reasonable to infer that the increasing aging time might have resulted in the transformation of Nd-allyl bond to a Nd-C σ-bond and thus reduced the yield of the reaction (Fig. 8).[34]

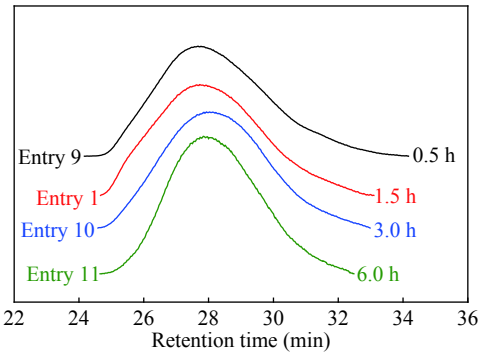


Fig. 7 GPC profiles of polybutadienes (Table 2, entries 1 and 9−11)

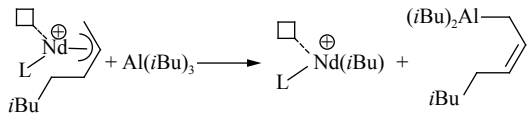


Fig. 8 Reformation of the Nd-allyl bond to a Nd-C σ-bond with prolonged aging time

The temperature of the polymerization had a great effect on the yield, M_w, and selectivity (Table 2, entries 2 and 12−14). When BD polymerization by the $Nd(CF_3SO_3)_3 \cdot H_2O \cdot 3TBP/Al(i\text{-}Bu)_3$ system was performed at low temperature of 20 °C, high *cis*-1,4- selectivity (99.8%) and relatively narrow PDI (2.28) of the polymer were observed (Table 2, entry 12). PDI increased from 2.28 to 4.22 with the increase of the temperature. In addition, M_w of the polymer rose from 1.7×10^6 to 3.2×10^6 when the temperature increased from 20 °C to 40 °C, and then decreased to 0.9×10^6 at 60 °C, which might be caused by the deactivation of the active species and enhanced chain transfer reaction at high temperature. It is noteworthy that the temperature of polymerization directly impacted the microstructure of the polymers.[35] Higher temperatures could result in the generation of the PBD with relatively high *trans*-1,4- and 1,2- contents. Based on the previous research,[36–40] it can be supposed that the "anti" configuration related to *cis*-1,4- selectivity was greatly affected by the temperature of polymerization. With the increase of temperature, the less stable "anti" configuration was facile to transform into more thermodynamically stable "syn" configuration related to *trans*-1,4- and 1,2- selectivity.

Possible Process and Active Species of Polymerization

To our knowledge, there are several mechanism studies on Nd-based polymerization of BD,[35,40–44] such as the studies reported by Hsieh and Iovu's groups. According to these investigations, the formation of the cationic active center of rare-earth metal such as Nd will accelerate the coordination and insertion of the monomer, and the activated Nd-based compound will be converted into an Nd-allyl compound after the first insertion of BD monomer. Fig. 9 presents the possible process of the formation of Nd-based sulfonates cationic active species, coordination and insertion in BD polymerization. In this study, it can be observed that the active center of the chain growth of Nd organic sulfonates catalytic system was highly sensitive to steric requirement of alkylaluminum. When the center metal was activated by a

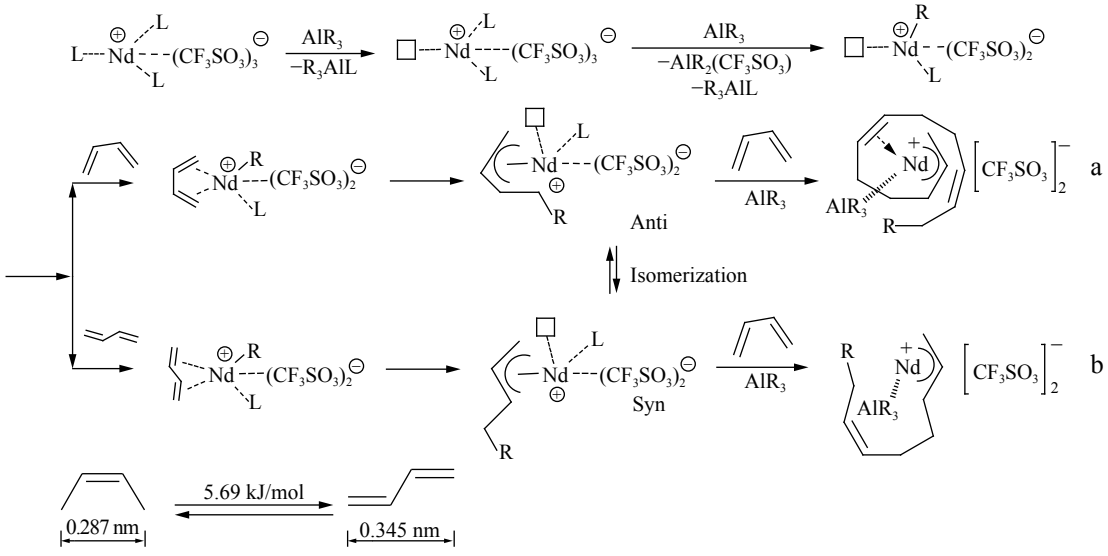


Fig. 9 Possible process of BD polymerization by Nd organic sulfonate cationic species (a: *cis*-regulatory coordination; b: *trans*-regulatory coordination)

https://doi.org/10.1007/s10118-019-2196-1

bulk alkylaluminum such as Al(*i*-Bu)$_3$, the butadiene monomer could insert into the growing chain with the smaller *cis*-regulatory configuration (0.287 nm), and high *cis*-1,4-PBD would be obtained (Fig. 9, process a). By contrast, when the relatively small alkylation reagents, such as AlEt$_3$, served as cocatalyst, the butadiene monomer would insert into the growing chain by *cis*-/*trans*- (0.345 nm) regulatory configuration, which resulted in the generation of *cis*-1,4-PBD containing a fraction of *trans*-1,4-PBD (Fig. 9, process b). In addition, it is generally accepted that *cis*-regulatory coordination is kinetically favored and *trans*-regulatory coordination is thermodynamically preferred.[45] The high temperature may cause isomerization of the active species from "*anti*" to "*syn*". It is noted that the terminal double bonds of the growing chain had strong capability of coordination to the cationic central metal in process a, which is called the back-biting coordination mechanism.[44] The monomer would be directed to the fixed structure of the cationic active center with a single configuration, which contributed to the formation of high *cis*-1,4-PBD.

CONCLUSIONS

In summary, a series of neodymium organic sulfonate complexes possessing characteristics of cation-anion ion pair can form cationic active species in the presence of alkylaluminum, affording the polymers with distinguished *cis*-1,4- selectivities (up to 99.9%) in the polymerization of butadiene. The electropositivity and steric hindrance of metal active sites can be adjusted by the variation of the ligands and alkylaluminum in order to achieve high *cis*-1,4-PBD. In addition, a precise control of the yield, molecular weight, and PDI of the resulting polymer can be conducted with the adjustment of [Al]/[Nd], aging time, aging temperature, and polymerization temperature. The active species and the possible process of polymerization have also been speculated. These neodymium organic sulfonate systems may provide more insights and possible strategies for the development of rare earth compounds with inherent characteristic of cation-anion ion pair for novel diene polymerization.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-019-2196-1.

ACKNOWLEDGMENTS

We acknowledge the National Natural Science Foundation of China (Nos. 51473156 and 51873203), Key Projects of Jilin Province Science and Technology Development Plan (Nos. 20180201086GX and 20160204028GX).

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