



Highly 3,4-selective living polymerization of 2-phenyl-1,3-butadiene with amidino N-heterocyclic carbene ligated rare-earth metal bis(alkyl) complexes

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Complete List of Authors:	Yao, Changguang; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, State Key Laboratory of Polymer Physics and Chemistry Xie, Hongyan; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, State Key Laboratory of Polymer Physics and Chemistry Cui, Dongmei; Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 1State Key Laboratory of Polymer Physics and Chemistry
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ARTICLE

Highly 3,4-selective living polymerization of 2-phenyl-1,3-butadiene with amidino N-heterocyclic carbene ligated rare-earth metal bis(alkyl) complexes

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Changuang Yao,^{a,b} Hongyan Xie^{a,b} and Dongmei Cui*^a

A series of amidino N-heterocyclic carbene ligands supported rare-earth metal bis(alkyl) complexes (2,6- $R^1_2C_6H_3N=CR^2NCH_2CH_2(NCHCHN(C_6H_2Me_3-2,4,6)C)Ln(CH_2SiMe_3)_2$ [$R^1 = 'Pr, R^2 = Ph, Ln = Lu$ (**1a**); $R^1 = 'Pr, R^2 = Ph, Ln = Sc$ (**1b**); $R^1 = 'Pr, R^2 = 'Bu, Ln = Lu$ (**2a**); $R^1 = Me, R^2 = Ph, Ln = Lu$ (**3a**)] were synthesized and characterized by NMR spectrum. On activation with $[(Ph_3C)][(B(C_6F_5)_4)]$, complexes **1a**, **2a** and **3a** exhibited high activities and high 3,4-selectivities (96.9%) for the polymerization of 2-phenyl-1,3-butadiene in a living mode to afford new plastic polydienes with high glass-transition temperatures (44.3~56.1 °C). The 3,4-selectivity decreased with increasing the polymerization temperature (25~60 °C), but increased with polarity of polymerization solvent in the order of chlorobenzene > toluene > cyclohexane. In contrast, complex **1b** was almost inert for the polymerization of 2-phenyl-1,3-butadiene owing to its steric bulkiness.

Introduction

It is well known that the versatile properties of polymeric materials are closely related to their microstructures, of which the regularity as the most critical aspect for determining polymer properties and applications has attracted the mostly wide concern¹. Therefore the specific selective coordination polymerization to precisely control stereo-regularity of polymer chains whenever relating to an olefinic monomer (at least three stereoregularities will be generated), has been a long-standing research project since the emergence of Ziegler-Natta coordination catalysts². Polydienes as one subcategory of polyolefins exhibit more isomeric structures than poly- α -olefins because they involve more complicated regio- and stereotacticity^{3,4}, which has sparked the research interest of polymer chemists for more than half a century.

2-Phenyl-1,3-butadiene (2-PB) is such a unique monomer, since it can be considered as either an α -vinyl-substituted styrene or a 2-phenyl-substituted 1,3-butadiene. Theoretically, 2-PB can be transferred to a plastic or an elastomer depending on whether the obtained P(2-PB) possesses 3,4-/1,2- (isotactic, syndiotactic or

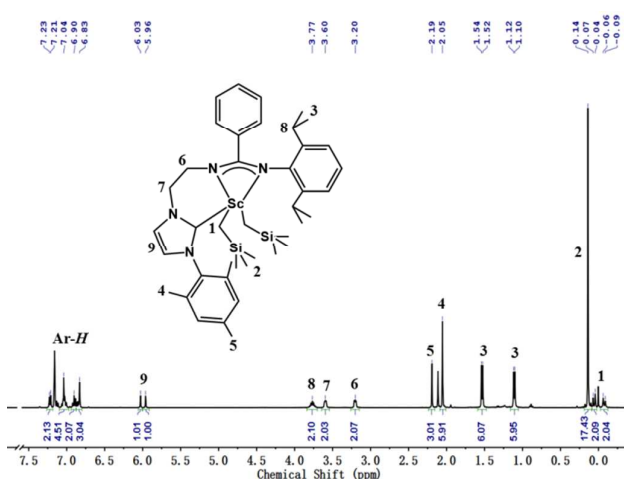
atactic) or *cis*-/*trans*-1,4-microstructures⁵. To date many studies on the polymerization of 2-PB have been reported, most of which relate to the ionic polymerization mechanism. Ambrose⁶ and Suzuki⁷ reported the living anionic polymerization of 2-PB with high *cis*-1,4 selectivity over a wide range of polymerization temperatures (-78~60 °C). The cationic polymerization of 2-PB reported by Hinashimura⁸ and Hasegawa⁹ also provided a 1,4-regulated product, but about half double bonds in the polymer main chains underwent further the cyclization reaction. The highly *cis*-1,4 (100%) regulated P(2-PB) was accessed by radical emulsion polymerization using the catalyst H_2O_2/Fe^{2+} in the presence of sodium pyrophosphate reported by Brosse¹⁰. Comparatively, the coordination polymerization of 2-PB was less investigated, which afforded the *cis*-1,4 enriched product reported by Vessel¹¹, Bruzzone¹² and Longo¹³ using titanium-based Ziegler-Natta catalysts. Noteworthy is that the polymerization of 2-PB always gives a 1,4-structure despite of the catalysts employed¹⁴, since for this bulky monomer the *cis*- η^4 coordination mode might be spacially preferred than 3,4- η^2 mode.

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin street, Changchun 130022, China. Fax: +86 431 85262774; Tel: +86 431 85262773; E-mail: dmcui@ciac.ac.cn

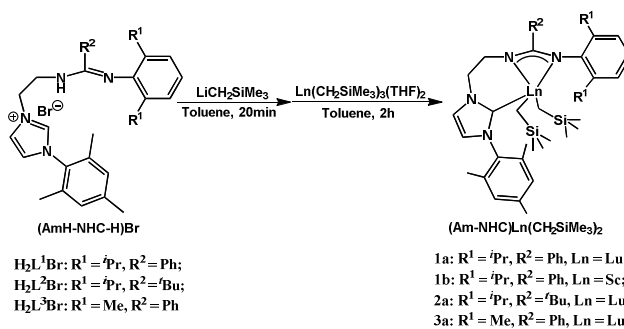
^b University of Chinese Academy of Sciences, Changchun Branch, Changchun 130022, China.

† Electronic Supplementary Information (ESI) available: ¹H NMR spectra of complexes **2a** and **3a**; ¹H and ¹³C NMR spectra of 2-phenyl-1,3-butadiene and selected polymer samples; DSC and GPC curves of selected polymer samples; polymerization data and conversion-time curve. See DOI: 10.1039/x0xx00000x

On the other hand, N-heterocyclic carbene (NHC) ligands have been widely used to stabilize various transition metals due to its low toxicity and strong σ -donor characters. The first example of a neutral lanthanide-NHC complex, $[\text{Y}^{\text{tBu}}(\text{O})\text{CHC}(\text{O})^{\text{tBu}}]_3(\text{C}\{\text{NMeCMe}_2\})_3^{15}$, was obtained by Arduengo et al. in 1994. Until 2003, Arnold et al. reported the first N-functionalized NHC yttrium complex, $[\text{tBuNCH}_2\text{CH}_2(\text{NCHCHN}^{\text{tBu}})\text{C}]\text{Y}[\text{N}(\text{SiMe}_3)_2]_2^{16}$, which could catalyze the ring-opening polymerization of *rac*-lactide to produce highly heterotactic poly(*rac*-lactide) with low polydispersity. Subsequently, they obtained a series of alkoxy and amido NHC ligands stabilized lanthanide complexes.¹⁷ Shen and co-workers prepared a trisphenoxo-tethered NHC supported yttrium complex and the lanthanide bromides bearing the salicylaldiminato functionalized NHC ligand.¹⁸ Okuda et al. documented several sterically hindered neutral and N-functionalized NHC rare-earth metal complexes and explored their property towards C–H bond activation.¹⁹ Xiao-Bing Lu et al. synthesized a kind of neutral scandium-NHC complexes, $[\{2,6\text{-C}_6\text{H}_3\text{R}_2\text{NCH}\}_2\text{CSc}(\text{CH}_2\text{SiMe}_3)_3]$, which showed excellent activities for the polymerization of 1-octene and copolymerization of 1-hexene with 1,5-hexadiene.²⁰ Our group synthesized a series of CCC-pincer bis(carbene) lanthanide dibromides²¹ and indenyl/fluorenyl,²² amidinato²³ and alkoxy²⁴ functionalized NHC ligated rare-earth metal bis(alkyl) complexes, and systematically investigated their (co)polymerization behaviours towards isoprene, butadiene derivatives, ethylene/norbornene and ethylene/ α -olefins. Herein, we report the synthesis and characterization of the lanthanide bis(alkyl) complexes bearing amidino N-heterocyclic



with equivalent rare-earth metal tris(alkyl) $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ ($\text{Ln} = \text{Sc}, \text{Lu}$), via protonolysis, to give the rare-earth-metal bis(alkyl) complex $(\text{Am-NHC})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2$ [$\text{R}^1 = i\text{Pr}, \text{R}^2 = \text{Ph}, \text{Ln} = \text{Lu}$ (**1a**); $\text{R}^1 = i\text{Pr}, \text{R}^2 = \text{Ph}, \text{Ln} = \text{Sc}$ (**1b**); $\text{R}^1 = i\text{Pr}, \text{R}^2 = t\text{Bu}, \text{Ln} = \text{Lu}$ (**2a**); $\text{R}^1 = \text{Me}, \text{R}^2 = \text{Ph}, \text{Ln} = \text{Lu}$ (**3a**)]. The pure complexes were isolated by recrystallizing from a mixture of toluene and hexane at -30°C . In the ^1H NMR spectra (Fig. 1 and S Figs. 3 and 4), the characteristic resonance of the ylidene protons of the ligands (10.38 ppm for $\text{H}_2\text{L}^1\text{Br}$, 10.02 ppm for



carbene ligands. For the first time, the highly 3,4-selective coordination polymerization of 2-PB has been achieved by using these rare-earth metal complexes, particularly in living fashion.

Results and Discussion

Synthesis and characterization of rare-earth metal bis(alkyl) complexes

In the precious work, we reported the amidino N-heterocyclic carbene ligand ($\text{H}_2\text{L}^1\text{Br}$) and its lutetium bis(alkyl) complex (**1a**), which showed excellent catalytic properties for isoprene polymerization.²³ Using the same method, another two ligands $\text{H}_2\text{L}^2\text{Br}$ and $\text{H}_2\text{L}^3\text{Br}$ were synthesized in this study. A general synthetic route for the amidino N-heterocyclic carbene ligands supported lanthanide bis(alkyl) complexes is shown in Scheme 1. The imidazolium bromide (AmH-NHC-H)Br ($\text{Am} = 2,6\text{-R}^1_2\text{C}_6\text{H}_3\text{N}=\text{CR}^2\text{NCH}_2\text{CH}_2$) was treated with one equiv of $\text{LiCH}_2\text{SiMe}_3$ to afford the ethylene-bridged amidino N-heterocyclic carbene ligand AmH-NHC, which further reacted

$\text{H}_2\text{L}^2\text{Br}$ and 10.28 ppm for $\text{H}_2\text{L}^3\text{Br}$) disappeared, suggesting the completeness of the reaction. The methylene protons of $\text{Ln}-\text{CH}_2\text{SiMe}_3$ species are complicated showing as two discrete AB spins in the upfield regions ($\delta -0.09/-0.06$ and $0.04/0.07$ for complex **1b**; $\delta -1.08/-1.05$ and $-0.88/-0.85$ for complex **2a**; $\delta -0.90/-0.87$ and $-0.68/-0.65$ for complex **3a**), which displayed as sharp singlets in the precursors $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$, suggesting the successful formation of the bis(alkyl) complexes **1b**, **2a** and

Scheme 1. General synthetic route for complexes 1-3.

Fig. 1 ^1H NMR spectrum of complex **1b**.

3a through alkyl abstraction. Since the ^1H NMR spectra of complexes **1b**, **2a** and **3a** have the similar topology to that of complex **1a**, we concluded that the overall molecular structure of these complexes is a solvent-free monomer analogous to **1a**.

Table 1 Polymerization of 2-PB by using the binary catalytic system (Am–NHC)Ln(CH₂SiMe₃)₂/[Ph₃C][B(C₆F₅)₄] under various conditions^a

entry	cat.	[2-PB]/[Lu]	T _p (°C)	time (h)	yield (%)	3,4- ^b (%)	M _{n, calcd} ^c × 10 ⁻⁴	M _{n, measd} ^d × 10 ⁻⁴	M _w /M _n ^d	T _g ^e (°C)
1	1a	200	25	4	>99	96.7	2.60	3.03	1.26	52.9
2	1b	200	25	4	-	-	-	-	-	-
3	2a	200	25	4	>99	96.6	2.60	3.40	1.33	51.7
4	3a	200	25	3	>99	92.2	2.60	3.58	1.43	48.9
5	1a	100	25	6	>99	96.9	1.30	1.84	1.28	53.2
6	1a	150	25	6	>99	96.9	1.95	2.41	1.27	53.2
7	1a	250	25	4	>99	96.6	3.25	3.47	1.27	53.1
8	1a	300	25	4	>99	96.3	3.91	4.72	1.32	52.5
9	1a	400	25	4	>99	95.9	5.21	7.08	1.27	52.4
10	1a	200	40	3	>99	93.2	2.60	3.50	1.66	51.9
11	1a	200	60	2	>99	91.5	2.60	3.89	1.61	50.8
12	1a	200	-20	24	42.3	96.9	1.10	3.67	1.17	56.1
13 ^f	1a	200	25	4	88.5	95.6	2.30	2.56	1.26	47.4
14 ^g	1a	200	25	4	76.9	93.2	2.01	2.38	1.23	44.3

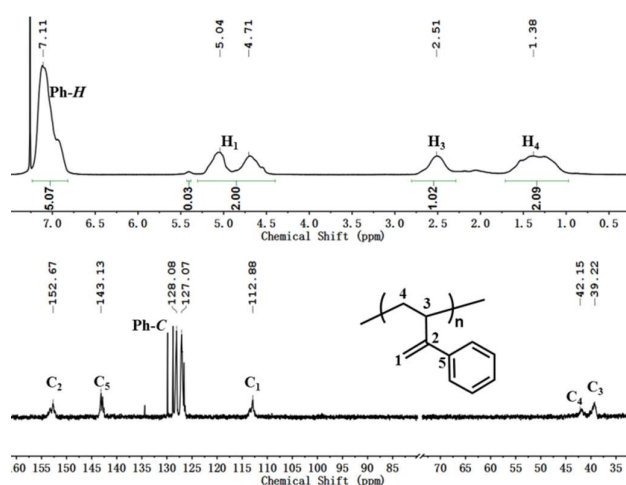
^aConditions: Ln 10 μmol, [Ph₃C][B(C₆F₅)₄] 10 μmol, chlorobenzene 2 mL. ^bDetermined by ¹H and ¹³C NMR spectroscopy in CDCl₃. ^cCalculated by ([2-PB]/[Ln]) × 130.19 × yield. ^dDetermined by GPC in THF at 40 °C against polystyrene standard. ^eMeasured by DSC. ^fToluene as solvent. ^gCyclohexane as solvent.

Polymerization of 2-phenyl-1,3-butadiene.

The binary catalytic system **1a**/[Ph₃C][B(C₆F₅)₄] showed high activity and high 3,4-selectivity for the polymerization of isoprene in a livingness mode²³. To explore whether or not this catalytic system has the similar properties for the polymerization of other conjugated diene derivatives, we performed the polymerization of 2-PB at room temperature with chlorobenzene as the solvent. As expected, the binary system exhibited high activity towards 2-PB polymerization (Table 1, entry 1). In the ¹H NMR spectrum of the obtained P(2-PB) sample (Fig. 2), the resonances at δ 5.04, 4.71 ppm are ascribed to the pendent vinyl protons of the 3,4-regularity and the resonances at 5.40 ppm is assignable to the internal olefinic protons of the 1,4-regularity. The integral intensity ratio of the the vinyl protons and the internal olefinic protons is 2: 0.03, suggesting an as high as 96.7% 3,4-selectivity of this catalytic system. Meanwhile the ratio of the resonances for phenyl, olefinic and aliphatic protons is 5:2:3, meaning the absence of the cyclization, etc., side reactions in the polymerization process. The signals at δ 152.67 and 112.88 ppm in the ¹³C NMR spectrum (Fig. 2) corresponding to the olefinic carbons of 3,4-units are both multiple, indicative of stereo-irregularity of the resulting P(2-PB). This represented the first 3,4-tactic P(2-PB). To the best of our knowledge, the 3,4-selectivity of the polymerization of conjugated diene based on rare-earth metal catalyst is closely related to the steric hindrance of the metal center. The sterically crowded complex will compel 1,3-diene monomer to coordinate to the central

metal in the η² mode. The coordinated monomer is attacked by the Ln–R active species to form a four-center metallocycle transition state, consequently leading to the 3,4-structured polymer chain formation.

In order to systematically investigate the influence of steric hindrance around the active metal center on the catalyst behaviour, the other three complexes **1b**, **2a** and **3a** based on Lu and Sc metals bearing different sizes of substituents were synthesized, which catalysis was studied under the same polymerization conditions (Table 1, entries 2, 3 and 4). As can

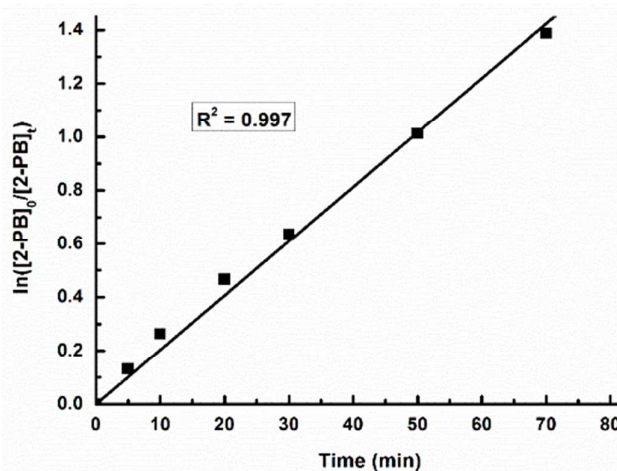
**Fig. 2** ¹H and ¹³C NMR spectra of 3,4-P(2-PB). (Table 1, entry 1).

be seen, the lutetium complex **2a** activated by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ showed high activity for the polymerization of 2-PB by transferring 200 equiv of 2-PB within 4 h in high 3,4-selectivity (96.4%) at room temperature comparable to that of **1a**; while the lutetium complex **3a** bearing the less steric substituent provided a much higher activity that a complete conversion was achieved in 3 h, suggesting that the less crowded environment around the active species preferred the bulky 2-PB monomer coordinating to accelerate the polymerization, which, naturally, wasn't facilitate the 3,4-selectivity (92.2%). Therefore switching to the small scandium central metal ($\text{Lu}^{3+} = 0.861\text{\AA}$ vs $\text{Sc}^{3+} = 0.745\text{\AA}$), the binary catalytic system

increased to 88.2% when using compound $(\text{Flu-NHC})\text{Lu}(\text{CH}_2\text{SiMe}_3)_2$ as a catalyst precursor.²⁵ All these results suggested the spatial effect of catalyst played a critical important role in determining the 3,4-selectivity of 2-PB polymerization.

As aforementioned, complex **1a** showed the highest 3,4-selectivity for the polymerization of 2-PB, so we further investigated the influence of different experimental conditions by using this precursor. The representative polymerization results were summarized in Table 1, entries 5-14.

The number average molecular weight (M_n) increased linearly from 1.84×10^4 to 7.08×10^4 with the increase of the



monomer-to-catalyst ratio changing from 100:1 to 400:1 (Table 1, entries 1, 5-9), while the molecular weight distribution (M_w/M_n) remained almost unchanged around 1.3, indicative of a single-sited catalytic system and the controllable polymerization fashion. Decreasing the reaction temperature to $-20\text{ }^\circ\text{C}$, the catalytic activity declined sharply such that monomer conversion was only 42.3% within 24 h, which increased at elevated temperatures such that complete conversion was achieved in 3 h at $40\text{ }^\circ\text{C}$ and 2 h at $60\text{ }^\circ\text{C}$ (Table 1, entries 10-11).

Interestingly, the 3,4-regularity (96.9%, Table 1, entry 12, SFig. 11) of the resulting polymer didn't changed any more when performing the polymerization at a lower temperature ($-20\text{ }^\circ\text{C}$) in contrary to our previous report that the 3,4-selectivity of isoprene polymerization increased with the decrease of

1b/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ did not induce the polymerization of 2-PB (Table 1, entry 2), owing to the sterically hindered coordination sphere of the small Sc^{3+} active site inhibited the monomer approaching and coordinating to it. Throughout these results, we could find that the steric hindrance of the metal center played a crucial role in controlling both the catalytic activity and the selectivity. Obviously, changing the substitutes (^iPr in **1a** = **2a** > Me in **3a**) at R^1 positions and the ionic radius displayed much stronger effects on the catalytic behaviour than varying the R^2 positioned substitute (Ph in **1a** < ^tBu in **2a**) that is relatively far from the active central metal. Therefore with the decreasing steric hindrance around the metal centers in the order of **1b** > **1a** \approx **2a** > **3a**, the 3,4-selectivity decreased correspondingly while the activity followed the contrary trend of **1b** < **1a** \approx **2a** < **3a**. This result was consistent with the polymerization of isoprene catalyzed by the half-metallocene rare-earth metal fluorenyl N-heterocyclic carbene precursors.^{22b} In the literature, the binary system $\text{CpTiCl}_3/\text{MAO}$ was used to catalyze 2-PB polymerization, the obtained polymer displayed high *cis*-1,4 selectivity (>99%),¹³ probably arising from the open environment around the central metal which benefits the monomer 2-PB coordination to titanium in the *cis*- η^4 mode. Comparatively, the sterically demanding lanthanide complexes $(\text{Flu-Py})\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ showed a little higher 3,4-regularity (45.7%) under the same polymerization conditions. Further improving the steric hindrance, the 3,4-selectivity

Fig. 3 Polymerization of 2-PB by using the binary catalytic system **1a**/ $[(\text{Ph}_3\text{C})][\text{B}(\text{C}_6\text{F}_5)_4]$: $\ln([2\text{-PB}]_t/[2\text{-PB}]_0)$ vs time. ($[\text{Lu}]_0 = 5.0\text{ }\mu\text{mol/mL}$, $[2\text{-PB}]_0/[\text{Lu}]_0 = 200$, Chlorobenzene, $25\text{ }^\circ\text{C}$), polymerization temperature²³, which dropped obviously to 91.5% when the polymerization temperature elevated to $60\text{ }^\circ\text{C}$, probably due to the fraction of *cis*- η^4 coordination mode increased⁷ to generate a thermally stable η^4 - π -butenyl species²⁶. In addition, the polymerization medium showed minor effect on the 3,4-selectivity that declined to 95.6% and 93.2% when the polymerization was performed in toluene and cyclohexane, respectively, as compared to 96.7% in

chlorobenzene. And the catalytic activity decreased with the polarity of the solvent in the order of chlorobenzene > toluene > cyclohexane (Table 1, entries 1, 13-14), which might be ascribed to the different ionization degrees of the active species $[(\text{Am-NHC})\text{Lu}(\text{CH}_2\text{SiMe}_3)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in different solvents. This was in line with the theory of anionic polymerization, the strong polar solvent generates the highly active looser ion-pairs.

The kinetics study demonstrated that the polymerization was rapid at the initial stage but became more and more sluggish when the monomer conversion was high, which could be explained by the slopes of the conversion vs time curves (SFig. 16). To establish the reaction order of 2-PB polymerization in chlorobenzene at 25 °C, the plot of $\ln([2\text{-PB}]_0/[2\text{-PB}]_t)$ vs time was drawn as Fig. 3. The straight line indicated the first-order dependence of the polymerization rate on the monomer concentration.

Moreover, the linear relationship between the monomer conversion and the number average molecular weight of the resulting polymer was also observed, while the molecular weight distribution stayed lower than 1.5 (Fig. 4), which are the typical features of a living polymerization mode. Thus the highly 3,4-selective living polymerization of 2-PB was achieved for the first time. All of the resultant 3,4-P(2-PB)s had high T_g s ranging from 44.3 °C to 56.1 °C, these thermodynamic properties are similar to those of the 3,4-polyisoprene obtained from the same catalytic system (SFig. 17)²³.

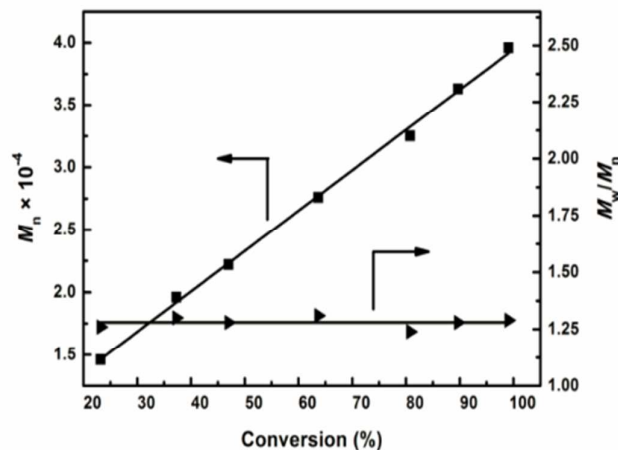


Fig. 4 Polymerization of 2-PB by using the binary catalytic system **1a**/[(Ph₃C)][(B(C₆F₅)₄)]: molecular weight vs conversion ($[\text{Lu}]_0 = 5.0 \mu\text{mol/mL}$, $[2\text{-PB}]_0/[\text{Lu}]_0 = 200$, PhCl, 25 °C).

Conclusions

A series of amidino N-heterocyclic carbene ligands ligated rare-earth metal bis(alkyl) complexes (Am-NHC)Ln(CH₂SiMe₃)₂ **1a-3a** were synthesized, characterized and investigated as efficient catalysts towards 2-phenyl-1,3-butadiene polymerization. The

activity and selectivity of the binary catalytic system (Am-NHC)Ln(CH₂SiMe₃)₂/[(Ph₃C)][(B(C₆F₅)₄)] were closely related to the steric hindrance of the metal center: the more sterically demanding of the metal center was, the lower activity but higher selectivity were obtained. For the first time, the 3,4-regioselectivity of 2-PB polymerization reached up to 96.9% at 25 °C in chlorobenzene although it declined slightly along with decreasing the solvent polarity or at the elevated polymerization temperatures. The resultant polymer had higher glass transition temperature of 56.1 °C, corresponding to a plastic material. The kinetic study declared that the polymerization of 2-PB was in accordance with the first-order dependence on the monomer concentration, and, in particular, exhibited living behaviour.

Experimental Section

General considerations

All manipulations were performed under a dried and oxygen-free argon atmosphere using standard high vacuum Schlenk techniques or in an Mbraun glovebox. All solvents were purified from Mbraun SPS system. Vinylmagnesium bromide (1.0 M in THF) was purchased from Aldrich. Acetophenone and pyridinium *p*-toluenesulfonate were purchased from the National Medicine Co. (China) and were used without further purification. The ligand (AmH-NHC-H)Br²³ and [Ph₃C][B(C₆F₅)₄]²⁷ were prepared according to literature. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 and 500. The number-average molecular weights (M_n) and

molecular weight distributions (M_w/M_n) of the polymer samples were measured by means of gel permeation chromatography (GPC) on a TOSOHHL-8220 GPC apparatus (Column: SuperHLM-Hx3) at 40 °C using THF as the eluent (the flowing rate is 0.35 mL/min) against polystyrene standards. Differential scanning calorimetry (DSC) analyses were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere.

Preparation of 2-phenyl-1,3-butadiene

To a stirred solution of vinylmagnesium bromide (240 mL, 1.0 M solution in THF, 240 mmol, 1.2 equiv) in THF (100 mL) at 0 °C, was added dropwise a solution of acetophenone (24.0 g, 200 mmol) in THF (100 mL) over 30 min under N₂ atmosphere. The reaction mixture was stirred at the same temperature for 2 h and then quenched with a saturated aqueous NH₄Cl (300 mL), diluted with saturated aqueous NaCl (100 mL), and extracted with ethyl acetate (300 mL). The extract was washed with saturated aqueous NaCl (200 mL), dried over Na₂SO₄ and concentrated to afford the alcohol 2-phenylbut-3-en-2-ol.

Under N₂ atmosphere, a solution of 2-phenylbut-3-en-2-ol (7.4 g, 50 mmol) and pyridinium *p*-toluenesulfonate (62.8 mg, 0.25 mmol, 0.005 equiv) in toluene (100 mL) was heated at 80 °C for 4 h. The reaction mixture was washed with saturated aqueous NaHCO₃ and saturated aqueous NaCl. The organic layer was dried over Na₂SO₄ and evaporated to give diene as a pale-yellow oil. ¹H NMR (400 MHz, 25 °C, CDCl₃) δ 7.35 (m, 2H, Ph-H), 6.65 (dd, 1H, =CH), 5.32~5.19 (m, 4H, =CH₂); ¹³C NMR (100 MHz, 25 °C, CDCl₃) δ 148.41, 139.88, 117.26, 116.97 (4C, olefin-C), 138.30, 128.40~127.59 (6C, Ph-C).

Synthesis of complex 1a.

Complex **1a** was synthesized according to the literature procedure.

Synthesis of complex 1b.

Following the procedure described for the formation of **1a**, the reaction of H₂L¹Br (0.287 g, 0.5 mmol) with LiCH₂SiMe₃ (0.047 g, 0.5 mmol) and Sc(CH₂SiMe₃)₃(THF)₂ (0.225 g, 0.5 mmol) afforded **1b** (0.205 g, 57.6%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ -0.09, -0.06 (AB, ²J_{H-H} = 11.2 Hz, 2H, Sc-CH₂SiMe₃), 0.04, 0.07 (AB, ²J_{H-H} = 11.2 Hz, 2H, Sc-CH₂SiMe₃), 0.14 (s, 18H, Sc-CH₂SiMe₃), 1.11 (d, ³J_{H-H} = 6.8 Hz, 6H, CH(CH₃)₂), 1.53 (d, ³J_{H-H} = 6.8 Hz, 6H, CH(CH₃)₂), 2.05 (s, 6H, C₆H₂Me₃), 2.19 (s, 3H, C₆H₂Me₃), 3.19-3.21 (m, 2H, CH₂CH₂), 3.58-3.61 (m, 2H, CH₂CH₂), 3.77 (sept, 2H, CH(CH₃)₂), 5.96 (d, ³J_{H-H} = 1.6 Hz, 1H, NCH), 6.01 (d, ³J_{H-H} = 1.6 Hz, 1H, NCH), 6.83-6.92 (m, 5H, C₆H₅), 7.00-7.06 (m, 3H, 2,6-Pr₂C₆H₃), 7.21-7.23 (m, 2H, C₆H₂Me₃).

Synthesis of complex 2a.

Following the procedure described for the formation of **1a**, the reaction of H₂L¹Br (0.277 g, 0.5 mmol) with LiCH₂SiMe₃ (0.047 g, 0.5 mmol) and LuCH₂SiMe₃(THF)₂ (0.290 g, 0.5 mmol) afforded **2a** (0.221 g, 53.9%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ -1.08, -1.05 (AB, ²J_{H-H} = 11.2 Hz, 2H, Lu-CH₂SiMe₃), -0.88, -0.85 (AB, ²J_{H-H} = 11.2 Hz, 2H, Lu-CH₂SiMe₃), 0.12 (s, 18H, Lu-CH₂SiMe₃), 1.11 (s, 9H, CMe₃), 1.38 (d, ³J_{H-H} = 6.8 Hz, 6H, CH(CH₃)₂), 1.49 (d, ³J_{H-H} = 6.8 Hz, 6H, CH(CH₃)₂), 1.95 (s, 6H, C₆H₂Me₃), 2.18 (s, 3H, C₆H₂Me₃), 3.52-3.54 (m, 2H, CH₂CH₂), 3.59 (m, 2H, CH(CH₃)₂), 3.66-3.68 (m, 2H, CH₂CH₂), 5.93 (s, 1H, NCH), 6.06 (s, 1H, NCH), 6.78 (s, 2H, C₆H₂Me₃), 7.09 (m, 5H, 2,6-Pr₂C₆H₃).

Synthesis of complex 3a.

Following the procedure described for the formation of **1a**, the reaction of H₂L³Br (0.259 g, 0.5 mmol) with LiCH₂SiMe₃ (0.047 g, 0.5 mmol) and Sc(CH₂SiMe₃)₃(THF)₂ (0.290 g, 0.5 mmol) afforded **3a** (0.195 g, 49.7%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ

-0.90, -0.87 (AB, ²J_{H-H} = 11.2 Hz, 2H, Lu-CH₂SiMe₃), -0.68, -0.65 (AB, ²J_{H-H} = 11.2 Hz, 2H, Lu-CH₂SiMe₃), 0.19 (s, 18H, Lu-CH₂SiMe₃), 2.03 (s, 6H, C₆H₂Me₃), 2.20 (s, 3H, C₆H₂Me₃), 2.49 (s, 6H, C₆H₃Me₂), 3.13 (m, 2H, CH₂CH₂), 3.52 (m, 2H, CH(CH₃)₂), 5.95 (s, 1H, NCH), 5.99 (s, 1H, NCH), 6.75-6.83 (m, 3H, C₆H₃Me₂), 6.86-6.91 (m, 5H, C₆H₅), 7.02 (m, 2H, C₆H₂Me₃).

Preparation of poly(2-phenyl-1,3-butadiene)

A typical polymerization procedure (Table 1, entry 1) was described as follows. Under a nitrogen atmosphere, a chlorobenzene solution (1.0 mL) of [Ph₃C][B(C₆F₅)₄] (9.2 mg, 10 μmol) was added to a well-stirred chlorobenzene solution (1.0 mL) of complex **1a** (8.4 mg, 10 μmol) in a flask. The reaction apparatus was placed in a bath at 25 °C. Then 0.26 g of 2-phenyl-1,3-butadiene (2 mmol) was added to the above system to start the polymerization. The system remained stirring for 4 h to give a viscous solution, which was poured into ethanol (ca. 30 mL) to terminate the polymerization. The resultant P(2-PB) precipitate was filtered, washed with ethanol, and dried under vacuum at 40 °C to a constant weight (0.26 g, 100%). The isolated P(2-PB) has a 96.7% 3,4-tacticity and a number-average molecular weight of 3.03×10⁴ with molecular weight distribution of 1.26. The glass transition temperature is 52.9 °C.

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Graphical abstract

