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PAPER

Highly *trans*-1,4 selective (co-)polymerization of butadiene and isoprene with quinolyl anilido rare earth metal bis(alkyl) precursors†

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The *N*-R-quinolinyl-8-amino ligands HL^{1-3} (R = 2,6-$^iPr_2C_6H_3$ (HL^1), 2,6-$Et_2C_6H_3$ (HL^2), 2,6-$Me_2C_6H_3$ (HL^3)) have been prepared, which reacted readily with one equiv. of rare earth metal tris(alkyl)s to afford the corresponding bis(alkyl) complexes $L^1Y(CH_2SiMe_3)_2(THF)$ (**1**) and $L^{1-3}Lu(CH_2SiMe_3)_2(THF)$ (**2–4**) *via* alkane elimination. Contrastingly, treatment of the *in situ* generated neodymium tri(alkyl)s with HL^1 afforded a mono(alkyl) neodymium complex (**5**). Complexes **1**, **2** and **5** in combination with aluminium alkyls and organoborates established homogenous ternary systems that exhibited versatile catalytic activities and *trans*-1,4 selectivities for the polymerization of butadiene, depending on the types of aluminium alkyl, organoborate and rare earth metal used. Furthermore, the *trans*-1,4 selective copolymerization of butadiene and isoprene was achieved by using the ternary system of **1**/$AlMe_3$/$[Ph_3C][B(C_6F_5)_4]$. Both the kinetics of copolymerization and the thermal behavior of the copolymers were investigated.

Introduction

During the past few decades, investigations into the stereospecific polymerization of 1,3-conjugated dienes promoted by rare earth metal complexes have gathered an upsurge in research interest in both academic and industrial environments,[1] among which extraordinary attention has been devoted to the *cis*-1,4-selective polymerization of 1,3-conjugated dienes because the given polymers are the most important rubbers used for tires and other elastic materials.[2] Only recently, *trans*-1,4 regulated polydienes have attracted renewed interest after the pioneering work of Natta,[3] since it became accepted that such polymers possess excellent dynamic properties, including excellent anti-fatigue properties, low rolling resistance, low heat buildup, good strength and low abrasion loss. They are now an important component of long-life “green” tires. Moreover, *trans*-1,4 polymerization may allow the incorporation of an α-olefin into a polydiene chain to afford highly value added copolymers.[4] However, *trans*-selective catalytic systems are much fewer in number than *cis*-selective ones, which might be because the 1,3-conjugated dienes prefer η^4-*cis* to η^4-*trans* coordination to the active metal center. Nevertheless, some catalyst systems have been designed for the *trans*-1,4-selective polymerization of isoprene, such as Ziegler–Natta catalysts based on Ti[5] and V[6] metals, and the recently reported $[Cp^*Ln(AlMe_4)_2]/B(C_6F_5)_3$,[7] $Y(allyl)_2Cl(MgCl_2)_2/AlR_3$,[2u] $[(C_5Me_4{}^nPr)Nd(BH_4)_2\text{-}(thf)_2]/Mg\text{-}(^nBu)_2$,[8] and $[Me_4C_2(C_5H_4)_2]Sm(allyl)_2Li(dme)$.[9] Comparatively, the catalyst systems that can initiate the *trans*-1,4-selective polymerization of butadiene are explored less, which are mainly Fe,[10] Ti,[11] and V[12] based precursors. To date, rare earth metal based catalysts have been limited to the lanthanocene aluminates,[2m,13] lanthanide bis(allyl)s,[14] and neodymium alkoxides.[15] Therefore, to innovate new rare earth metal catalysts for *trans*-1,4 (co-)polymerizations of 1,3-conjugated dienes is an obviously interesting but very tough project.

Rare earth metal bis(alkyl) complexes supported by monoanionic ancillary ligands have been demonstrated to be highly active single-component catalysts and excellent precursors for the polymerization of conjugated dienes and olefins.[1d–f] We recently reported the synthesis of quinolinyl anilido scandium bis(alkyl) complexes, which are the first non-Cp ligated rare earth metal precursors, providing high syndioselectivity for styrene polymerization.[16] Herein, we wish to report the isolation of quinolinyl anilido yttrium, lutetium and neodymium complexes, which, under the activation of organoborates and aluminium alkyls, exhibited distinguished catalytic activity and *trans*-1,4 selectivity for both butadiene and isoprene homo- and co-polymerizations.

Results and Discussion

Synthesis and characterization of quinolinyl anilido rare-earth metal complexes

The ligands *N*-R-quinolin-8-amines (HL^1: R = diisopropylphenyl; HL^2: R = diethylphenyl; HL^3: R = dimethylphenyl)

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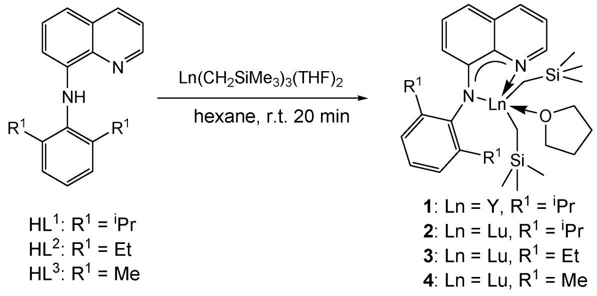
† Electronic supplementary information (ESI) available: ORTEP drawing of complex **3** and ^{13}C NMR spectra of the selected polybutadiene sample and polyisoprene sample. CCDC reference numbers 780668 (**1**), 780669 (**2**), 780670 (**3**) and 780671 (**5**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10100e

were prepared following the previously reported procedure.[16] The acid–base reaction between the yttrium tris(alkyl) complex, $Y(CH_2SiMe_3)_3(THF)_2$, and one equiv. of HL^1 in hexane at room temperature afforded the corresponding yttrium bis(alkyl) complex **1** in a medium yield. Similarly, treatment of $Lu(CH_2SiMe_3)_3(THF)_2$ with one equiv. of HL^{1-3} in hexane gave the analogous lutetium bis(alkyl) complexes **2–4**, respectively (Scheme 1). The ^1H NMR spectra of complexes **1–4** are displayed in Fig. 1. The methylene protons of $Y–CH_2SiMe_3$ in **1** give a doublet resonance at $\delta = -0.10$ due to coupling with the yttrium ion (J_{Y-C-H} = 3.0 Hz). Meanwhile, the methylene protons of the metal alkyl $Lu–CH_2SiMe_3$ in **2** exhibits an AB spin at $\delta = -0.35$ and -0.27 (J_{H-H} = 8.4 Hz), indicating that the methylene protons are diastereotopic, whereas the methylene protons of $Lu–CH_2SiMe_3$ in **3** and **4** show up as singlets at $\delta = -0.33$ and -0.34, respectively, suggesting that the two alkyl ligands are equivalent. As the neodymium tri(alkyl) complex is not stable, the synthesis of the quinolinyl anilido neodymium alkyl complex did not follow the alkane elimination method described above for the syntheses of lutetium and yttrium alkyl complexes, but employed a one-pot reaction: $NdCl_3(THF)_2$ was first treated with three equiv. of $LiCH_2SiMe_3$ in THF and then to this one equiv. of ligand HL^1 was added *in situ* . However, repeated attempts to isolate the neodymium bis(alkyl) complex from this reaction failed, as they gave the mono(alkyl) complex **5** as the major product owing to the ligand redistribution (Scheme 2).



Scheme 1 The synthesis of complexes **1–4**.

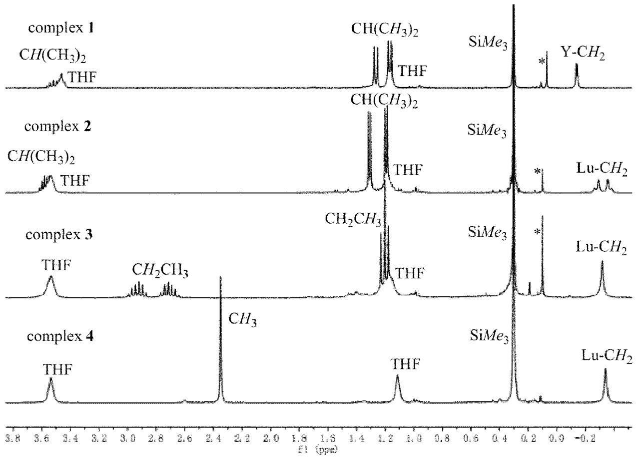
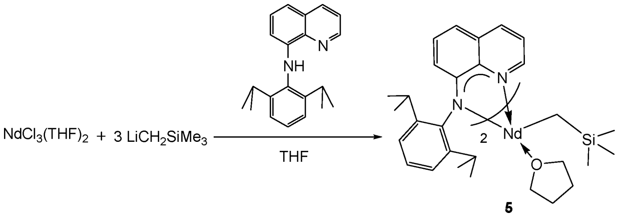


Fig. 1 ^1H NMR spectra of complexes **1–4**. (*: impurity).



Scheme 2 The synthesis of complex **5**.

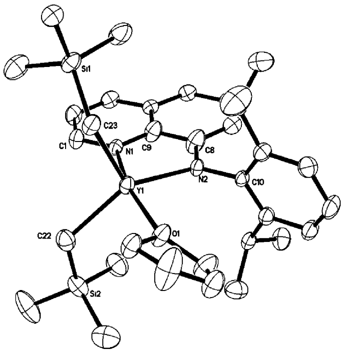


Fig. 2 An ORTEP drawing of complex **1** with a 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y(1)–N(1) = 2.445(4), Y(1)–N(2) = 2.314(4), Y(1)–O(1) = 2.336(3), Y(1)–C(22) = 2.400(6), Y(1)–C(23) = 2.380(5), N(1)–C(9) = 1.364(7), N(2)–C(8) = 1.374(7), N(2)–C(10) = 1.422(6), O(1)–Y(1)–N(1) = 161.72(13), C(23)–Y(1)–C(22) = 106.9(2), N(2)–Y(1)–N(1) = 68.87(13).

The solid-state structures of complexes **1**, **2** and **5** were confirmed by X-ray diffraction (Fig. 2–4). Complexes **1** and **2** are five-coordinate isostructural monomers, adopting a distorted trigonal bipyramidal geometry. The nitrogen atom in the quinolinyl ring and the THF molecule are axial (N(1)–Y(1)–O(1) = 161.72° for **1**; N(1)–Lu(1)–O(1) = 161.94° for **2**) and the two alkyl carbon atoms and the N(2) atom of the ligand occupy the equatorial positions. While the six-coordinate complex **5** adopts a twisted tetragonal bipyramidal geometry with the alkyl carbon and the nitrogen atom N(1) axial and the THF oxygen and the other three nitrogen atoms equatorial. It is noteable that in complexes **1**, **2** and **5** the bond length of N(1)–C(9) (average 1.365 Å) is close to that of N(2)–C(8) (average. 1.371 Å), suggesting that the electrons delocalize within the N(1)–C(9)–C(8)–N(2) fragment. The NN ligand chelates to the metal ion in a η^2-mode, leading to the N–aryl ring and the quinolinyl ring perpendicular to each other. The average bond length of Ln–C is 2.390 Å for **1**, 2.342 Å for **2**, and 2.528 Å for **5**, whilst, the Ln–N(2) bond lengths of 2.314(4) Å for **1**, 2.267(4) Å for **2**, and 2.381(3) Å for **5**, respectively. Both fall within the normal values.[17] The bond angles of C–Ln–C 106.9(2)° (**1**) to 107.22(18)° (**2**) are comparable to those found in other rare-earth metal bis(alkyl) complexes.[18]

Polymerization of butadiene

Recently, we have been engaged in the stereospecific polymerizations of 1,3-conjugated dienes,[19] which is a very important process in the chemical industry to afford products that are among the most significant and widely used rubbers. Therefore complexes **1**, **2** and **5** were employed as precursors in the polymerization of butadiene (BD) upon the activation of aluminium alkyls and organoborates. The generated homogeneous catalysts showed

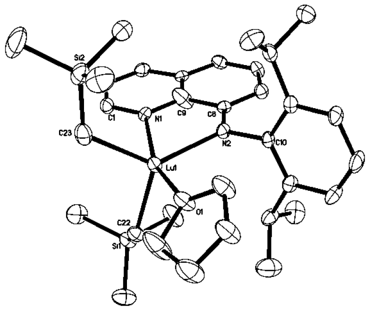


Fig. 3 An ORTEP drawing of complex **2** with a 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Lu(1)–N(1) = 2.387(4), Lu(1)–N(2) = 2.267(4), Lu(1)–O(1) = 2.286(3), Lu(1)–C(22) = 2.338(5), Lu(1)–C(23) = 2.346(5), N(1)–C(9) = 1.365(7), N(2)–C(8) = 1.368(5), N(2)–C(10) = 1.428(5), O(1)–Lu(1)–N(1) = 161.94(12), C(22)–Lu(1)–C(23) = 107.22(18), N(2)–Lu(1)–N(1) = 70.22(13).

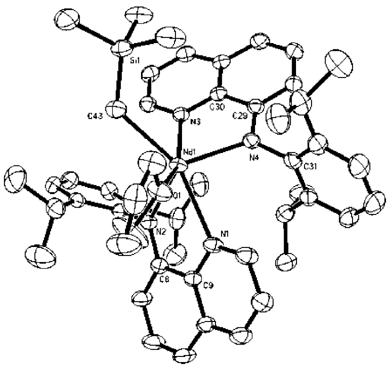


Fig. 4 An ORTEP drawing of complex **5** with a 35% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Nd(1)–N(1) = 2.619(3), Nd(1)–N(2) = 2.381(3), Nd(1)–N(3) = 2.559(3), Nd(1)–N(4) = 2.397(3),Nd(1)–O(1) = 2.603(3), Nd(1)–C(43) = 2.528(4), N(3)–C(30) = 1.371(5), N(4)–C(29) = 1.376(4), N(4)–C(31) = 1.436(5).

versatile catalytic performances depending on the type of aluminium alkyl, organoborate, and rare earth metal center. The selected polymerization data are summarized in Table 1.

The type of aluminium alkyl seemed to have no influence on the catalytic activity. All of the ternary systems **1**/AlR_3/$[Ph_3C][B(C_6F_5)_4]$ exhibited similar high activities, reaching complete conversion within 3 h, whichever aluminium alkyl (Al^iBu_3 or $AlMe_3$ or $AlEt_3$) was employed. In striking contrast, the type of aluminium alkyl played a significant role in control of the selectivity. The catalytic system **1**/$AlMe_3$/$[Ph_3C][B(C_6F_5)_4]$ was highly selective to providing polybutadiene (PBD) with up to 91% *trans*-1,4 regularity. When $AlMe_3$ was replaced by Al^iBu_3, the resultant system afforded 78% *cis*-1,4 regulated PBD and when complex **1** was activated by $AlEt_3$, the resultant PBD had equal *cis*-1,4 and *trans*-1,4 content (entries 1–3). The fluorinated borates also significantly influenced the catalytic performances.

When applying $[PhNMe_2H][B(C_6F_5)_4]$ instead of $[Ph_3C][B(C_6F_5)_4]$ as the activator, the ternary system **1**/$AlMe_3$/$[PhNMe_2H][B(C_6F_5)_4]$ showed low activity and the borates had a negligible effect on the selectivity (entry 6).

Besides the types of co-activators, the central metal also exerted an obvious influence on the catalytic performances. Thus, complexes based on various lanthanide elements bearing the *o*-isopropyl substituent of the *N*-aryl ring of the ligand were examined when combined with $AlMe_3$ and $[Ph_3C][B(C_6F_5)_4]$. By using the yttrium precursor, a complete conversion could be achieved within 3 h and up to 91% *trans*-1,4 regulated PBD was obtained. Comparatively, both the catalytic activity and the *trans*-1,4 selectivity (68%) obviously dropped for the lutetium-based systems (entry 4). Whilst the larger neodymium-based mono(alkyl) precursor **5** displayed a lower activity and *trans*-1,4 selectivity (71%) compared to the yttrium system, which might be attributed to the more sterically hindered environment around the neodymium center bearing the two ligands (entry 5).

As the catalytic system based on yttrium precursor **1**/$AlMe_3$/$[Ph_3C][B(C_6F_5)_4]$ displayed distinguished catalytic activity and selectivity, it was used to further investigate the kinetics of the polymerization at room temperature under a monomer-to-Y ratio of 1000. The results demonstrated that the amount of monomer conversion increased with polymerization time, which displayed a nearly linear correlation with the molecular weight of the obtained polymer (Fig. 5). Meanwhile, the molecular weight distribution remained constant (PDI = 1.26–1.58). This meant that the polymerization was pseudo-living and controllable. Intrigued

Table 1 *Trans*-1,4 polymerization of butadiene by complex/AlR_3/borate[a]

								microstructure(%)[c]		
entry	cat.	AlR_3	[BD]/[Ln]	time (h)	yield (%)	M_n[b] ($/10^{-4}$)	M_w/M_n[b]	*cis*-1,4	*trans*-1,4	1,2-
1	**1/A**	Al^iBu_3	1000	3	> 99	3.4	1.58	78	19	3
2	**1/A**	$AlEt_3$	1000	3	> 99	3.9	1.14	47	49	4
3	**1/A**	$AlMe_3$	1000	3	> 99	33.6	1.50	6	91	3
4	**2/A**	$AlMe_3$	1000	3	41	12.7	1.55	23	68	9
5	**5/A**	$AlMe_3$	1000	3	76	16.6	1.80	25	71	4
6	**1/B**	$AlMe_3$	1000	3	31	14.2	1.61	7	89	4
7	**1/A**	$AlMe_3$	500	2	> 99	22.7	1.37	6	91	3
8	**1/A**	$AlMe_3$	2000	6	> 99	46.3	1.56	7	89	4
9	**1/A**	$AlMe_3$	3000	9	> 99	52.4	1.72	8	88	4
10	**1/A**	$AlMe_3$	5000	15	> 99	78.4	2.09	8	88	4

[a] General conditions: 10^{-5} mol of Ln complex; in toluene; monomer/solvent = 1 : 5 (v/v); T_p, 20 °C; [Al]/[Ln] = 10; [Ln]/[activator] = 1 : 1 (activator = $[Ph_3C][B(C_6F_5)_4]$ (**A**), $[PhMe_2NH][B(C_6F_5)_4]$ (**B**)). [b] Determined by GPC in THF at 40 °C against a polystyrene standard. [c] Determined by ^{13}C NMR and ^1H NMR.

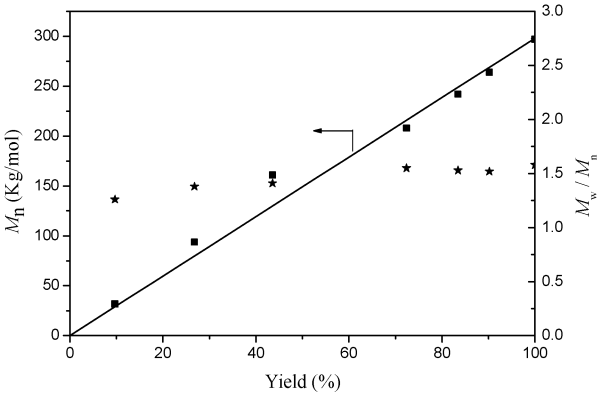


Fig. 5 A plot of the number average molecular weight of PBD as a function of the butadiene conversion. Conditions: [BD]/[Y] = 1000, $[Y]_0$ = 1.15 μmol mL^{-1}, $[AlMe_3]/[Y]$ = 10, toluene, 20 °C.

by this finding, we carried out polymerizations of butadiene under monomer-to-initiator ratios varying from 500 to 5000, anticipating that high molecular weight *trans*-1,4 PBD would be obtained. All of the polymerizations went smoothly, indicating that the active species was stable and its lifetime was long, although with the ratio over 2000 a prolonged polymerization time was needed because the catalyst concentrations became lower and the system turned extremely viscous. The molecular weight of the resultant PBD increased with the ratios, from 22.7×10^4 g mol^{-1} up to 78.4×10^4 g mol^{-1}, albeit with a slightly broadened molecular weight distribution (from 1.37 to 2.09), which might be attributed to the difficulty of monomer diffusion in a sticky system. Noteably, the *trans*-1,4 tacticity of the resultant polymers did not change obviously over the entire range of the monomer-to-Y ratios (entries 7–10).

Copolymerization of isoprene and butadiene using complex 1/AlMe$_3$/borate

The copolymerization of butadiene with isoprene is usually adopted as an efficient way to reduce the crystallinity and lower the melting temperature of *trans*-1,4 PBD, in order to improve its processing and mechanical properties. However, a catalyst that is active for butadiene polymerization is not guaranteed to show the same performance in isoprene polymerization.[10,12a] To our delight, the system **1**/$AlMe_3$/$[Ph_3C][B(C_6F_5)_4]$ was able to initiate isoprene polymerization with a similar activity in a *trans*-1,4 selective manner. Thus, the copolymerization of butadiene and isoprene was explored under various monomer feed ratios. The representative polymerization data are listed in Table 2. From Table 2 it can be seen that all of the copolymerizations could reach complete conversion, the resultant copolymers were random, the composition of the copolymers was consistent with the monomer feed ratio and the *trans*-1,4 regularity of both PBD and PIP sequences dropped slightly compared with their homopolymers, as shown by the ^1H NMR spectroscopy analysis (Fig. 6). In addition, the monomer competitive polymerization ratios were calculated with the Fineman–Ross equation, based on data from the copolymerization at low monomer conversions, to be r_1 = 1.11 (BD) and r_2 = 0.44 (IP) (Fig. 7).[20] This result indicated that butadiene was more active than isoprene.[21] To our knowledge, this represents the first rare earth metal based catalyst showing *trans*-1,4 selectivity for the copolymerization of butadiene and isoprene.

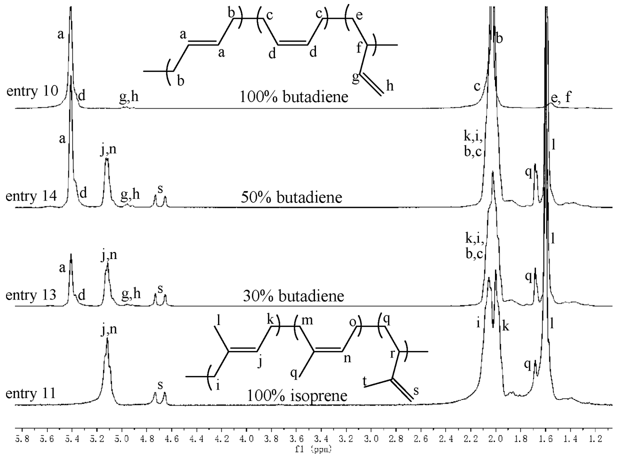


Fig. 6 ^1H NMR spectra (400 MHz) of the resulting polymers.

It is known that *trans*-1,4 PBD may exist in two different forms. One form is stable at room temperature and is characterized by a monoclinic unit cell. By heating the polymer, an endothermic transition occurs leading to a second form, characterized by a hexagonal mesophase.[22] The thermal behavior of the obtained butadiene–isoprene copolymers was examined by DSC. We found that the copolymer composition strongly influenced the monoclinic–hexagonal transition and the melting temperature (T_t and T_m, respectively). Fig. 8 shows the DSC curves of the butadiene homopolymer and of some selected butadiene–isoprene copolymers. It can be observed that the values of T_t and T_m in the copolymers (Fig. 8b) shift to lower temperatures

Table 2 The copolymerization of isoprene (IP) and butadiene (BD) using complex **1**/$AlMe_3$/borate[a]

							BD microstructure(%)[c]			IP microstructure(%)[c]		
Entry	BD/IP (mmol/mmol)	time [h]	yield [%]	M_n[b] ($/10^{-4}$)	M_w/M_n[b]	BD content (mol%)	*cis*-1,4	*trans*-1,4	1,2-	*cis*-1,4	*trans*-1,4	3,4-
11	0/50	15	> 99	68.9	1.71	0	—	—	—	5	87	8
12	5/45	15	> 99	63.3	1.86	10	17	78	5	11	79	10
13	15/35	15	> 99	64.2	1.83	30	15	81	4	12	79	9
14	25/25	15	> 99	63.5	1.89	50	14	82	4	15	76	9
15	35/15	15	> 99	71.1	1.84	70	14	82	4	17	74	9
16	45/5	15	> 99	71.6	2.04	90	12	84	4	18	73	9

[a] General conditions: 10^{-5} mol of the Y complex; in toluene (25 mL); T_p (20 °C); [Al] = $AlMe_3$; [Al]/[Ln] = 10; [Ln]/[activator] = 1 : 1 (activator = $[Ph_3C][B(C_6F_5)_4]$ (**A**)). [b] Determined by GPC in THF at 40 °C against a polystyrene standard. [c] Determined by ^{13}C NMR and ^1H NMR.

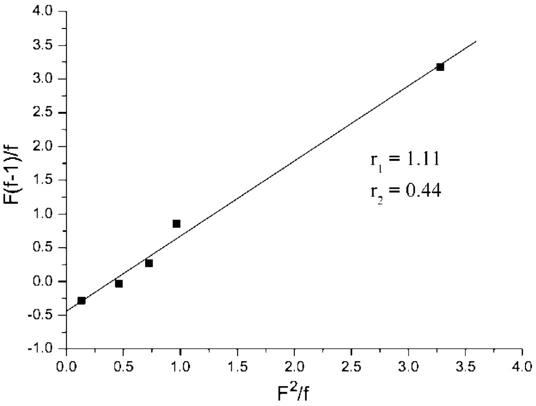


Fig. 7 A Fineman–Ross plot for the copolymerization of butadiene and isoprene with **1**/$AlMe_3$/$[Ph_3C][B(C_6F_5)_4]$ at 20 °C (F = [BD]/[IP] in the feed, f = [BD]/[IP] in the copolymer).

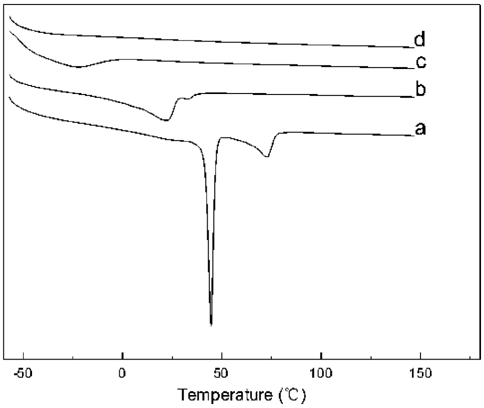


Fig. 8 DSC curves of the resulting polymers. (a) Polybutadiene (Table 1, entry 10, 100% butadiene); (b) butadiene–isoprene copolymer (Table 2, run 16, 90% butadiene); (c) butadiene–isoprene copolymer (Table 2, run 15, 70% butadiene); (d) butadiene–isoprene copolymer (Table 2, run 14, 50% butadiene).

with respect to those of pure *trans*-1,4 polybutadiene (Fig. 8a). Moreover, the temperature interval between the two endothermic events is progressively reduced by increasing the isoprene content, and for a certain copolymer composition (isoprene content 30%) only one endothermic peak can be detected (Fig. 8c). A possible explanation for such a behavior is that T_t and T_m become so close with increasing isoprene content that it is no longer possible to distinguish between them. Finally, no transition is observed for the copolymers in which the isoprene content is 50% (Fig. 8d).

Conclusions

We have demonstrated that rare earth metal bis(alkyl)s complexes bearing a non-Cp quinolinyl aniline ligand, upon the activation by aluminium alkyls and organoborates, generated single-site, homogeneous cationic systems for the (co-)polymerization of 1,3-conjugated dienes. The optimum catalytic system of yttrium precursor/$AlMe_3$/$[Ph_3C][B(C_6F_5)_4]$ provided a high activity and up to 91% *trans*-1,4 selectivity for butadiene polymerization. Such good performances occurred for a broad range of monomer-to-initiator ratios, therefore a high molecular weight, *trans*-1,4 regulated polybutadiene was obtained. Remarkably, the system also exhibited similar activity and selectivity towards isoprene polymerization. Thus, random copolymers with controlled compositions and both *trans*-1,4 regulated monomer sequences could be achieved swiftly, owing to the comparable competitive polymerization ratios of r_1 = 1.11 and r_2 = 0.44.

Experimental Section

General Considerations

All manipulations were performed under a dry and oxygen-free argon atmosphere using standard high vacuum Schlenk techniques or in a glove box. All solvents were purified *via* a SPS system. Anilines, NaO^tBu, bis[2-(diphenylphosphino)phenyl] ether, 8-bromoquinoline, $Pd(OAc)_2$, and aluminium alkyls were purchased from Aldrich and used without further purification. Butadiene (99%, Changchun Northern Special Gases Co., Ltd.) was dried by passing it through a column filled with activated molecular sieves (4 Å). Isoprene (Aldrich) was purified by distillation over calcium hydride under a nitrogen atmosphere. $[Ph_3C][B(C_6F_5)_4]$ and $[PhNHMe_2][B(C_6F_5)_4]$ were prepared according to the published procedures.[23] All ligands were prepared following the previously reported procedure.[16] All complexes were stored at a low temperature (–30 °C). ^1H, ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) or AV300 (FT, 300 MHz for ^1H; 75 MHz for ^{13}C). The molecular weight (M_n) was measured by TOSOH HLC-8220 GPC at 40 °C using THF as the eluent (the flow rate was 0.35 mL min^{-1}) against polystyrene standards. Elemental analyses were performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry. Differential scanning calorimetry (DSC) analyses were carried out on a Q100 DSC from TA Instruments under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The thermal history difference in the polymers was eliminated by first heating the specimen to 150 °C, cooling at 10 °C min^{-1} to –60 °C, and then a second heating from –60°C to 150 °C at 10 °C min^{-1} was performed.

X-ray analysis was performed at –86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The determination of crystal class and the unit cell parameters was carried out by the SMART program package. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method.

The reactivity ratios r_1 and r_2 were determined using the Fineman–Ross method and the following linear relationship:

$$F(f-1)/f = r_1 - r_2\,(F^2/f)$$

where F and f are the butadiene/isoprene molar ratios in the feed and the polymer (by ^1H NMR analysis), respectively.

Preparation of the complex $L^1Y(CH_2SiMe_3)_2(THF)$ (1)

To a 3 mL hexane solution of $Y(CH_2SiMe_3)_3(THF)_2$ (0.20 g, 0.4 mmol), an equivalent of HL^1 (0.12 g, 0.4 mmol in 4 mL hexane) was added dropwise at room temperature. The resulting red solution was stirred for 20 min at room temperature, and then concentrated to about 2 mL. The residue was cooled to –30 °C for 12 h to afford red crystalline solids that were washed carefully with a small amount of cold hexane (0.5 mL) to remove impurities and dried *in vacuo* to give red powders of complex **1** (0.16 g, 64%). Red crystals for X-ray analysis grew from a solution of hexane at −30 °C after several days. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ −0.10 (d, $^2J_{Y\text{–}C\text{–}H}$ = 3.0 Hz, 4H, CH_2SiMe_3), 0.34 (s, 18H, $SiMe_3$), 1.20 (br, 4H, THF), 1.21 (d, $^3J_{H\text{–}H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.31 (d, $^2J_{H\text{–}H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 3.50 (br, 4H, THF), 3.56 (m, 2H, $CH(CH_3)_2$), 6.22 (dd, $^3J_{H\text{–}H}$ = 7.8 Hz, $^4J_{H\text{–}H}$ = 0.9 Hz, 1H, quinoline), 6.74 (d, $^3J_{H\text{–}H}$ = 7.2 Hz, 1H, quinoline), 6.90 (q, $^3J_{H\text{–}H}$ = 4.5 Hz, 1H, quinoline), 7.20–7.32 (m, 4H, $NC_6H_3{}^i Pr_2$, quinoline), 7.68 (dd, $^3J_{H\text{–}H}$ = 8.4 Hz, $^4J_{H\text{–}H}$ = 1.2 Hz, 1H, quinoline), 9.06 (dd, $^3J_{H\text{–}H}$ = 4.5 Hz, $^4J_{H\text{–}H}$ = 1.5 Hz, 1H, quinoline).^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.74 (6C, $SiMe_3$), 25.46 (4C, $CH(CH_3)_2$), 26.06 (2C, THF), 28.95 (2C, $CH(CH_3)_2$), 36.75 (d, $^3J_{H\text{–}H}$ = 53 Hz, 2C, CH_2SiMe_3), 70.90 (2C, THF), 110.05, 110.94, 120.94 (3C, quinoline), 124.93 (2C, $NC_6H_3{}^i Pr_2$), 125.44 (1C, $NC_6H_3{}^i Pr_2$), 130.57, 131.47, 140.49 (3C, quinoline), 141.68 (1C, $NC_6H_3{}^i Pr_2$), 146.36 (1C, $NC_6H_3{}^i Pr_2$), 145.35, 146.49, 155.68 (3C, quinoline). Anal. calcd for $C_{33}H_{53}N_2OSi_2Y$(%): C, 62.04; H, 8.36; N, 4.38. Found: C, 62.92; H, 8.09; N, 4.13.

Preparation of the complex $L^1Lu(CH_2SiMe_3)_2(THF)$ (2)

Following a similar procedure to that described for the preparation of **1**, the reaction of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.23 g, 0.4 mmol in 3 mL hexane) with an equivalent of HL^1 (0.12 g, 0.4 mmol in 4 mL hexane) gave **2** (0.24 g, 81%). Red crystals for X-ray analysis grew from a solution of hexane at −30 °C after several days. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ −0.35, −0.27 (AB, $^2J_{H\text{–}H}$ = 8.4 Hz, 4H, CH_2SiMe_3), 0.32 (s, 18H, $SiMe_3$), 1.19 (br, 4H, THF), 1.21 (d, 6H, $CH(CH_3)_2$), 1.32 (d, 6H, $CH(CH_3)_2$), 3.55 (br, 4H, THF), 3.60 (m, 2H, $CH(CH_3)_2$), 6.22 (d, $^3J_{H\text{–}H}$ = 5.4 Hz, 1H, quinoline), 6.72 (d, $^3J_{H\text{–}H}$ = 6.0 Hz, 1H, quinoline), 6.92 (q, $^3J_{H\text{–}H}$ = 3.6 Hz, 1H, quinoline), 7.20–7.33 (m, 4H, $NC_6H_3{}^i Pr_2$, quinoline), 7.68 (dd, $^3J_{H\text{–}H}$ = 6.0 Hz, $^4J_{H\text{–}H}$ = 1.2 Hz, 1H, quinoline), 9.03 (dd, $^3J_{H\text{–}H}$ = 3.3 Hz, $^4J_{H\text{–}H}$ = 1.2 Hz, 1H, quinoline).^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.81 (6C, $SiMe_3$), 25.16 (2C, $CH(CH_3)_2$), 26.22 (2C, $CH(CH_3)_2$), 25.46 (br, 2C, THF), 28.93 (2C, $CH(CH_3)_2$), 43.18 (2C, CH_2SiMe_3), 71.36 (br, 2C, THF), 110.99, 120.96 (2C, quinoline), 124.87 (2C, $NC_6H_3{}^i Pr_2$), 125.40 (1C, $NC_6H_3{}^i Pr_2$), 130.68, 131.51, 140.54 (3C, quinoline), 141.50 (1C, $NC_6H_3{}^i Pr_2$), 146.24 (1C, $NC_6H_3{}^i Pr_2$), 146.55, 146.71, 156.00 (3C, quinoline). Anal. calcd for $C_{33}H_{53}N_2OSi_2Lu$(%): C, 54.68; H, 7.37; N, 3.86. Found: C, 55.03; H, 7.51; N, 3.67.

Preparation of the complex $L^2Lu(CH_2SiMe_3)_2(THF)$ (3)

Following a similar procedure to that described for the preparation of **1**, the reaction of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.23 g, 0.4 mmol in 3 mL hexane) with an equivalent of HL^2 (0.11 g, 0.4 mmol in 4 mL hexane) gave **3** (0.19 g, 83%). Red crystals for X-ray analysis grew from a solution of hexane at −30 °C after several days.^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ −0.33 (s, 4H, CH_2SiMe_3), 0.29 (s, 18H, $SiMe_3$), 1.16 (br, 4H, THF), 1.19 (t, $^3J_{H\text{–}H}$ = 7.5 Hz, 6H, CH_2CH_3), 2.71 (m, 2H, CH_2CH_3), 2.91 (m, 2H,CH_2CH_3), 3.53 (br, 4H, THF), 6.19 (dd, $^3J_{H\text{–}H}$ = 8.1 Hz, $^4J_{H\text{–}H}$ = 1.2 Hz, 1H, quinoline), 6.70 (dd, $^3J_{H\text{–}H}$ = 7.8 Hz, $^4J_{H\text{–}H}$ = 0.9 Hz, 1H, quinoline), 6.89 (q, $^3J_{H\text{–}H}$ = 4.8 Hz, 1H, quinoline), 7.14–7.24 (m, 4H, $NC_6H_3Et_2$, quinoline), 7.67 (dd, $^3J_{H\text{–}H}$ = 8.4 Hz, $^4J_{H\text{–}H}$ = 1.5 Hz, 1H, quinoline), 8.29 (dd, $^3J_{H\text{–}H}$ = 4.8 Hz, $^4J_{H\text{–}H}$ = 1.5 Hz, 1H, quinoline). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.78 (6C, $SiMe_3$), 15.56 (2C, CH_2CH_3), 25.24 (2C, THF), 25.47 (2C, CH_2CH_3), 43.56 (2C, CH_2SiMe_3), 70.85 (2C, THF), 109.26, 110.85, 120.96 (3C, quinoline), 124.71 (1C, $NC_6H_3Et_2$), 128.26 (2C, $NC_6H_3Et_2$), 131.04, 131.55, 140.48 (3C, quinoline), 140.99 (2C, $NC_6H_3Et_2$), 141.60 (1C, $NC_6H_3Et_2$), 146.41, 148.24, 155.04 (3C, quinoline). Anal. calcd for $C_{31}H_{49}N_2OSi_2Lu$(%): C, 53.43; H, 7.09; N, 4.02. Found: C, 53.58; H, 6.96; N, 4.17.

Preparation of the complex $L^3Lu(CH_2SiMe_3)_2(THF)$ (4)

Following a similar procedure to that described for the preparation of **1**, the reaction of $Lu(CH_2SiMe_3)_3(THF)_2$ (0.23 g, 0.4 mmol in 3 mL hexane) with an equivalent of HL^3 (0.10 g, 0.4 mmol in 4 mL hexane) gave **4** (0.20 g, 74%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ −0.34 (4H, CH_2SiMe_3), 0.30 (s, 18H, $SiMe_3$), 1.11 (br, 4H, THF), 2.35 (s, 6H, *o*-$NC_6H_3Me_2$), 3.54 (br, 4H, THF), 6.19 (d, $^3J_{H\text{–}H}$ = 7.8 Hz, 1H, quinoline), 6.74 (d, $^3J_{H\text{–}H}$ = 8.1 Hz, 1H, quinoline), 6.95 (q, $^3J_{H\text{–}H}$ = 4.5 Hz, 1H, quinoline), 7.04 (t, 1H, $^3J_{H\text{–}H}$ = 7.4 Hz, $NC_6H_3Me_2$), 7.17 (d, $^3J_{H\text{–}H}$ = 7.5 Hz, 2H, $NC_6H_3Me_2$), 7.23 (t, 1H, $^3J_{H\text{–}H}$ = 7.8 Hz, quinoline), 7.72 (d, $^3J_{H\text{–}H}$ = 8.1 Hz, 1H, quinoline), 8.94 (d, $^3J_{H\text{–}H}$ = 4.5 Hz, 1H, quinoline). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 4.84 (6C, $SiMe_3$), 19.38 (2C, *o*-$NC_6H_3Me_2$), 25.21 (2C, THF), 43.72 (2C, CH_2SiMe_3), 70.91 (2C, THF), 108.32, 110.96, 120.95 (3C, quinoline), 124.24 (1C, $NC_6H_3Me_2$), 129.31 (2C, $NC_6H_3Me_2$), 131.29, 131.61 (2C, quinoline), 135.51 (2C, $NC_6H_3Me_2$), 140.47 (1C, quinoline), 141.70 (1C, $NC_6H_3Me_2$), 146.37, 149.40, 153.80 (3C, quinoline). Anal. calcd for $C_{29}H_{45}N_2OSi_2Lu$(%): C, 52.08; H, 6.78; N, 4.19. Found: C, 52.23; H, 6.57; N, 4.02.

Preparation of the complex $L^1{}_2Nd(CH_2SiMe_3)$ (THF) (5)

Anhydrous $NdCl_3$ (0.17 g, 0.68 mmol) was suspended in 10 mL of THF and the suspension was stirred overnight. A solution of $LiCH_2SiMe_3$ (0.19 g, 2.04 mmol in 10 mL of THF) was added to the above suspension at ambient temperature, and a bright blue solution formed in 10 min. The reaction mixture was stirred for 2 h and then cooled to 0 °C. HL^1 (0.21 g, 0.68 mmol) in 5 mL of THF was then added. The reaction solution was stirred for 2 h at 0 °C. The volatiles were removed under vacuum, and the residue was extracted with 30 mL of hexane. Concentration of the extract solution *in vacuo* to approximately 2 mL and cooling to −10 °C afforded **5** as red crystals (0.13 g, 42% yield). The NMR spectrum of complex **5** was not available due to paramagnetism. Anal. calcd for $C_{50}H_{65}N_4OSiNd$(%): C, 65.96; H, 7.20; N, 6.15. Found: C, 66.18; H, 7.04; N, 6.01.

Polymerization of butadiene

A typical procedure for the polymerization was as follows (Table 1, entry 3): in a glovebox, a toluene solution of **1** (2.0 mL, 10 μmol, 6.4 mg), 100 μmol $AlMe_3$, a toluene solution of $[PhC_3][B(C_6F_5)_4]$ (1.0 mL, 10 μmol, 9.2 mg) and a toluene solution of butadiene (2.0 mL, 10 mmol, 0.54 g) were added into a 25 mL reactor. After a designated time, methanol was injected into the system to quench the polymerization, and the reaction mixture was poured into a large quantity of methanol containing a small amount of hydrochloric acid to precipitate the white solids. The precipitated polymer was collected by filtration, washed with methanol and dried under vacuum at 40 °C to a constant weight to afford 0.54 g (100% yield) of polybutadiene.

Copolymerization of butadiene and isoprene

A typical procedure for the copolymerization was as follows (Table 2, entry 14): in a glovebox, a toluene solution of **1** (12.5 mL, 10 μmol, 6.4 mg), 0.1 mmol $AlMe_3$, a toluene solution of $[PhC_3][B(C_6F_5)_4]$ (5.0 mL, 10 μmol, 9.2 mg), a toluene solution of butadiene (5.0 mL, 25 mmol, 1.35 g), and isoprene (2.5 mL, 25 mmol, 1.70 g) were added into a 50 mL reactor. After a designated period of time, methanol was injected into the system to quench the polymerization, and the reaction mixture was poured into a large quantity of methanol containing a small amount of hydrochloric acid to precipitate the white solids. The precipitated polymer was collected by filtration, washed with methanol and dried under vacuum at 40 °C to a constant weight to afford 3.05 g (100% yield) of polybutadiene.

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