

High *Trans*-1,4 (Co)Polymerization of β -Myrcene and Isoprene with an Iminophosphonamide Lanthanum Catalyst^{*}

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Abstract β -Iminophosphonamide ligated lanthanum bis(benzyl) complex (NPN^{Dipp})La(CH₂Ph-4-Me)₂(THF) (NPN^{Dipp} = Ph₂P(NC₆H₃Pr₂-2,6)₂), upon activation of AlEt₃ and [Ph₃C][B(C₆F₅)₄], exhibited high catalytic activity and high *trans*-1,4 stereoselectivity for the polymerization of bio-sourced β -myrcene (MY). Based on which, a series of novel *trans*-1,4 regulated elastomers could be generated by random/block copolymerization of MY and isoprene (IP).

Keywords: Lanthanum; β -Myrcene; Stereoselectivity.

INTRODUCTION

The synthesis of polymers from biomass-derived monomers is driven by the desire to reduce our dependence on petro-sourced polymeric materials^[1–4]. Great progress has been achieved for the development of renewable polymers. For example, polylactide has been one of the most industrially produced biobased polymers. However, most of efforts have focused on various kinds of biodegradable polyesters generated by coordination or step-growth polymerization of methylene butyrolactones^[5–8], lactide^[9–12], large-ring lactones^[13] and long-chain fatty acid esters *etc*^[14–16]. β -Myrcene (MY) as a kind of readily available natural terpene from plants or from the pyrolysis of pinene was only explored by anionic or free radical polymerization to produce low tactic polymer several decades ago^[17–19]. Until recently, the stereoselective coordination polymerization of MY was achieved by Visseaux's group using rare-earth metal based catalysts to give *cis*-1,4 and *trans*-1,4 regulated poly(β -myrcene) (PMY)^[20–23] and our group reported first perfect isotactic and syndiotactic enriched 3,4-PMY with cationic lutetium alkyl species^[24, 25]. Except for the above-mentioned examples, very few transition metal catalysts were reported to show highly catalytic activity and high stereoselectivity for MY polymerization to our best knowledge, which were in sharp contrast to other conjugated diene monomers such as isoprene and butadiene^[26–36].

For many years, we have pursued the coordination polymerization of conjugated dienes to prepare highly stereoregular polymeric materials with rare-earth metal catalysts^[37]. A series of high *cis*-1,4 *trans*-1,4 and 3,4-selective rare-earth metal catalysts for isoprene/butadiene polymerization have been developed^[26–33]. Recently, a

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cationic lanthanum benzyl catalyst bearing iminophosphonamide ligand have demonstrated highly catalytic activity and high *trans*-1,4 selectivity for the isoprene polymerization in a living fashion^[38]. Intrigued by the exceptional catalytic performance of the cationic iminophosphonamide lanthanum benzyl species, herein we examined the polymerization behaviors of this catalyst in MY homopolymerization and its copolymerization with IP.

EXPERIMENTAL

General Methods

All manipulations were performed under a dry and oxygen-free argon atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. All solvents were purified *via* a SPS system. ClPPh₂, 2,6-diisopropylaniline, AlR₃ (R = ^tBu, Et, Me), MgⁿBu₂ (1 mol/L in hexane), ZnEt₂ (1 mol/L in hexane) and ⁿBuLi were purchased from Aladdin and used without further purification. Isoprene and myrcene were purified by distillation over calcium hydride under a nitrogen atmosphere overnight. Azide^[39], [Ph₃C][B(C₆F₅)₄]^[40] and NPN^{dpp}H^[41] were prepared according to the published procedures. Complex **1** was synthesized according to the previous report (Chart 1)^[38]. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ¹H; 100 MHz for ¹³C) spectrometer. The molecular weight (*M_n*) was measured by TOSOH HLC-8220 GPC at 40 °C using THF as eluent (the flow rate is 0.35 mL/min) against polystyrene standards. Differential scanning calorimetry (DSC) analyses were carried out on a Q100 DSC from Mettler-Toledo Instruments under a nitrogen atmosphere.

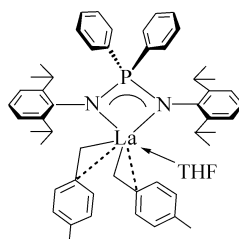


Chart 1 β -Iminophosphonamide-ligated lanthanum bis(benzyl) complex **1**

β -Myrcene Polymerization

A typical polymerization procedure (Table 1, run 1) was described as follows. MY (0.68 g, 5 mmol), **1** (9.6 mg, 10 μ mol), a toluene solution of AlEt₃ (0.05 mmol, 0.1 mL $\times$ 0.5 mol/L), and a toluene solution (2 mL) of [Ph₃C][B(C₆F₅)₄] (9.2 mg, 10 μ mol) were charged into a flask. After 2 h, the viscous reaction solution was poured into ethanol (~40 mL) containing a small amount of hydrochloric acid to terminate the polymerization. PMY was precipitated, filtered, washed with ethanol, and dried under vacuum at 40 °C to a constant weight (0.68 g, 100%).

β -Myrcene and Isoprene Copolymerization

A typical copolymerization procedure (Table 2, run 15) was described as follows. **1** (9.6 mg, 10 μ mol), a toluene solution of AlEt₃ (0.10 mmol, 0.2 mL $\times$ 0.5 mol/L), and a toluene solution (4 mL) of [Ph₃C][B(C₆F₅)₄] (9.2 mg, 10 μ mol) were charged into a flask. The mixture was stirred for 5 min and then MY (0.68 g, 5 mmol) and IP (0.34g, 5 mmol) were added into this mixture. After 2 h, the viscous reaction solution was poured into ethanol (~40 mL) containing a small amount of hydrochloric acid to terminate the polymerization. The copolymer was precipitated, filtered, washed with ethanol, and dried under vacuum at 40 °C to a constant weight (1.02 g, 100%).

RESULTS AND DISCUSSION

The representative polymerization data were summarized in Table 1. The neutral complex **1** was inert to the polymerization of MY. Upon activation with 1 equiv of [Ph₃C][B(C₆F₅)₄] and 5 equiv of AlEt₃, complex **1**

demonstrated highly catalytic activity at room temperature and 500 equiv of MY were completely converted into *trans*-1,4-PMY (94.5%) in 2 h (Fig. 1) (run 1), which showed higher activity than lanthanide borohydride-based catalysts reported by Visseaux's group^[20, 21]. The resultant polymer had a moderate molecular weight ($M_n = 2.8 \times 10^4$) and a narrow molecular weight distribution ($M_w/M_n = 1.21$) (Table 1, run 1), suggesting a living mode of the polymerization, which was further evidenced by sequential monomer addition (Table 1, run 2). The catalytic activity increased with polymerization temperature, so that a complete conversion needed only half an hour at 60 °C (Table 1, run 4). In contrast, lowered temperature facilitated the catalytic selectivity and *trans*-1,4 selectivity of 97.5% was observed at 0 °C (Table 1, run 3) close to the value of cyclopentadienyl ligated neodymium borohydride complex (98.5%)^[21]. For this catalyst system, the type of co-catalysts had dramatic influence on both catalytic activity and selectivity. When AlMe_3 was used, much lower molecular weight of the resultant polymer was observed with a relatively narrow molecular weight distribution (Table 1, run 5), suggesting rapid reversible chain transfer reaction between lanthanum active species and AlMe_3 existed in the

Table 1. Homopolymerization of β -myrcene by using complex **1** under various conditions^a

Run	AlR ₃	T _p (°C)	Time (h)	Yield (%)	Microstructure ^b <i>trans</i> -1,4/ <i>cis</i> -1,4/3,4-	M _n ^c (10 ⁴)	M _w /M _n ^c	T _g ^d (°C)
1	AlEt ₃ (5)	20	2	> 99	94.5/1.0/4.5	2.8	1.21	−69
2 ^e	AlEt ₃ (5)	20	2/2	> 99	95.0/1.1/3.1	5.3	1.25	−69
3	AlEt ₃ (5)	0	2	45	97.9/0.9/1.2	4.5	1.34	−69
4	AlEt ₃ (5)	60	0.5	> 99	90.1/4.3/5.6	1.9	1.28	−64
5	AlMe ₃ (5)	20	2	> 99	88.2/2.7/9.1	0.9	1.25	−60
6	Al ⁱ Bu ₃ (5)	20	2	> 99	64.9/19.1/17.0	6.2	1.83	−55
7	ZnEt ₂ (5)	20	2	40	92.1/2.6/5.3	1.9	1.17	−62
8	Mg ⁿ Bu ₂ (5)	20	2	9	90.2/4.8/5.0	n.d.	n.d.	n.d.
9	AlEt ₃ (10)	20	2	> 99	94.9/4.1/1.0	1.3	1.22	−69
10	AlEt ₃ (20)	20	2	> 99	96.3/0.6/3.1	0.9	1.28	−69
11	AlEt ₃ (40)	20	2	> 99	95.9/0.8/3.3	0.6	1.25	−69

^a Conditions: toluene 2 mL, Cat 10 μmol , [MY]/[Cat] = 500, [Cat]/[Ph₃C][B(C₆F₅)₄] = 1:1, unless otherwise noted;

^b Measured by means of ¹H-NMR and ¹³C-NMR spectroscopy in CDCl₃; ^c Determined by means of gel permeation chromatography (GPC) against polystyrene standards at 40 °C; ^d Determined by differential scanning calorimetry (DSC); ^e Polymerization of 500 equiv of MY for 2 h followed by 500 equiv of MY for another 2 h

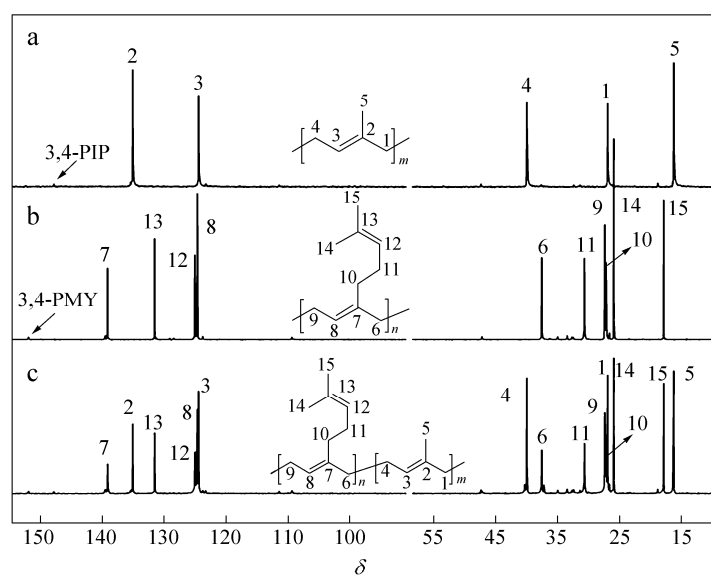


Fig. 1 ¹³C-NMR (100 MHz, CDCl₃, 25 °C) of (a) *trans*-1,4-PIP, (b) *trans*-1,4-PMY (Table 1, run 1), (c) *trans*-1,4-PMY-*b*-*trans*-1,4-PIP (Table 2, run 17)

system. Switching to the bulky Al^iBu_3 led to a substantial reduction of the *trans*-1,4 selectivity (64.9%) (Table 1, run 6). Replace with ZnEt_2 and Mg^nBu_2 deeply reduced the catalytic activity of $1/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ but had a little effect on the selectivity (Table 1, run 7 and 8). It is known that except as a co-catalyst to activate the main precursor, AlR_3 sometimes also behaves as a chain transfer agent to adjust the molecular weight^[42, 43]. Similarly, using the system $1/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{AlEt}_3$, with increasing the Al/La ratio from 10 to 20 and 40, the molecular weight of PMY decreased in an inverse proportion and the molecular weight distribution remained almost unchanged, suggesting a coordinative chain transfer polymerization (CCTP) (Table 1, runs 9–11). Unlike *trans*-1,4 polyisoprene (PIP), a crystalline plastic with about 46 °C of melting point^[31], *trans*-1,4 PMY is an elastomer with a glass transition temperature ($T_g = -69$ °C) (Fig. 2) and could be easily dissolved in CHCl_3 , CH_2Cl_2 and THF *etc.* due to the long alkyl side chains. To our knowledge, complex **1** is the first non-cyclopentadienyl (non-Cp) lanthanum complex to show a high *trans*-1,4 selectivity towards MY polymerization.

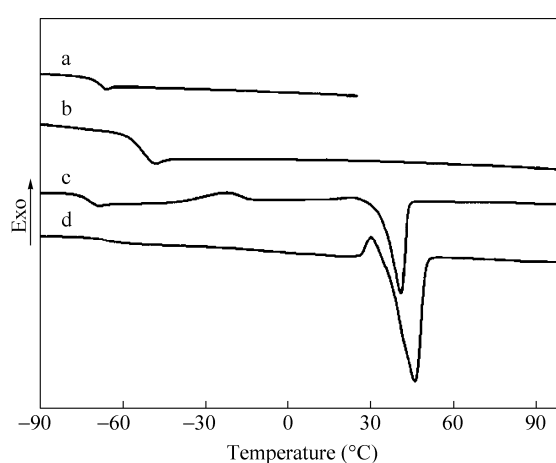


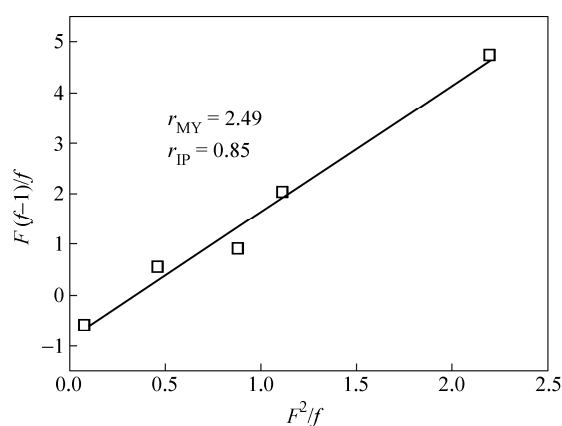
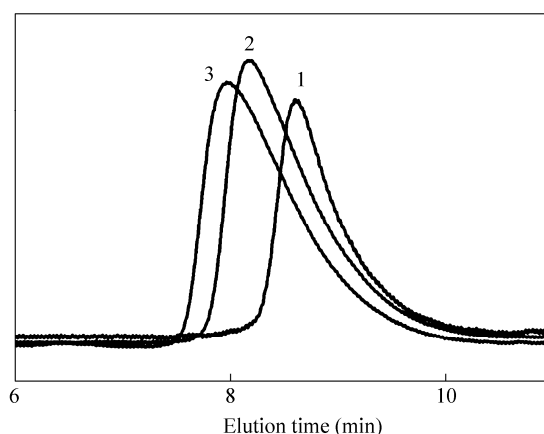
Fig. 2 DSC charts of (a) *trans*-1,4-PMY (Table 1, run 1), (b) PMY-*co*-PIP (Table 2, run 13), (c) PMY-*b*-PIP (Table 2, run 17) and (d) *trans*-1,4-PIP

The copolymerization of two or more different monomers is an efficient strategy to modify the properties of manufactured polymers to meet specific needs, for example to reduce crystallinity, modify glass transition temperature or synthesize new elastomers. Thus, we explored the copolymerization of MY and IP using the catalyst system $1/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{AlEt}_3$ under MY feeding fraction varying from 80% to 10%. The representative polymerization data are listed in Table 2. All the copolymerization could reach complete conversion in 2 h with moderate molecular weights ($M_n = 1.5 \times 10^4$ – 2.4×10^4) and relatively narrow molecular weight distributions ($M_w/M_n = 1.18$ – 1.77) (Table 2, run 12–16). IP and MY united together to generate new type of elastomer with low glass transition temperature and the incorporation of MY with a low dosage could efficiently destroy the crystallinity of *trans*-1,4-PIP (Table 2, run 16). The *trans*-1,4 regularity of both PIP and PMY sequence dropped slightly compared with their homopolymers, as shown by NMR spectroscopy analyses. Monomer reactivity ratios were calculated with the Fineman-Ross equation, based on the data from the copolymerization at low monomer conversions, to be $r_{\text{MY}} = 2.49$ and $r_{\text{IP}} = 0.85$ (Fig. 3). This result indicated that MY was more active than IP. In addition, the sequential addition of two monomers can produce diblock and triblock copolymers thanks to the living polymerization character. GPC curve of the crude copolymer without extraction was unimodal with a narrow molecular weight distribution ($M_w/M_n = 1.22$) (Fig. 4), which was further conformed by ^{13}C -NMR spectroscopy analyses (Fig. 1). The diblock copolymer showed a T_g at -65 °C and a melting point at 40 °C arising from the high *trans*-1,4-PMY block and crystalline *trans*-1,4-PIP block (Fig. 2). The unprecedented PIP-*b*-PMY-*b*-PIP triblock copolymer is one kind of novel thermoplastic elastomer, which has remained unexplored to date, as far as we are aware.

Table 2. Copolymerization of β -myrcene and isoprene by using $1/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{AlEt}_3$ ^a

Run	[MY]/ [IP]	Time (h)	Yield (%)	MY structure ^b (%) <i>trans</i> -1,4/ <i>cis</i> -1,4/3,4	IP structure ^b (%) <i>trans</i> -1,4/ <i>cis</i> -1,4/3,4	M_n^c (10 ⁴)	M_w/M_n^c	T_g/T_m^d (°C)
12	80/20	2	> 99	84.1/14.2/1.7	79.8/12.1/8.1	2.2	1.48	−66/−
13	60/40	2	> 99	80.9/11.0/8.1	76.3/20.3/3.4	1.6	1.46	−66/−
14	50/50	2	> 99	79.0/7.2/13.8	82.5/12.2/5.3	1.5	1.77	−64/−
15	30/70	2	> 99	82.5/10.9/6.6	84.0/3.7/12.3	2.0	1.26	−64/−
16	10/90	2	> 99	77.2/8.9/13.9	88.9/5.5/5.6	2.4	1.18	−69/−
17 ^e	50/50	2/2	> 99	94.6/−/5.4	95.2/0.5/4.3	3.9	1.20 ^f /1.22	−65/40
18 ^g	50/50/50	2/2/2	> 99	92.5/0.7/6.8	95.0/1.0/4.0	4.8	1.22 ^h /1.24	−66/34

^a Conditions: toluene 4 mL, Cat 10 μmol , AlEt_3 100 μmol , $[\text{MY}]/[\text{IP}]/[\text{Cat}] = 500:500:1$ $[\text{Cat}]/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4] = 1:1$, unless otherwise noted; ^b Measured by means of ^1H -NMR and ^{13}C -NMR spectroscopy in CDCl_3 ; ^c Determined by means of gel permeation chromatography (GPC) against polystyrene standards at 40 °C; ^d Determined by differential scanning calorimetry (DSC); ^e Polymerization of 500 equiv of IP for 2 h followed by 500 equiv of MY for another 2 h; ^f M_w/M_n of PIP in the diblock copolymer; ^g Polymerization of 500 equiv of IP for 2 h followed by 500 equiv of MY for another 2 h and followed by 500 equiv of IP for another 2 h; ^h M_w/M_n of PIP-*b*-PMY in the triblock copolymer

**Fig. 3** Fineman-Ross plot for copolymerization of myrcene (MY) and isoprene (IP) with $1/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{AlEt}_3$ at 20 °C ($F = [\text{MY}]/[\text{IP}]$ in feed, $f = [\text{MY}]/[\text{IP}]$ in copolymers, $r_{\text{MY}} = 2.49$ and $r_{\text{IP}} = 0.85$)**Fig. 4** GPC traces of (1) *trans*-1,4-PMY (Table 1, run 1), (2) diblock copolymer (Table 2, run 12) and (3) triblock copolymer (Table 2, run 18)

CONCLUSIONS

We have demonstrated that iminophosphonamide lanthanum bis(benzyl) complex, upon the activation with organoborate and aluminium alkyls, displays high *trans*-1,4 selectivity for the β -myrcene polymerization and the copolymerization with isoprene in a living mode. For the first time, the random copolymerization of β -myrcene and isoprene generated high *trans*-1,4 elastomers with the β -myrcene incorporation rate varied from 10% to 80% and, in addition, a new kind of thermoplastic elastomer, isoprene- β -myrcene-isoprene triblock copolymer, can be obtained *via* sequential monomer addition.

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