

Renewable β -Myrcene Polymerization Initiated by Lutetium Alkyl Complexes Ligated by Imidophosphonamido Ligand*

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Abstract β -Imidophosphonamido ligated lutetium alkyl complex (NPN^{Dipp})Lu(CH₂SiMe₃)₂(THF) (NPN^{Dipp} = Ph₂P(NC₆H₃ⁱPr₂-2,6)₂) with the activation of AlⁱBu₃ and [Ph₃C][B(C₆F₅)₄] exhibited high catalytic activity, medium syndio- (rr = 66%) but remarkably high 3,4-regioselectivity for the polymerization of β -myrcene (MY). In sharp contrast, high isotactic 3,4-polymyrcene (PMY) (mm = 95%) was obtained by the precursor (NPN^{Et})Lu(CH₂SiMe₃)₂(THF) (NPN^{Et} = PPh₂(NC₆H₃ⁱPr₂-2,6)(NC₆H₄-Et-2)) with less bulky substituents on the *N*-aryl ring.

Keywords: Lutetium; β -Myrcene; Regioselectivity.

INTRODUCTION

Investigation of efficient catalyst systems for precise controlling the microstructures of synthetic polymer materials has been a target of macromolecule science, which could provide polymers with versatile properties. For instance, syndiotactic polypropylene (*s*-PP) and syndiotactic polystyrene (*s*-PS) have higher melting points and strength than atactic analogues^[1–3]. Regarding polymerization of conjugated 1,3-dienes (isoprene, butadiene), there exist more complicated regio- and stereospecifically selective polymerization modes (*cis*-1,4, *trans*-1,4, 1,2 or 3,4)^[4–7].

β -Myrcene (MY, CH₃CH₂CH=C(CH₃)₂-1,3-CH₂=CCH=CH₂), a dimer of isoprene (IP), is extracted from natural plant oils, which is a promising candidate of the petroleum-dependent materials, owing to increasing burdens of gradual exhaustion of petroleum resource and environment pollution^[8]. However, polymerization of MY is mainly limited to anionic or free radical polymerization to be transferred to PMY with low tacticity such as 70%–80% 1,4-*cis* enchainment^[9, 10]. Until 2010, highly *cis*-1,4 and *trans*-1,4 regulated PMY were first reported by Visseaux and co-workers using the rare-earth metal borohydride complexes^[11–13].

Very recently, our group reported the first perfect isotactic 3,4-PMY with the lutetium dialkyl complex bearing NSN-bidentate β -diimidodisulfonate ligand^[14]. However, the syndiotactic 3,4-PMY has not been reported yet, meanwhile the syndiotactic 3,4-PIP can be obtained by fluorenyl-modified *N*-heterocyclic carbene and

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β -imidophosphonamido supported rare earth metal bis(alkyl) complexes^[15, 16]. Intrigued by the excellent catalytic performance of cationic β -diimidosulfonate-supported lutetium complex, we examined cationic β -imidophosphonamido ligated lutetium alkyl species for β -myrcene polymerization. We demonstrate that by adjustment of substituents on *N*-aryl ring, the stereoselectivity of lutetium catalysts can be shifted from syndiotacticity to isotacticity.

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 and Li^{*n*}Bu were purchased from Aladdin and used without further purification. Isoprene was purified by distillation over calcium hydride under a nitrogen atmosphere. Azide, [Ph₃C][B(C₆F₅)₄], [PhMe₂NH][B(C₆F₅)₄], B(C₆F₅)₃, Lu(CH₂SiMe₃)₃(THF)₂, NPN^{dipp}H were prepared according to the published procedures^[17–19]. Complexes **1**, **2** and **3** were synthesized according to the previous report^[16, 20]. 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.

β -Myrcene Polymerization

A typical polymerization procedure (Run 1, Table 1) was described as follows. β -Myrcene (0.68 g, 5 mmol), **1** (9.6 mg, 10 μ mol), a toluene solution of Al^{*i*}Bu₃ (0.10 mmol, 0.2 mL $\times$ 0.5 mol/L), and a toluene solution (3 mL) of **B** (9.2 mg, 10 μ mol) were charged into a flask. After 10 min, the viscous reaction solution was poured into ethanol (*ca.* 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%).

RESULTS AND DISCUSSION

The neutral complexes **1**, **2** and **3** were inert to the polymerization of MY, which upon activation with [Ph₃C][B(C₆F₅)₄] and Al^{*i*}Bu₃ showed different catalytic performances in respect of the types of the steric bulkiness on NPN-ligand frame-work (Chart 1). The representative polymerization data are summarized in Table 1. Complex **1** showed high activity at 20 °C to transfer 500 equiv MY completely into 3,4-PMY in 30 min (run 1). The regio- and stereoselectivities of the resultant polymer were determined by NMR method, which was similar to that of polyisoprene^[14]. In the ¹H-NMR spectrum of the obtained polymer (Fig. 1), two singlets at δ = 4.67 and 4.70 can be assigned to the olefinic protons. This is further proven by ¹³C-NMR spectrum (Fig. 2). The signals from δ = 152.41 to 153.21, from δ = 151.13 to 153.20 and from 149.82 to 151.10 were arising from the isotactic sequence, atactic sequence and syndiotactic sequence while the resonances at δ = 150.80 could be assigned to the syndiotactic pentad rrr^[15]. Based on this, the obtained 3,4-PMY has a moderate syndiotacticity (rr = 66%, rrrr = 30%) (run 2). As far as we know, this is the first example of syndiotactic 3,4-PMY.

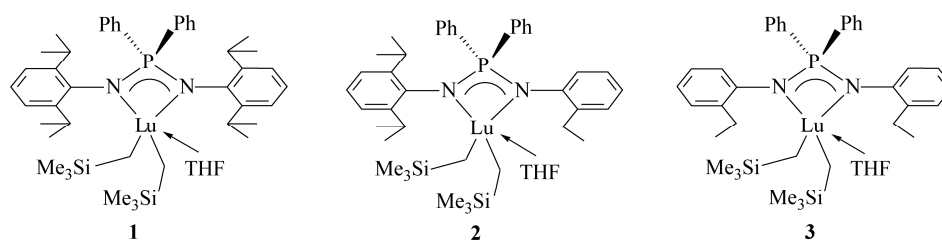


Chart 1 β -imidophosphonamido-ligated lutetium dialkyl complex **1**, **2** and **3**

Increase and decrease of the polymerization temperature ($-30\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$) for this system seemed a little influence of 3,4 selectivity (100% and 94%), but big influence of the catalytic activity (Fig. 1) (runs 2 and 3). Increasing the monomer-to-catalyst molar ratio from 500:1 to 2000:1 the polymerization performed fluently albeit at a prolonged polymerization time when the ratio was over 2000, whilst the molecular weight of the obtained PMY increased correspondingly from 11.5×10^4 to 42.1×10^4 , suggesting the controllable polymerization characteristics (runs 1, 4 and 5). Switching the co-activator from Al^iBu_3 to AlEt_3 and AlMe_3 resulted in decrease of the 3,4-content owing to the formation of the different active species, and the dramatic drop of the molecular weight ascribed to the strong chain transfer characteristics of AlEt_3 and AlMe_3 (runs 6, 7)^[21]. The trityl and anilinium borate activators **A** and **B** showed similar influences on the polymerization activity; while the neutral borane compound **C** showed lower activity (runs 8 and 9). Surprisingly, switching the more bulkier 2, 6-diisopropyl substituent to 2-ethyl one on the aryl ring of complex **1** to form complex **2** not only exhibited extreme 3, 4-regioselectivity (100%), but a distinguishing isospecific selectivity ($\text{mm} = 95\%$) as compared to the more steric NPN^{Dipp} complex **1** in chlorobenzene (Fig. 1 and Fig. 2) (run 13). Switching the *ortho*-positions of Ar to a ethyl group gave a modest 3, 4-selectivity (90%) (run 14). The stereoselectivity switching is mostly attributed to the different transition states that MY coordinates to the active species and the polymerization medium, the similar phenomenon has been observed in the isoprene polymerization^[16]. We postulate that the polar solvent (chlorobenzene) might make the loose ion-pair (the catalytic active species), which facilitates the allyl polymeric active species swinging back to the enantio site of the former MY monomer occupied, leaving the other site adopting the second incoming MY to avoid epimerization or MY coordination in different *re* or *si* faces; meanwhile the more opened space increases the chance to form the *exo-endo* geometry (steric demanding than the *exo-exo* geometry), that increases the isoselectivity^[22]. Both syndiotactic and isotactic polymers are amorphous and soluble in most organic solvents (THF, CHCl_3 or toluene) due to the long alkyl side chains. Somewhat interestingly, syndiotactic PMY also has a higher glass transition temperature ($-30\text{ }^{\circ}\text{C}$) compared with that of isotactic polymer ($-43\text{ }^{\circ}\text{C}$) in accordance with that of syndiotactic and isotactic 3,4-PIP (Fig. 3)^[16].

Table 1. Polymerization of β -myrcene by complexes **1**, **2** and **3**^a

Run	Cat.	[MY]/[Lu]	Temp ($^{\circ}\text{C}$)	Time (h)	Yield (%)	M_n^b ($\times 10^4$)	M_w/M_n^b	Microstructures ^c (%)			T_g^d ($^{\circ}\text{C}$)
								3,4-	rr/rrrr	mr/mm	
1	1	500	20	0.5	100	11.5	1.8	97	58/25	38/4	-32
2	1	500	-30	6	100	26.4	1.7	100	66/30	34/-	-30
3	1	500	60	0.1	100	6.4	2.0	94	50/22	45/5	-35
4	1	1000	20	1	100	27.3	1.8	97	59/25	32/9	-30
5	1	2000	20	3	100	42.1	1.7	98	58/23	34/8	-31
6 ^e	1	500	20	1	100	4.4	1.8	92	48/20	45/7	-30
7 ^f	1	500	20	6	60	3.4	1.5	75	-	-	-47
8 ^g	1	500	20	0.5	86	13.0	1.4	96	56/27	39/5	-32
9 ^h	1	500	20	0.5	trace	-	-	-	-	-	-
10 ⁱ	1	500	-30	6	100	23.1	1.7	100	56/27	37/7	-30
11	2	500	20	0.5	100	7.9	1.8	96	7	51/42	-42
12 ⁱ	2	500	20	0.5	100	8.9	2.1	97	-/-	14/86	-42
13 ⁱ	2	500	-30	6	100	16.9	1.9	100	-/-	5/95	-43
14	3	500	20	0.5	100	8.0	2.2	90	33	23/44	-40

^a Conditions: 3 mL of toluene, 10 μmol of **1**, **2** or **3**, $[\text{Lu}]/[\text{B}]/[\text{Al}^i\text{Bu}_3] = 1:1:5$ (**B** = $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$); ^b Determined by GPC in THF at $40\text{ }^{\circ}\text{C}$ against polystyrene standards; ^c Determined by ^1H -NMR and ^{13}C -NMR spectroscopy in CDCl_3 ; ^d Measured by DSC; ^e In chlorobenzene; ^f AlEt_3 used; ^g AlMe_3 used; ^h **B** = $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$; ⁱ In chlorobenzene

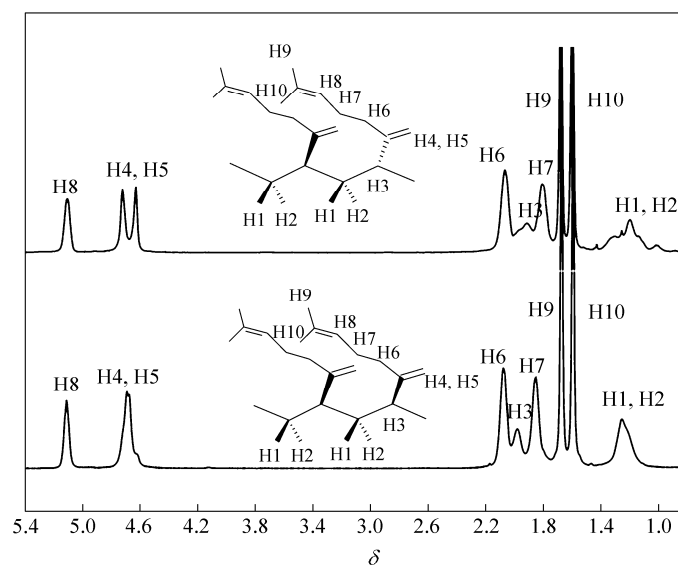


Fig. 1 Overlay of ^1H -NMR spectra (CDCl_3 , 400 MHz, 25 $^\circ\text{C}$) of PMY produced by complex **1** (top, run 2) and complex **2** (bottom, run 13)

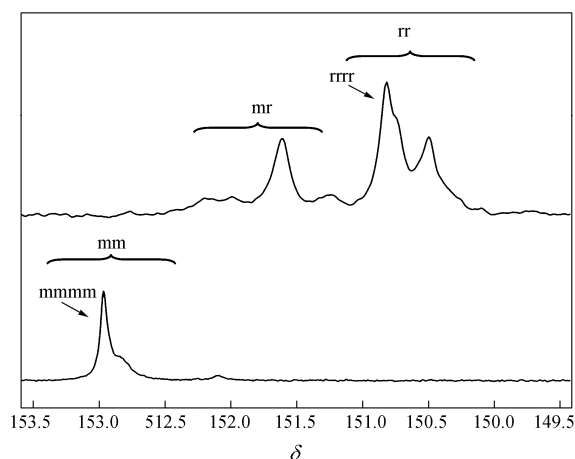


Fig. 2 Overlay of ^{13}C -NMR spectra (CDCl_3 , 100 MHz, 25 $^\circ\text{C}$) of PMY produced by complex **1** (top, run 2) and complex **2** (bottom, run 13)

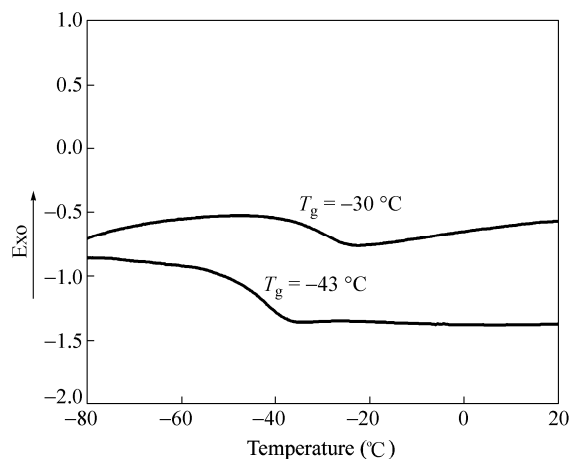


Fig. 3 DSC charts of syndiotactic (top, run 2) and isotactic (bottom, run 13) 3,4-PMY

CONCLUSIONS

In conclusion, we have demonstrated that β -imidophosphonamido-supported lutetium alkyl complexes, in combination with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and alkylaluminum, generated the first example featuring high 3,4-regio and moderate syndiotactic selectivity for the polymerization of β -myrcene. When the substituted group on aryl ring was changed, the high catalytic activity was maintained, but the stereoselectivity changed to highly isotactic. The syndiotactic 3,4-PMY has a higher T_g than isotactic 3,4-PMY.

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