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Ioselective 3,4-(co)Polymerization of Biorenewable Myrcene Using NSN-Ligated Rare-earth Metal Precursors: Approach to New Elastomer

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Polymerization of biorenewable myrcene (MY) by using the cationic β -diimidosulfonate lutetium catalyst in high activity, afforded the unprecedented isotactic 3,4-polymyrcene (PMY) with a low T_g (-42°C), based on which, the random and block copolymerization of myrcene and isoprene (IP) gave the novel elastomers comprising the amorphous *iso*-3,4-PMY and *iso*-3,4-PIP sequences.

Due to the increasing burdens of gradual exhaustion of petroleum resource and environment pollution nowadays, there has been a growing demand for finding alternatives of the petroleum-dependent materials.¹ For instance, the biodegradable and biocompatible polyesters that can be easily synthesized from the bioresourced monomers such as methylene butyrolactones (MBL),² lactide,³ large-ring lactones⁴ or long-chain fatty acid esters⁵ *etc.* by ring-opening polymerizations or polycondensation, have been found wide applications such as the daily used plastics to replace polyolefins. Meanwhile, polydienes have versatile stereoregularities, for instance, *cis*-1,4 polyisoprene (PIP) can be used as a promising candidate to replace natural rubber (NB) for tires manufacture;⁶ *trans*-1,4 PIP⁷ is usually employed as an important component of tire-sides; 3,4-PIP⁸ and 1,2-PBD⁹ can be used to prepared high-value-added rubbers or long-life “green” tires, however, all are from the petroleum-resourced monomers.

β -Myrcene (MY, $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2-1,3-\text{CH}_2=\text{CCH}=\text{CH}_2$), a dimer of IP, is found in many natural plant oils.¹⁰ Although having the similarity to IP, MY is limited to anionic or free radical polymerization to be transferred to PMYs with low tacticity such as 70%–80% 1,4-*cis* enchainment.¹¹ Recently, the first stereoselective coordination polymerization of MY has been achieved by Visseaux and co-workers using neodymium and lanthanum borohydride-based catalysts to give highly *cis*-1,4 and

trans-1,4 regulated PMY albeit with low solubility in common solvents, probably owing to the presence of crosslinking.¹² To date no catalysts are reported to show high 3,4-selectivity for β -MY polymerization.

During our previous studies on IP polymerization, we found that the lutetium dialkyl complex **1** (Chart 1) bearing NSN-bidentate β -diimidosulfonate ligand under the activation of organoborate exhibited perfect 3,4-regio- and isospecific stereo-selectivity for IP polymerization.^{8c} Herein, we wish to report that by using the in-situ generated cationic β -diimidosulfonate lutetium alkyl species, the polymerization of MY with perfect 3,4-regio- (> 99%) and isospecific stereo-selectivity (*mmmm* > 99%) can be achieved for the first time, as far as we are aware. Surprisingly, this new PMY is an elastomer with a low T_g . In addition, this cationic catalyst has also exhibited highly efficient dual catalysis towards the regio- and stereo-selective copolymerization of MY and IP.

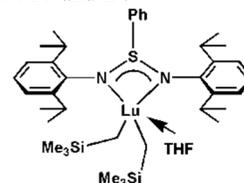


Chart 1. β -Diimidosulfonate-ligated Lutetium Dialkyl Complex 1.

The representative polymerization data are summarized in Table 1. Activated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and Al^iBu_3 , complex **1** showed a high activity for the polymerization of MY at 20°C by transferring 500 equiv. of MY completely in a short time (30 min) into 3,4-PMY (99%) ($\delta = 4.69$ ppm for the two vinyl protons in ^1H NMR; $\delta = 153.00$ ppm for the tertiary carbon C3 (Fig. 1) in ^{13}C NMR) with an excellent isotacticity (*mmmm* = 96%)¹³ and a relatively narrow molecular weight distribution ($M_w/M_n = 1.60$) (run 1). The catalytic activity increased with polymerization temperature that a complete conversion needs only 6 min at 60°C (run 2). In contrast, performing the polymerization at -30°C facilitated catalytic selectivity that a perfect isotactic 3,4-PMY was obtained (3,4-selectivity = 100%, *mmmm* = 100%) evidenced by the strong and sharp singlet appearing at $\delta = 153.00$ ppm and the absence of the other pentad resonances (run 3) (Fig. 1, SFigs. 1-3 DEPT HSQC).^{11b} 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 12.5×10^4 to 46.1×10^4 , suggesting the

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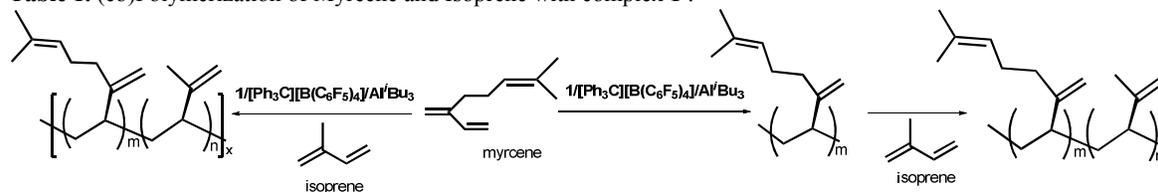
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Table 1. (co)Polymerization of Myrcene and Isoprene with complex **1**.^a

Run	[MY]/[IP]	Temp (°C)	T (h)	Yield (%)	Microstructure (%) ^b			M_n ($\times 10^4$) ^c	M_w/M_n ^c	T_g (°C) ^d
					3,4-/3,4-	<i>mm</i>	<i>mmmm</i>			
1	500/0	25	0.5	100	99/-	96	96	12.5	1.60	-42
2	500/0	60	0.1	100	94/-	90	90	4.6	2.43	-42
3	500/0	-30	12	100	100/-	100	100	22.7	1.41	-42
4	1000/0	25	0.5	100	99/-	96	96	27.9	1.49	-43
5	2000/0	25	3	100	99/-	94	94	46.1	1.46	-40
6 ^e	500/0	25	1	100	97/-	93	30	2.8	1.92	-37
7 ^f	500/0	25	6	27	77/-	n.d.	n.d.	3.0	1.45	-41
8 ^g	500/0	25	0.5	100	99/-	93	93	11.8	1.63	-42
9 ^h	500/0	25	6	46	80/-	n.d.	n.d.	2.2	1.50	-40
10 ⁱ	500/0	25	1	100	99/-	46	23	12.9	2.21	-38
11	0/500	-30	6	100	-/99	100	99	15.1	1.80	30/170 ^j
12	500/500	25	0.5	100	98/96	95/92	83/78	14.3	1.63	-15
13 ^k	500/500	25	1	100	98/96	96/91	96/65	18.1	1.62	-35/25 ^l
14 ^k	500/500	-30	12	100	100/100	99/99	99/99	25.3	1.46	-37/24 ^l

^a Conditions: 2 mL of C₆H₅Cl, 10 μ mol of **1**, [Lu]/B/AlR₃ = 1:1:5 (B = [Ph₃C][B(C₆F₅)₄]). ^b Determined by ¹H NMR and ¹³C NMR spectroscopy in CDCl₃.

^c Determined by GPC in THF at 40 °C against polystyrene standard. ^d Measured by DSC. ^e AlEt₃ used. ^f AlMe₃ used. ^g B = [PhMe₂NH][B(C₆F₅)₄]. ^h B = B(C₆F₅)₃.

ⁱ In toluene. ^j T_g/T_m ^k Sequential addition of 500 equiv of myrcene and 500 equiv of isoprene. ^l T_g/T_m

controllable polymerization characteristics (runs 1, 4 and 5).

Switching the co-activator from AlⁱBu₃ to AlEt₃ and AlMe₃ 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 AlEt₃ and AlMe₃ (runs 6,7).¹⁴ The anilinium borate [PhMe₂NH][B(C₆F₅)₄] behaved in the similar performance to the trityl one [Ph₃C][B(C₆F₅)₄], however, on the contrary, the neutral borane compound B(C₆F₅)₃ was a very poor activator (runs 8,9), similar behaviors of these borates have been found in many rare-earth metal catalyzed conjugated dienes systems reported previously.¹⁵ When the polymerization medium was changed to the non-polar toluene, an obvious drop of the stereo isoselectivity was observed although the 3,4-regioselectivity seemed to be unaffected, which was in accordance with our previous report that the polar chlorobenzene solvent facilitated the stereo isoselective 3,4-polymerization of IP (run 10).^{8c} Noteworthy was that unlike isotactic 3,4-PIP that is a crystalline plastic having a high melting point (run 11), isotactic 3,4-PMY is an elastomer with a low glass transition temperature ($T_g = -42$ °C, S Figs. 13, 14) and can be easily dissolved in CHCl₃, CH₂Cl₂ and THF *etc* (run 2) due to the long alkyl side chains. Nevertheless, in no case, gel-formation was observable during the MY polymerization with this cationic complex **1** system, suggesting

that it was absolutely inert to the remained double bonds. The excellent catalytic performances of **1**/[Ph₃C][B(C₆F₅)₄]/AlⁱBu₃ towards both highly regio- and isospecific polymerizations of IP and MY prompted us to attempt their copolymerization. The copolymerization was firstly performed in chlorobenzene at room temperature by mixing equivalent MY and IP together. Delighted to us, both the high regio and stereoselectivities were maintained although slightly lower than those in the corresponding homopolymerizations. Only one T_g was found in the obtained copolymer, and no melting temperature T_m was observable, indicating a random microstructure (run 12) (S Figs. 8, 9). Whilst sequential addition of the two monomers into the system, block copolymer was achieved (runs 13,14). More obviously, the block copolymer displays strong and sharp singlets at $\delta = 153.01$ ppm and $\delta = 149.24$ ppm assigned to the isotactic 3,4-PMY block (*mmmm* = 99%) and the isotactic 3,4-PIP block (*mmmm* = 99%), respectively (S Fig. 10). In addition, the block copolymer has two T_g s at 24 °C and -37 °C (or -35 °C and 25 °C) owing to the two different long monomer sequences, which, however, are close to but different from those of their homopolymers. No T_m arising from the isotactic 3,4-PIP sequence is observed (isotactic 3,4-PIP is crystalline with $T_m = 160$ °C), which might be ascribed to the amorphous PMY interrupting the crystallinity of the isotactic PIP (S Fig. 15). To distinguish further the random and block

microstructures, low molecular weight block or random copolymers were prepared following the sequential or concurrent monomer addition manner but in the very low molar ratio of the monomers against complex **1** (IP:MY: **1** = 12.5:12.5:1). The very weak new signal around 33.9 ppm is attributed to the joint of PMY and PIP (SFig. 11a), indicating the diblock structure. The

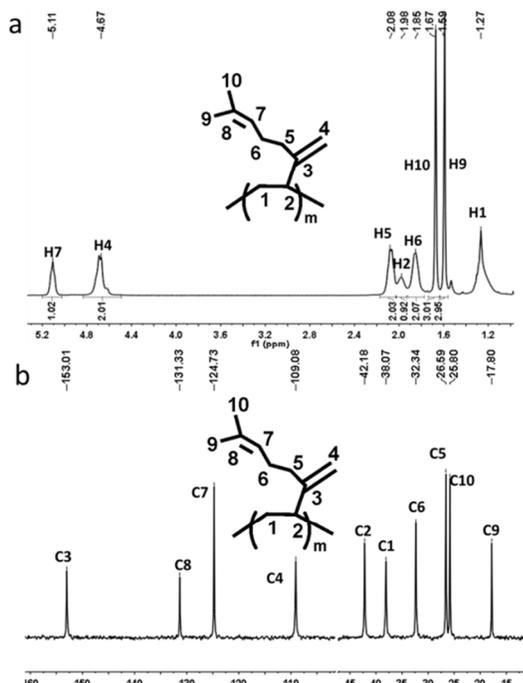


Fig. 1 ^1H NMR and ^{13}C NMR of 3,4 isotactic PMY (run 3)

random copolymer gives broadened multiple resonances around 42.0 ppm, 32.4 ppm and 18.2 ppm, which are assigned to the connections of PMY-PMY-PIP and PIP-PMY-PIP overlapping with the corresponding signals arising from PIP and PMY units (SFig. 11b), in contrary to the sharp singlet resonances in the block one.

To spread more lights on the morphology of the copolymers, atomic force microscopy (AFM) and transmission electron micrograph (TEM) characterizations were employed, which revealed that the copolymers are microphase-separated with the isotactic 3,4-PIP as the dispersed phase and the amorphous 3,4-PMY as the matrix (SFigs.16 and 17).

In summary, we have demonstrated that by means of a cationic lutetium-based coordination complex bearing the β -diimidisulfonate ligand, coordination polymerization of MY with high activity and the absence of cross-linking has been achieved for the first time. More strikingly, the polymerization is perfect 3,4-regio- and isospecific stereo-selective (3,4-selectivity > 99%, *mmmm* > 99%). This unprecedented polymer is a new elastomer having a lower glass transition temperature, in contrast to isotactic 3,4-PIP that is crystalline. Moreover, the isoprene-myrcene diblock copolymers, (*iso*-3,4-PMY)-*b*-(*iso*-3,4-PIP), composed of the amorphous elastic *iso*-3,4-PMY unit and the *iso*-3,4-PIP unit, as well as the random copolymers, have been obtained through sequential addition or mixing the two monomers in one pot.

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= $\{I(mmmm)/I(mmmr) + I(mmrr) + I(mmmm)\} \times 100$ (see in SFigs 1-3).

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