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

Bo Liu, Lei Li, Guangping Sun, Dongtao Liu, Shihui Li and Dongmei Cui

Polymerization of biorenewable myrcene (MY) by using the cationic β-dimidosulfonate lutetium catalyst in high activity, afforded the unprecedented isotactic 3,4-polymyrcene (PMY) with a low Tg (−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. For instance, the biodegradable and biocompatible polyesters that can be easily synthesized from the biorenewable monomers such as methylene butyrolactones with a low Tg afford the unprecedented isotactic 3,4-polymyrcene (PMY) with perfect 3,4-regio- (> 99%) and isospecific stereo-selectivity (mammam = 99%) can be achieved for the first time, as far as we are aware. Surprisingly, this new PMY is an elastomer with a low Tg. 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-Dimidosulfonate-ligated Lutetium Dialkyl Complex I.

The representative polymerization data are summarized in Table 1.Activated with [Ph3C][B(C6F5)4] and Al′Bu3, complex I 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%) (δ = 4.69 ppm for the two vinyl protons in 1H NMR; δ = 153.00 ppm for the tertiary carbon C3 (Fig. 1) in 13C NMR) with an excellent isotacticity (mammam = 96%) and a relatively narrow molecular weight distribution (Mw/Mn = 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 cationic selectivity that a perfect isoacatic 3,4-PMY was obtained (3,4-selectivity = 100%, mammam = 100%) evidenced by the strong and sharp singlet appearing at 153.00 ppm and the absence of the other pentad resonances (run 3) (Fig. 1, SFig. 1-3 DEPT HSQC). 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 × 10⁶ to 46.1 × 10⁶, suggesting the...
Table 1. (co)Polymerization of Myrcene and Isoprene with complex 1.

| Run | [MY]/[IP] | Temp (°C) | T (h) | Yield (%) | 3,4-/3,4- | Microstructure (%) | $M_n$ ($10^4$) | $M_n/M_w$ | $T_g$ (°C)
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<td>12</td>
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<td>100/-</td>
<td>100/100</td>
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<td>-43</td>
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<td>3</td>
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<td>97/-</td>
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<td>100</td>
<td>99/-</td>
<td>93/93</td>
<td>11.8</td>
<td>1.63</td>
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<td>99/99</td>
<td>25.3</td>
<td>1.46</td>
<td>-37/24</td>
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- Conditions: 2 mL of $C_6H_{13}Cl$, 10 μmol of 1, [Lu]/[AIR] = 1:1.5 (B = [Ph₆C][B(C₆F₅)₃]).
- Determined by $^1$H NMR and $^{13}$C NMR spectroscopy in CDCl₃.
- Determined by GPC in THF at 40 °C against polystyrene standard.
- Measured by DSC. "AIE₃ used. "AlMe₃ used. "B = [PhMe₃NH][B(C₆F₅)₃]. "B = [Ph₆C][B(C₆F₅)₃].
- In toluene.
- $T_g/T_n$. "Sequential addition of 500 equiv of myrcene and 500 equiv of isoprene. "$T_g/T_s$ measured by DSC.

Switching the co-activator from AlEt₃ to AIE₃ 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 AIE₃ and AlMe₃ (runs 6, 7). The anilinium borate [PhMe₃NH][B(C₆F₅)₃] behaved in the similar performance to the triyl one [Ph₆C][B(C₆F₅)₃], 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. 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). Noteworthy was that unlike isotactic 3,4-PPI 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, SFigs. 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/[Ph₆C][B(C₆F₅)₃]/AlBu₃ 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) (SFigs. 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 (mmm = 99%), respectively (SFig. 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 (SFig. 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

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 micro-phase-separated with the isotactic 3,4-PMY as the dispersed phase and the amorphous 3,4-PMY as the matrix (SFig.s 16 and 17).

In summary, we have demonstrated that by means of a cationic lutetium-based coordination complex bearing the β-dimidoisulfonate 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 elastomeric material with a lower glass transition temperature, in contrast to isotactic 3,4-PIP that is crystalline. Moreover, the isoprene–isoprene 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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Notes and references


7. Selected trans-1,4 Selective catalyst systems for isoprene polymerization, see: (a) M. Zimmermann, K. W. Tomroost and R. Anwander, Angew. Chem., Int. Ed., 2008, 47, 775; (b) W. Rong, D. Liu, H. Zuo, Y. Pan, Z. Jian, S. Li, and D. Cui, Organometallics, 2013, 32, 1166; (c) H. Liu, J. He, Z. Liu, G. Du, S. Zhang, and X. Li, Macromolecules, 2013, 46, 3257.


13. The regioselectivity was determined by 1H NMR and 13C NMR. First, the 3,4 regioselectivity can be easily determined by 1H NMR. Stereoregularity of mycetene was determined by the C3 (Fig. 1) resonances in 13C NMR spectrum. The mmmm pentad peak (δ = 153.00 ppm (C3)) appears at the lowest field region compared with the other mnnm, mnmm, mnmn and mrmr pentads. 3.4% = [(I-C=C-3-M-3-4 motif)]/I(C=C-3-M-3-4 motif)] + 2[2C-FM=C-1-M-4-4 motif)] x 100, mm% = [I(mm)/I(mm) x I(mn) + I(mn)] x 100, mm%
\[ \frac{I(mmnr)}{I(mmnr) + I(mmrr) + I(mmnnn)} \times 100 \text{ (see in SFigs 1-3).} \]

14 (a) R. L. Kuhlman; T. T. Wenzel, Macromolecules, 2008, 41, 4090;

15. (a) D. Li; Li, S.; D. Cui; X. Zhang, Organometallics, 2010, 29, 2186;
(b) K. Lv; D. Cui, Organometallics, 2008, 27, 5438.