

# Regio- and Stereoselective Polymerization of Bio-based Ocimene by Rare-Earth Metal Catalysts

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## Electronic Supplementary Information

**Abstract** Coordination polymerization of renewable  $\beta$ -ocimene has been investigated using asymmetric diiminophosphinate lutetium complex **1**,  $\beta$ -diketiminate yttrium complex **2**, bis(phosphino)carbazolide yttrium complex **3**, half-sandwich benzyl fluorenyl scandium complex **4** and pyridyl-methylene-fluorenyl rare-metal complexes **5a–5c**. Complexes **1**, **4** and **5a–5c** show *trans*-1,2-regioselectivities and high activities, of which **5c** exhibits excellent isoselectivity (*mmmm*>99%). Conversely, complexes **2** and **3** promote  $\beta$ -ocimene polymerization to produce isotactic *cis*-1,4-polyocimenes (*cis*-1,4>99%, *mm*>95%). Diblock copolymers *cis*-1,4-PIP-block-*cis*-1,4-POc and *cis*-1,4-PBD-block-*cis*-1,4-POc are obtained in one-pot reactions of  $\beta$ -ocimene with isoprene and butadiene using complex **3**. Epoxidation and hydroxylation of polyocimene afford functionalized polyolefins with enhanced  $T_g$  (from  $-20$  °C to  $79$  °C and  $74$  °C) and hydrophilicity.

**Keywords** Biobased monomer; Terpenes; Ocimene; Rare-earths; Polymerization; Regio/stereoselectivity; Elastomer

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## INTRODUCTION

Polymer-based materials have pervaded every aspect of our daily lives and it's hard to imagine the life without it.<sup>[1,2]</sup> Nevertheless, dwindling fossil resources present a big challenge for the fossil-based polymers industry. On the other hand, the increasing strict requirements from regulators and demands by consumers also drive us to explore sustainable polymers from the renewable natural resources. Thus, the substitution of fossil resources by sustainable resources has gained a massive amount of attention over the last few decades. Accordingly, a large amount of bio-based polymers have been synthesized using renewable monomers, stemming from nature resources.<sup>[3–14]</sup>

Terpenes are a family of naturally occurring compounds available from many conifer species, etc., and formally consist of multiple isoprene units according to the “isoprene rule” of Ruzicka.<sup>[15]</sup> Owing to the 1,3-diene structure, linear terpenes like  $\beta$ -ocimene,<sup>[16–23]</sup>  $\beta$ -myrcene,<sup>[24–43]</sup> and  $\beta$ -farnesene<sup>[15,44–49]</sup> (Scheme 1), etc., have been polymerized us-

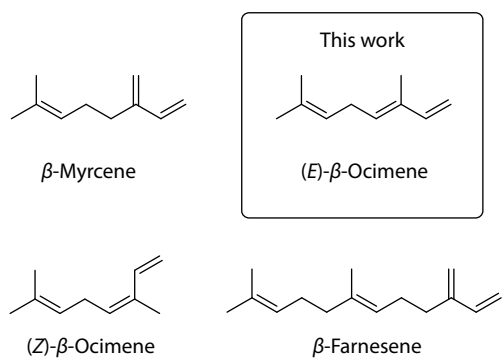
ing various polymerization techniques, such as coordination polymerization,<sup>[50]</sup> to afford polymers with a range of stereochemistries and microstructures. These polymers are potential substitutes for fossil-based synthetic rubber. In contrast to  $\beta$ -myrcene and  $\beta$ -farnesene,  $\beta$ -ocimene, mainly originating from basil and lavender oil, has a unique substitution pattern at the 1,3-diene segment featuring a 3,4-disubstituted 1,3-diene. This variation endows it different polymerization behaviors during coordination polymerization. Li and coworkers<sup>[19]</sup> firstly prepared syndiotactic *cis*-1,4-polyocimene (*cis*-1,4 unit=100%, *rrrr*=100%) at  $-40$  °C with a chiral half-sandwich scandium dialkyl precursor and isotactic *trans*-1,2-polyocimenes (*trans*-1,2-unit=100%, *mm*=100%) at  $30$  °C with  $\text{Cp}^*\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ . Valencia *et al.*<sup>[22]</sup> demonstrated that the neodymium-based catalysts only produced 1,4-rich polyocimenes (1,4-unit $\leq$ 79%). Capacchione and coworkers<sup>[23]</sup> found that the *tert*-butyl substituted [OSSO] titanium catalyst gave a *trans*-1,4 rich polyocimene (70%) at  $70$  °C and the bulky 2-phenyl-2-propyl substituted [OSSO] titanium catalyst generated an isotactic 1,2-polyocimene (>99%) at  $0$  °C. Overall, insight regarding the coordination polymerization of ocimene remain scarce.

Rare-earth metal catalysts have demonstrated excellent catalytic performances for the selective polymerization of

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conjugated dienes, such as isoprene,<sup>[51–53]</sup> butadiene,<sup>[54–56]</sup>  $\beta$ -myrcene,<sup>[23,27–30,33,39]</sup> (*E*)-4,8-dimethyl-1,3,7-nonatriene,<sup>[12]</sup> 1-substituted-1,3-butadiene<sup>[13]</sup> as well as polar 1,3-dienes.<sup>[57]</sup> It is well-known that the microstructures of resultant polymers are closely related with the coordination environments around the metal active centers endowed by different kinds of ligands and metal types. In this contribution, the polymerization behaviors of  $\beta$ -ocimene were investigated using various rare-earth metal catalysts (Scheme 2), which show different regio- and stereoselectivity for isoprene polymerization. The first isotactic *cis*-1,4-polyocimene was generated. The post-functionalization of resultant polyocimenes were also carried out.

## EXPERIMENTAL

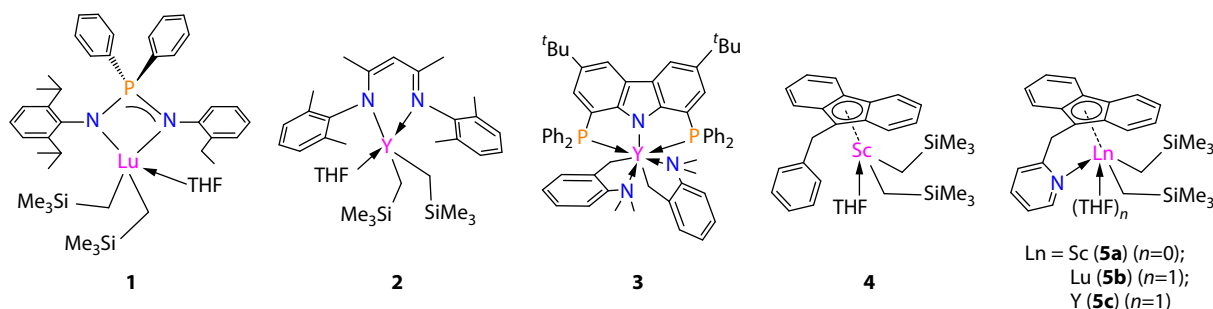
### Materials and Instruments

All manipulations were performed under a dry and oxygen-free nitrogen atmosphere using standard high-vacuum Schlenk

techniques or in a glovebox. All solvents were purified via a SPS system.  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  are purchased from Energy Chemical. The monomer ocimene was a mixture of isomers and purchased from Sigma-Aldrich, dried over  $\text{CaH}_2$ , distilled twice before use.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker AV400 (400 MHz for  $^1\text{H}$ ; 100 MHz for  $^{13}\text{C}$ ) or AV500 (500 MHz for  $^1\text{H}$ ; 125 MHz for  $^{13}\text{C}$ ) spectrometer. The molecular weight ( $M_n$ ) was measured by TOSOHHL-8420 GPC at 40 °C using THF as eluent (the flow rate is 0.175 mL/min) against polyisoprene standards. The glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of the polymer was measured through differential scanning calorimetry (DSC) analyses, which was carried out on a METTLER TOPEM DSC instrument under nitrogen atmosphere. Any thermal history difference in the polymers was eliminated by first heating the specimen to above 140 °C, cooling at 10 °C/min to –100 °C, and then recording the second DSC scan from –100 °C to 100 °C at 10 °C/min.

### Ocimene Polymerization

A typical polymerization procedure (Table 1, run 3) was described as follow. In the glove box, ocimene (0.68 g, 5 mmol) was added into a 10 mL flask. Then, 10 equiv. of  $\text{Al}^i\text{Bu}_3$  (0.20 mL, 0.5 mol/L), a toluene solution (2.0 mL) of complex **3** (10.0 mg, 10  $\mu\text{mol}$ ), and 1 equiv. of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (9.2 mg, 10  $\mu\text{mol}$ ) were added to the flask at 25 °C. After the reaction was stirred for 1.5 h, methanol (containing 1 wt% butylhydroxytoluene (BHT) as a stabilizing agent) was injected to terminate the polymerization. The mixture was poured into a large quantity of methanol (50 mL). The obtained polymer was dried under vacuum at 40 °C to a constant weight. The isomer contents of the polyocimene products were calculated from the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra according to the following equations (Eqs. 1–4):



**Table 1** Polymerization of  $\beta$ -ocimene with various rare-earth metal complexes.<sup>a</sup>

Run	Cat.	Time (h)	Conv. (%)	Microstructure <sup>b</sup> (%)		$M_n^c$ ( $10^4$ )	$M_w/M_n^c$	$T_g^d$ (°C)
				<i>cis</i> -1,4 ( <i>mm</i> )	<i>trans</i> -1,2 ( <i>mmmm</i> )			
1	<b>1</b>	0.5	71	–	>99(32)	8.9	2.83	–29
2	<b>2</b>	1	65	>99(95)	–	15.8	1.61	–22
3	<b>3</b>	1.5	73	>99(99)	–	10.5	1.16	–21
4	<b>4</b>	0.5	66	17	83	7.4	1.56	–29
5	<b>5a</b>	0.5	67	8	92(0)	3.7	1.60	–29
6	<b>5b</b>	0.5	66	–	>99(22)	5.4	1.67	–28
7	<b>5c</b>	0.5	68	–	>99(99)	6.1	1.33	–29/76, 93 <sup>e</sup>

Conditions: <sup>a</sup> Complex 10  $\mu\text{mol}$ ;  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  10  $\mu\text{mol}$ ;  $\text{Al}^i\text{Bu}_3$  100  $\mu\text{mol}$ ; Toluene 2 mL; Ocimene 5 mmol; Temperature 25 °C; <sup>b</sup> Determined by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy; <sup>c</sup> Determined by GPC in THF at 40 °C against a polystyrene standard; <sup>d</sup> Determined by DSC; <sup>e</sup>  $T_g/T_m$ .

$$\text{Mol } cis\text{-}1,4\text{-Oc}\% = [I_{\text{Hd}} / (I_{\text{Hd}} + I_{\text{He}'} / 2)] \times 100\% \quad (1)$$

$$\text{Mol } trans\text{-}1,2\text{-Oc}\% = [0.5I_{\text{He}'} / (I_{\text{Hd}} + I_{\text{He}'} / 2)] \times 100\% \quad (2)$$

where  $I_{\text{Hd}}$  is the integration of the resonance at 2.50 ppm (one proton of the *cis*-1,4-ocimene unit), and  $I_{\text{He}'}$  is the integration of the resonance at 2.63 ppm (two protons of the *trans*-1,2-ocimene unit).

$$\text{Mol isotactic } cis\text{-}1,4\text{-Oc}\% = [I_{mm} / IC_i] \times 100\% \quad (3)$$

$$\text{Mol isotactic } trans\text{-}1,2\text{-Oc}\% = [I_{mmmm} / IC_r] \times 100\% \quad (4)$$

where  $I_{mm}$  is the integration of the signals around 136.7–137.3 ppm assigned as the *mm* unit of the olefinic carbon C1 of the isotactic *cis*-1,4-ocimene unit, while  $IC_i$  is the integration of the signals around 135.0–137.5 ppm.  $I_{mmmm}$  is the integration of the signals at 138.5 ppm assigned as the *mmmm* unit of the olefinic carbon C1' of the isotactic *trans*-1,2-ocimene unit, while  $IC_r$  is the integration of the signals around 137.0–139.0 ppm.

### Copolymerization of Ocimene and Isoprene

Under nitrogen atmosphere, ocimene (0.68 g, 5 mmol) and isoprene (0.34 g, 5 mmol) were added into a 10 mL flask. Then, 10 equiv. of  $\text{Al}^i\text{Bu}_3$  (0.20 mL, 0.5 mol/L) in toluene, a toluene solution (4.0 mL) of complex **3** (10.0 mg, 10  $\mu\text{mol}$ ), and 1 equiv. of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (9.2 mg, 10  $\mu\text{mol}$ ) were added to the flask at 25 °C. After the reaction was stirred for 3.5 h, methanol (containing 1 wt% butylhydroxytoluene (BHT) as a stabilizing agent) was injected to terminate the polymerization. The mixture was poured into a large quantity of methanol (50 mL). The obtained polymer was dried under vacuum at 40 °C to a constant weight. The copolymerization process of ocimene with butadiene resembles that described above.

### Epoxidation of Polyocimene

In a 100 mL flask, 0.3 g of a POC was dissolved into 25 mL of dichloromethane by stirring. *m*-Chloroperbenzoic acid (760 mg, 4.4 mmol) was added to the solution at 0 °C, and then the resulting solution was stirred for 3 h. The reaction mixture was quenched by the addition of saturated aqueous  $\text{Na}_2\text{SO}_3$  under vigorous stirring. The organic layer was separated and washed for three times with 1 mol/L aqueous NaOH. The solvent was evaporated under reduced pressure and the epoxidation polymer (POc-EO) was dried in high vacuum until constant weight.

### Hydroxylation of Polyocimene

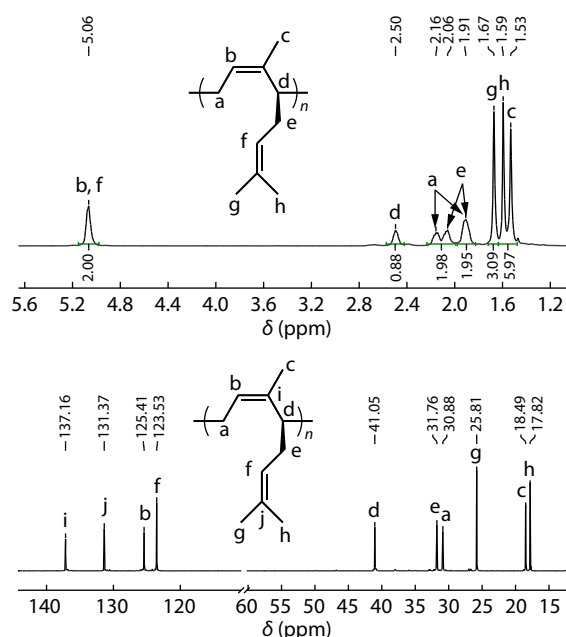
POc-EO (0.1 g, 1.22 mmol of epoxy groups) was dissolved in 30 mL of acetone/chloroform (2/1, V/V) at room temperature. HCl (3 mmol, 36 wt% aqueous solution) was added dropwise to the polymer solution, and stirred for 5 h at room temperature. The reaction was terminated by adding plenty of deionized water, and then the solution was washed with deionized water to neutral. The organic layer was separated and evaporated under reduced pressure and the hydroxylated product (POc-OH) was dried in high vacuum until constant weight.

## RESULTS AND DISCUSSION

### Polymerization of $\beta$ -Ocimene with Various Rare-earth Metal Catalysts

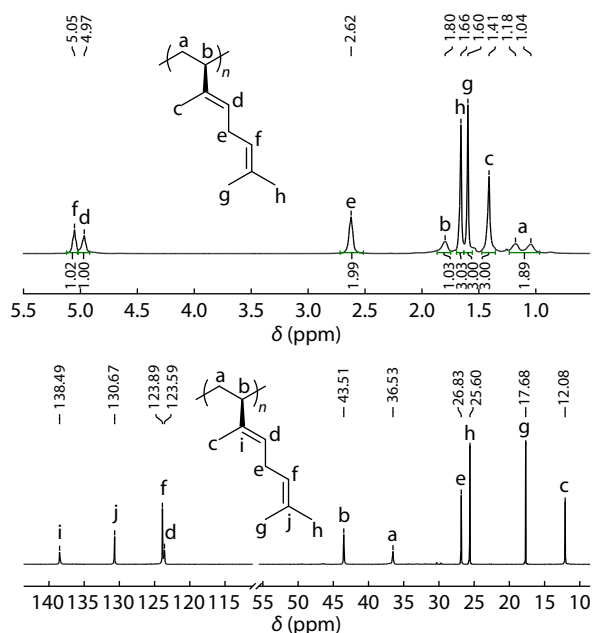
The asymmetric diiminophosphinate complex **1**, a 3,4-selective

catalyst for isoprene/ $\beta$ -myrcene polymerization, was utilized to catalyze the  $\beta$ -ocimene polymerization, giving perfect *trans*-1,2-polyocimene featuring a relatively low isotacticity (*mmmm*=32%) at a conversion of 71% in 0.5 h (Table 1, run 1, Figs. S1 and S2 in the electronic supplementary information, ESI).  $\beta$ -Diketiminato yttrium complex **2** and bis(phosphino)carbazolido yttrium complex **3**, high *cis*-1,4-selective catalysts for isoprene polymerization, showed excellent *cis*-1,4-regioselectivity (>99%) and high isoselectivity (*mm*=95% for **2**, 99% for **3**) for  $\beta$ -ocimene polymerization (Table 1, runs 2 and 3), as evidenced by the strong and sharp singlet observed at  $\delta$ =137 ppm (Fig. 1 and Figs. S3–S9 in ESI). In addition, the methine protons  $H_b$  and  $H_f$  nearly overlap at 5.06 ppm, which is in sharp contrast with the two separated triplet peaks of syndiotactic *cis*-1,4 polyocimene.<sup>[19]</sup> The isotactic conformation also causes the resonance peaks of methene protons  $H_d$  and  $H_e$  appear at 1.91, 2.16 ppm and 1.91, 2.06 ppm, respectively.



**Fig. 1**  $^1\text{H}$ - (upper) and  $^{13}\text{C}$ -NMR (lower) spectra of isotactic *cis*-1,4-POc generated by complex **3** in  $\text{CDCl}_3$  at 25 °C (Table 1, run 3).

When the half-sandwich benzyl fluorenyl complex **4** was used to initiate the  $\beta$ -ocimene polymerization, a *trans*-1,2 rich polyocimene (83%) was produced (Figs. S10 and S11 in ESI), which is close to the literature value of 78% obtained by  $\text{Cp}^*\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ <sup>[19]</sup> due to similar coordination environment around the scandium active centers. Switching to the bulky constrained geometry configuration scandium complex **5a**, the *trans*-1,2 selectivity is boosted to 92% and the catalytic activity remains almost constant. However, the molecular weight of the resultant polyocimene is only a half of the  $M_n$  value obtained by complex **4** with similar narrow molecular weight distributions (1.60 for **5a**, 1.56 for **4**). Unexpectedly, the regio- and isoselectivity increase from 92% (*mmmm*=0%) to 99% (*mmmm*=22%) and 99% (*mmmm*>99%), respectively (Fig. 2 and Figs. S12–S15 in ESI), with the increment of ionic radius of rare-earth metal atoms from 0.89 Å (Sc) to 1.00 Å (Lu) and 1.04 (Y) Å. All the catalysts **5a–5c** re-



**Fig. 2**  $^1\text{H}$ - (upper) and  $^{13}\text{C}$ -NMR (lower) spectra of isotactic *trans*-1,2-POc generated by complex **5c** in  $\text{CDCl}_3$  at 25 °C (Table 1, run 7).

main almost same catalytic activities and the molecular weight of resultant polyocimenes increase from  $3.7 \times 10^4$  g/mol (**5a**) to  $5.4 \times 10^4$  g/mol (**5b**) and  $6.1 \times 10^4$  g/mol with narrow molecular weight distributions (1.33–1.67). The perfectly isotactic *trans*-1,2-regioregularity (*mmmm* > 99%) generated by **5c** endow the polymer with good crystalline ability, as evidenced by the two melting peaks observed at 76 and 93 °C, respectively, in the DSC curve (Fig. S42 in ESI).

### Homopolymerization and Copolymerization of $\beta$ -ocimene Initiated by Complexes **3** and **5c**

In view of the outstanding catalytic performances of complexes **3** and **5c**, their polymerization behaviors were explored under various reaction conditions. For complex **3**, raising the polymerization temperature from 25 °C to 80 °C obviously enhanced the polymerization process but the *cis*-1,4 selectivity is not influenced along with a slight decrease in isoselectivity from 99% (25 °C) to 96% (40 °C), 94% (60 °C) and 90% (80 °C) (Figs. S16–S18 in ESI), exhibiting strong tolerance to high reaction temperatures. In addition, the resultant molecular

weights vary over the range of  $9.3 \times 10^4$  g/mol to  $10.5 \times 10^4$  g/mol with narrow molecular weight distributions (1.31–1.62), suggesting low chain transfer efficiency. Upon increasing the monomer-to-catalyst ratio from 500:1 to 1500:1, the resultant molecular weights were boosted from  $10.5 \times 10^4$  g/mol to  $46.9 \times 10^4$  g/mol with narrow molecular weight distributions (1.16–1.25), suggesting controllable polymerization characteristics (Table 1, run 3 and Table 2, runs 4 and 5). For complex **5c**, only the isoselectivities are slightly influenced by the elevated temperatures and drop from 99% (25 °C) to 98% (40 °C), 97% (60 °C) and 90% (80 °C). The maximum monomer conversion of 70% is reached 60 °C in 0.5 h and remains constant despite of elevated reaction temperatures. The molecular weights slightly decline from  $6.1 \times 10^4$  g/mol to  $5.2 \times 10^4$  g/mol with narrow molecular weight distributions (1.27–1.46).

Due to the livingness characteristics of complex **3** for the polymerization of isoprene, butadiene or ocimene, the one-pot copolymerizations of  $\beta$ -ocimene with isoprene or butadiene were carried out and diblock copolymers were obtained, as evidenced by narrow molecular weight distributions ( $M_w/M_n=1.17$  and 1.08) (Figs. S31 and S32 in ESI) and two distinct glass transition temperatures ( $T_g=-57$  and  $-23$  °C for PIP-*b*-POc;  $-97$  and  $-18$  °C for PBD-*b*-POc) (Figs. S43 and S44 in ESI) observed in DSC curves. Furthermore, nearly no signals arising from the IP-Oc or BD-Oc joints were observed in the  $^{13}\text{C}$ -NMR spectra of PIP-*b*-POc or PBD-*b*-POc, indicating the diblock microstructure. In addition, the  $^{13}\text{C}$ -NMR spectral analyses demonstrate that both isoprene/butadiene and  $\beta$ -ocimene units incorporated into copolymer chains have high *cis*-1,4 regularity (Table 3, runs 1 and 2; Figs. S25 and S29 in ESI).

### Epoxidation and Hydroxylation of *Cis*-1,4-polyocimene

The treatment of *cis*-1,4-polyocimene with *meta*-chloroperbenzoic acid in  $\text{CH}_2\text{Cl}_2$  at 0 °C afforded epoxidized polymers (POc-EO) (Scheme 3), which is soluble in strongly polar solvents like ethanol. The olefinic protons at  $\delta=5.07$  ppm in the  $^1\text{H}$ -NMR spectrum disappear along with the appearance of the epoxide protons at  $\delta=2.55$ – $3.07$  ppm, suggesting the completeness of the epoxidation reaction (Fig. S30 in ESI). The introduction of epoxy groups dramatically reduces the chain

**Table 2** Polymerization of ocimene with complexes **3** and **5c**.<sup>a</sup>

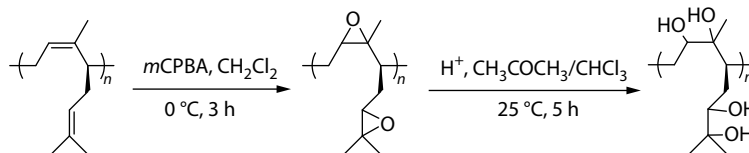
Run	Cat.	[M]:[Ln] (mol:mol)	Time (h)	Temp. (°C)	Conv. (%)	Microstructure <sup>b</sup> (%)		$M_n$ <sup>c</sup> ( $10^4$ )	$M_w/M_n$ <sup>c</sup>	$T_g$ <sup>d</sup> (°C)
						<i>cis</i> -1,4 ( <i>mm</i> )	<i>trans</i> -1,2 ( <i>mmmm</i> )			
1	<b>3</b>	500	1.5	40	84	>99(96)	–	10.1	1.31	–20
2	<b>3</b>	500	1	60	94	>99(94)	–	9.5	1.39	–20
3	<b>3</b>	500	0.67	80	95	>99(90)	–	9.3	1.62	–18
4	<b>3</b>	1000	3.5	25	71	>99(99)	–	25.6	1.20	–19
5	<b>3</b>	1500	8	25	65	>99(99)	–	46.9	1.25	–20
6	<b>5c</b>	500	0.5	40	68	–	>99(98)	5.6	1.27	–29/76, 94 <sup>e</sup>
7	<b>5c</b>	500	0.5	60	70	–	>99(97)	5.4	1.32	–31/76, 94 <sup>e</sup>
8	<b>5c</b>	500	0.5	80	70	–	>99(90)	5.2	1.46	–30/76, 93 <sup>e</sup>

Conditions: <sup>a</sup> Complex 10  $\mu\text{mol}$ ;  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  10  $\mu\text{mol}$ ;  $\text{Al}^i\text{Bu}_3$  100  $\mu\text{mol}$ ;  $[\text{M}]$  2.5 mol/L; <sup>b</sup> Determined by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy; <sup>c</sup> Determined by GPC in THF at 40 °C against a polystyrene standard; <sup>d</sup> Determined by DSC; <sup>e</sup>  $T_g/T_m$ .

**Table 3** Copolymerization of  $\beta$ -ocimene and isoprene or butadiene with complex **3**.<sup>a</sup>

Run	[Oc]:[IP] (mol:mol)	Conv. (%)	$f_{Oc}^b$ (mol%)	$cis\text{-}1,4_{Oc}/cis\text{-}1,4_{IP}$ (%)	$mm_{Oc}^b$ (%)	$M_n^c$ ( $10^4$ )	$M_w/M_n^c$	$T_g^d$ ( $^{\circ}C$ )
1	500:500	83	47	>99/98	65	13.2	1.17	−57, −23
2 <sup>e</sup>	500:500	77	56	>99/96	62	19.4	1.08	−97, −18

Conditions: <sup>a</sup> Complex **3** 10  $\mu$ mol;  $[Ph_3C][B(C_6F_5)_4]$  10  $\mu$ mol;  $Al^iBu_3$  100  $\mu$ mol; Toluene 1 mL; Time 3.5 h; Temperature 25  $^{\circ}C$ ; <sup>b</sup> Determined by  $^1H$ - and  $^{13}C$ -NMR spectroscopy; <sup>c</sup> Determined by GPC in THF at 40  $^{\circ}C$  against a polystyrene standard; <sup>d</sup> Determined by DSC; <sup>e</sup> Copolymerization of Oc and BD.

**Scheme 3** Epoxidation and hydroxylation of *cis*-1,4-POc.

flexibility and thus the glass transition temperature increase from  $-20$   $^{\circ}C$  to  $79$   $^{\circ}C$  (Fig. S45 in ESI). The reaction of POC-EO with hydrochloric acid in acetone/chloroform (2/1, V/V) at room temperature gave white solids, indicating the higher polarity. The  $^1H$ -NMR spectral analysis shows that epoxy groups completely transform into hydroxyl moieties, as evidenced by the appearance of new signal at  $\delta=3.22\text{--}4.27$  ppm in the  $^1H$ -NMR spectrum. The presence of hydroxyl group was also confirmed by the O—H stretching vibration band at  $3450\text{ cm}^{-1}$  in the FTIR spectrum (Fig. S35 in ESI). Moreover, the introduction of polar groups greatly improved the hydrophilicity of POC-EO and POC-OH with the obvious reduction in the water contact angle from  $116^{\circ}$  to  $69^{\circ}$  and  $60^{\circ}$ , respectively (Fig. S47 in ESI).

## CONCLUSIONS

In summary, a new type of isotactic *cis*-1,4-polyocimene is synthesized for the first time using rare-earth metal complexes. We also demonstrated that the tacticity of the resultant polyocimenes strongly depends on the coordination environment around the metal active centers and the type of metal elements. The yttrium complexes bearing pincer-type ligands like  $\beta$ -diketiminate and bis(phosphino)carbazolide ligands, high *cis*-1,4-selective for diene polymerization, exhibit high isotactic *cis*-1,4 selectivity for  $\beta$ -ocimene polymerization, forming isotactic *cis*-1,4-polyocimene. With respect to the rare-earth metal complexes supported by bulky diiminophosphinate, benzyl fluorenyl and pyridyl-methylene-fluorenyl ligands, *trans*-1,2-regulated polyocimenes were produced and especially the pyridyl-methylene-fluorenyl yttrium complex **5c** in a suitable coordination environment gave isotactic *trans*-1,2-polyocimene ( $mmmm>99\%$ ) with two melting points. One-pot copolymerizations of  $\beta$ -ocimene with isoprene and butadiene afforded high *cis*-1,4 regulated diblock copolymers featuring distinct phase separation due to the rather different reactivity ratios. The *cis*-1,4-polyocimene is readily transformed into epoxidized and hydroxylated plastics with elevated glass transition temperatures and improved hydrophilicity.

## Conflict of Interests

The authors declare no interest conflict.

## Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-3047-7>.

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