# Achieving Isopropenyl-Enriched Polyisoprene: Unraveling the Role of Bidentate vs. Tridentate Iron Precatalysts Through Ligand Framework Design

Sunny Sohail<sup>a,b,c</sup>, Yanping Ma<sup>a,\*</sup>, Qaiser Mahmood<sup>b,\*</sup>, Zexu Hu<sup>b</sup>, Yizhou Wang<sup>a,c</sup>, Tongling Liang<sup>c</sup>, Wen-Hua Sun<sup>a,b,c,\*</sup>

<sup>a</sup> Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: myanping@iccas.ac.cn, whsun@iccas.ac.cn,

<sup>b</sup> Chemistry and Chemical Engineering Guangdong Laboratory, Shantou 515031, China. Email: qaiser@ccelab.com.cn

<sup>c</sup> CAS Research/Education Center for Excellence in Molecular Sciences and International School, University of Chinese Academy of Sciences, Beijing 100049, China

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#### 1. General consideration and materials

The synthesis of iron catalysts and the isoprene polymerization process were typically carried out under an inert atmosphere of dry argon using standard Schlenk techniques. Toluene was dried using sodium metal, and all other solvents were subjected to reflux over CaH<sub>2</sub> under an argon atmosphere before use. The co-catalysts, namely AlMe<sub>2</sub>Cl (0.9 M in heptane), and AlEt<sub>2</sub>Cl (2.0 M in hexane), and MAO (1.67 M in toluene), were purchased from Shanghai Macklin Biochemical Co. Ltd. and Anhui Botai Electronic Materials Co. and were used as received without any further modifications. Analytical grade isoprene was purchased and subjected to purification by distillation over CaH<sub>2</sub> under an argon atmosphere, after which it was stored at low temperature. All other commercially available chemicals were used without the need for additional purification. <sup>1</sup>H and <sup>13</sup>C NMR measurements were performed using a Bruker Avance Neo 600 MHz spectrometer, with deuterated chloroform (CDCl<sub>3</sub>) as the internal standard and tetramethylsilane (TMS) as the internal reference. Chemical shifts are reported in ppm, while J values in Hz. Fourier transform infrared (FT-IR) analysis was performed using a Bruker Tensor II FT-IR spectrometer. The elemental analysis of iron complexes was determined using a Thermoscientific Flashsmart instrument micro-analyzer. Gel permeation chromatography (GPC) was conducted using a 1260 Infinity II High Temperature GPC System equipped with a refractive index detector. The GPC system utilized mixed columns with a combined length of 650 and an internal diameter of 7.5 mm. The samples were dissolved in 1, 2, 4-trichlorobenzene (TCB) at a temperature of 120 °C, and elution of TCB occurred at a flow rate of 1.0 ml/min. The columns were calibrated using standard polystyrene samples. UV-Vis measurements were conducted at 25 °C using the PerkinElmer LAMBDA 850+ spectrophotometer with wavelength range of 250-850 nm, with the samples prepared at  $6.04 \times 10^{-5}$  M in ethanol.

#### 2. Synthesis and characterization of ligands

L-NMe<sub>2</sub>: A mixture of 5,6,7-trihydroquinolin-8-one (2.94 g, 20 mmol), N,Ndimethylethane-1,2-diamine (2.12 g, 24 mmol, 1.2 eq.), and sodium triacetoxyborohydride (6.33 g, 30 mmol, 1.5 eq.) in 1,2-dichloroethane (100 mL) was stirred at 30 °C for 12 hours. The reaction was then quenched with a saturated aqueous NaHCO<sub>3</sub> solution (100 mL, pH > 8), and the mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over NaSO<sub>4</sub> and concentrated. The residue was purified by silica gel column chromatography (dichloromethane/methanol, 500/1 to 100/1), yielding L-NMe<sub>2</sub> as a yellow oil (3.12 g, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 (d, J = 4.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.97 (dd, J = 7.7, 4.7 Hz, 1H), 3.72 (d, J = 5.4 Hz, 1H), 3.70 (s, 1H), 2.78 – 2.61 (m, 4H), 2.42 (td, J = 6.4, 3.3 Hz, 2H), 2.17 (s, 6H), 2.09 – 2.00 (m, 1H), 1.95 – 1.87 (m, 1H), 1.78 – 1.58 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.36, 146.73, 136.85, 132.39, 121.88, 59.43, 57.85, 45.63, 45.50, 44.99, 28.83, 28.56, 19.53. FT-IR (cm<sup>-1</sup>): 3361 (b), 2936 (m), 2857 (w), 2818 (w), 2766 (w), 1664 (w), 1445 (m), 1356 (w), 1342 (w), 1273 (w), 1244 (w), 1161 (w, RC-NH), 1042 (w, R'C-NH), 959 (w), 827 (w), 784 (w), 711 (w).

L-N<sup>*i*</sup>Pr<sub>2</sub>: Using a similar procedure and molar ratios to that described for L-NMe<sub>2</sub>, L-N<sup>*i*</sup>Pr<sub>2</sub> was obtained as a yellow oil (4.45 g, 80%). <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  8.40 (d, J = 4.6 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.06 (dd, J = 7.6, 4.8 Hz, 1H), 3.84 – 3.77 (m, 1H), 3.22 (dd, J = 11.3, 5.6 Hz, 1H), 3.03 (dt, J = 13.1, 6.6 Hz, 2H), 2.79 (ddd, J = 20.1, 15.6, 7.3 Hz, 4H), 2.69 – 2.64 (m, 2H), 2.18 (dt, J = 10.6, 5.3 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.87 – 1.70 (m, 2H), 1.04 (d, J = 6.6 Hz, 12H). <sup>13</sup>C NMR (101 MHz, DMSO-d)  $\delta$  157.07, 146.93, 137.26, 132.41, 122.46, 58.15, 47.95, 47.02, 44.06, 28.59, 21.58, 20.54, 19.67. FT-IR (cm<sup>-1</sup>): 3055 (b), 2989 (w), 2930 (w), 2855 (w), 1425 (w), 1267 (s, RC-NH), 1123 (w, R'C-NH), 896 (w), 735 (s) 705 (w)

L-NH<sub>2</sub>: A solution of picolinaldehyde (10.0 g, 93.35 mmol) in methanol (100 mL) was prepared, and ethane-1,2-diamine (11.0 g, 186.7 mmol) was added slowly over 1 hour. The mixture was stirred for an additional hour before NaBH<sub>4</sub> (5.65 g, 149.35 mmol) was added in portions over 2 hours, followed by another hour of stirring. The reaction mixture was then refluxed for 10 hours, cooled, and concentrated under reduced pressure to remove volatiles. The resulting mixture was washed with aqueous NaOH (60 mL, 20 wt%), and the product was extracted with toluene (3 × 70 mL), followed by a second wash with aqueous NaOH (60 mL, 10 wt%). The crude product was passed through a short alumina column, and the solvent was evaporated. The product was distilled to yield a colorless liquid (7.1 g, yield 50%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (dd, J = 4.9, 1.9 Hz, 1H), 7.13 (td, J = 7.6, 1.9 Hz, 1H), 6.83 (d, J = 7.9 Hz, 1H), 6.64 (dd, J = 7.7, 4.9 Hz, 1H), 3.41 (s, 2H), 2.32 (t, J = 6.0 Hz, 2H), 2.24 – 2.18 (m, 2H), 1.44 (s, 3H, N*H or* N*H*<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.6, 148.7, 135.9, 121.7, 121.4, 54.6, 51.8, 41.3. FT-IR (cm<sup>-1</sup>):

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3353 (b), 3286 (w), 3053 (w), 3007 (w), 2922 (w), 2829 (w), 1593 (s), 1566 (m), 1475 (m), 1433 (s), 1354 (w), 1297 (w), 1127 (w), 1044 (w, RC-NH), 995 (s, R'C-NH), 874 (w), 755 (s), 630 (w), 606 (w).

**L-OH**: Following the same procedure used for **L-NH**<sub>2</sub> synthesis, **L-OH** was prepared without heating or reflux. The pure product was obtained by vacuum distillation as a colorless liquid (3.5 g, 25% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.42 (d, J = 4.5, 1H), 7.06 (td, J = 7.6, 1.7, 1H), 6.94 (d, J = 7.7, 1H), 6.62 (dd, J = 7.0, J = 5.4, 1H), 3.77 (s, 2H), 3.67 – 3.52 (m, 2H), 3.13 (br, 2H), 2.71 – 2.48 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  169.5, 149.8, 136.9, 122.7, 121.4, 61.6, 55.2, 51.9. FT-IR (cm<sup>-1</sup>): 3378 (b), 3051 (w), 2926 (m), 2853 (w), 1645 (s), 1591 (m), 1568 (w), 1473 (w), 1435 (s), 1265 (s), 1147 (w), 1086 (w, RC-NH), 1048 (w, R'C-NH), 997 (w), 791 (w), 734 (s), 701 (w).

**L-CH<sub>2</sub>Ph:** Using a similar procedure and molar ratios to that described for **L-NMe<sub>2</sub>**, **L-CH<sub>2</sub>Ph** was obtained as a yellow oil (2.25 g, 93%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 8.34 (d, J = 4.1 Hz, 1H), 7.38 (d, J = 7.4 Hz, 2H), 7.29 (dd, J = 14.3, 7.1 Hz, 3H), 7.22 – 7.16 (m, 1H), 7.00 (dd, J = 7.6, 4.8 Hz, 1H), 3.94 (s, 1H), 3.82 (dd, J = 7.3, 5.6 Hz, 1H), 3.01 (s, 1H), 2.85 – 2.74 (m, 1H), 2.73 – 2.64 (m, 1H), 2.15 (dt, J = S5 12.1, 5.1 Hz, 1H), 2.04 – 1.93 (m, 1H), 1.83 – 1.74 (m, 1H), 1.72 – 1.61 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.4, 146.8, 140.5, 140.5, 136.9, 132.5, 128.4, 128.3, 127.1, 126.9, 121.9, 57.6, 51.8, 28.9, 28.6, 19.7. FT-IR (cm<sup>-1</sup>): 3345 (b), 3284 (w), 3202 (w), 3007 (w), 2918 (w), 2829 (w), 1593 (s), 1566 (m), 1473 (w), 1433 (m), 1352 (w), 1297 (w), 1125 (w), 1048 (w, RC-NH), 997 (w, R'C-NH), 872 (w), 758 (s), 630 (w), 608 (w).

**L-NHPh:** A solution of 5,6,7-trihydroquinolin-8-one (1.47 g, 10 mmol) and freshly distilled phenylhydrazine (1.08 g, 10 mmol) in ethanol (10 mL) was heated on a steam bath for 6 hours. After cooling to room temperature, yellow crystals of the product were collected by suction filtration, washed with cold ethanol (5–10 mL), and dried to yield **L-NHPh** as a yellow solid (1.20 g, 50%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  14.00 (s, 1H), 8.51 (d, J = 4.7 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.31 –7.26 (m, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.15 (dd, J = 7.6, 4.9 Hz, 1H), 6.83 (dd, J = 8.8, 4.3 Hz, 1H), 2.88 (t, J = 6.1 Hz, 2H), 2.85 – 2.80 (m, 2H), 2.05 – 1.95 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  151.1, 151.0, 145.3, 145.0, 136.8, 135.3, 133.0, 129.2, 121.8, 119.6, 112.8, 112.8, 34.1, 30.2, 22.8. FT-IR (cm<sup>-1</sup>): 3216 (b), 3098 (w), 3026 (w), 2930 (w), 1605 (s, C=N), 1575 (m), 1555 (s), 1519 (m), 1452 (m), 1426 (s), 1332 (w), 1298 (w), 1255 (s),

1189 (w), 1142 (s), 1084 (w), 1064 (w), 1036 (w), 895 (w), 820 (w), 794 (w), 775 (w), 751 (w), 731 (w), 690 (w), 591 (w).

#### 3. Procedure for isoprene polymerization

Isoprene polymerization was conducted using a Schlenk technique under argon atmosphere. The precatalysts such as  $Fe-NMe_2$  (10 µmol), and toluene (5 ml) were added sequentially into the schlenk flask, then required amount of MAO was added, stirred for 1 minute at the desired temperature and then immediately isoprene (2 ml) was added into the solution. After the desired reaction time, the polymerization was quenched with 10% hydrochloric acid in ethanol. The polymer was washed with excess of ethanol three times, filtered and then dried under vacuum at room temperature to constant weight.

#### 4. X-Ray Crystallographic Studies

Single crystals of Fe-NMe<sub>2</sub> and Fe-NHPh, suitable for X-ray determinations, were grown through the slow diffusion of n-hexane into a solution of the corresponding complexes in dichloromethane at room temperature. Single crystal X-ray diffraction analysis of Fe-NMe<sub>2</sub> and Fe-NHPh was carried out using a Rigaku Sealed Tube CCD (Saturn 724+) diffractometer. This diffractometer utilized graphite-monochromated Cu-K $\alpha$  radiation with a wavelength ( $\lambda$ ) of 1.54184 Å. The measurements were conducted at a temperature of 169.98 (±10) K. The determination of cell parameters involved the global refinement of the positions of all collected reflections. Intensities obtained from the X-ray diffraction analysis were corrected for Lorentz and polymerization effects, and an empirical absorption correction was applied. The structure of both complexes was solved using direct methods and subsequently refined through full-matrix least squares fitting on Fe-NMe<sub>2</sub> and Fe-NHPh. Nonhydrogen atoms in each complex were refined anisotropically, while the positions of all hydrogen atoms were determined based on calculated positions. Data collected during the analysis were processed using the Olex2 program [1]. The solvent molecules, which do not influence the geometry of the main compound, were also solved. The crystal data and processing parameters for FeNMe2 and Fe-NHPh are presented in Table S1.

## 5. Crystal data and structure refinement

Identification code	Fe-NMe <sub>2</sub>	Fe-NHPh	
Empirical formula	C <sub>13</sub> H <sub>20</sub> Cl <sub>2</sub> FeN <sub>3.5</sub> O <sub>0.12</sub>	C <sub>45</sub> H <sub>45</sub> Cl <sub>3.5</sub> Fe <sub>2</sub> N <sub>9</sub>	
Formula weight	354.07	947.67	
Temperature/K	170.0(4)	170.0(6)	
Crystal system	trigonal	triclinic	
Space group	ce group C2/c		
a/Å	14.8062(4)	12.3257(3)	
b/Å	10.1238(3)	13.4312(3)	
c/Å	21.3450(7)	15.1114(3)	
$\alpha/^{\circ}$	90	89.086(2)	
β/°	90.579(3)	70.721(2)	
$\gamma^{\prime}$	90	85.196(2)	
Volume/Å <sup>3</sup>	3199.35(17)	2352.91(9)	
Z	8	2	
$\rho_{calc}g/cm^3$	1.470	1.338	
µ/mm <sup>-1</sup>	10.578	7.095	
F(000)	1468.0	979.0	
Crystal size/mm <sup>3</sup>	$0.150 \times 0.120 \times 0.100$	0.15  imes 0.12  imes 0.08	
Radiation	Cu Ka ( $\lambda = 1.54184$ )	Cu Ka ( $\lambda = 1.54184$ )	
$2\Theta$ range for data collection/°	8.286 to 151.916	6.196 to 153.058	
Index ranges	$-14 \le h \le 17,$ $-12 \le k \le 12,$ $-26 \le l \le 26$	$-15 \le h \le 15,$ $-16 \le k \le 16,$ $-18 \le 1 \le 18$	
Reflections collected	9671	32307	
Independent reflections	$\begin{array}{ll} 3203 & [R_{int} = & 0.0409, \\ R_{sigma} = 0.0409] \end{array}$	9490 [ $K_{int} = 0.060$ /, $K_{sigma} = 0.0513$ ]	
Data/restraints/parameters	3203/0/179	9496/0/538	
Goodness-of-fit on F <sup>2</sup>	1.052	1.085	
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0488, wR_2 = 0.1314$	$R_1 = 0.0669, wR_2 = 0.1948$	
Final R indexes [all data]	$R_1 = 0.0536, wR_2 = 0.1361$	$R_1 = 0.0748, wR_2 = 0.2045$	
Largest diff. peak/hole/e Å-3	0.92/-0.70	0.95/-1.20	

Table S1. Crystal data and structure refinement for Fe-NMe<sub>2</sub>, and Fe-NHPh

## 6. <sup>1</sup>H and <sup>13</sup>C NMR spectra for polyisoprenes



Figure S2. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the polyisoprene obtained using Fe-NMe<sub>2</sub>/MAO (Table 4, entry 1).



Figure S3. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the polyisoprene obtained using Fe-N<sup>*i*</sup>Pr2/MAO (Table 4, entry 2).



Figure S4. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the polyisoprene obtained using  $Fe-NH_2/MAO$  (Table 4, entry 3).



**Figure S5.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the polyisoprene obtained using **Fe-OH**/MAO (Table 4, entry 4).



Figure S6. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the polyisoprene obtained using Fe-NHPh/MAO (Table 4, entry 5).





Figure S7. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the polyisoprene obtained using Fe-CH<sub>2</sub>Ph/MAO (Table 4, entry 6).

### 7. GPC curves for iron obtained polyisoprene



Figure S8. GPC curves for iron complexes Fe-NMe<sub>2</sub> (table 4, entry1).



**Distribution Plots** 

Figure S9. GPC curves for iron complexes Fe-N<sup>7</sup>Pr<sub>2</sub> (table 4, entry2).



Figure S10. GPC curves for iron complexes Fe-NH<sub>2</sub> (table 4, entry 3).



Figure S11. GPC curves for iron complexes Fe-OH (table 4, entry 4).



Figure S12. GPC curves for iron complexes Fe-NHPh (table 4, entry 5).



Figure S13. GPC curves for iron complexes Fe-CH<sub>2</sub>Ph (table 4, entry 6).

### 8. Mass spectrum of iron complexes



Figure S14. Mass spectrum of Fe-NMe<sub>2</sub>



Figure S15. Mass spectrum of Fe-N<sup>i</sup>Pr<sub>2</sub>



Figure S16. Mass spectrum of Fe-NH<sub>2</sub>



Figure S17. Mass Spectrum of Fe-OH



Figure S18. Mass spectrum of Fe-NHPh



Figure S19. Mass spectrum of Fe-CH<sub>2</sub>Ph

### 9. Elemental analysis data

Table S2. Elemental analysis results

Entry	N%质量百分数	C%质量百分数	H%质量百分数
Fe-NHPh	10.5646286	50.11384323	4.8479
Fe-CH2Ph	6.27573	54.375336	6.77196
Fe-lpr2	6.5569	36.179114	5.56999
Fe-NH2	11.754998	30.102564	4.42822
Fe-OH	8.250633	40.45255	6.20125
Fe-NMe2	9.42355	39.35236	5.00125

# 10. FIIR of ligands and iron complexes



Figure S20. FTIR spectra of prepared ligands



Figure S21. FTIR spectra of prepared iron complexes

### 11. UV-vis spectroscopy spectra



Figure S22. UV-vis spectra of iron compelxes

### References

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