

Supporting Information

**Highly 3,4-selective living polymerization of 2-phenyl-1,3-butadiene
with amidino N-heterocyclic carbene ligated rare-earth metal
bis(alkyl) complexes**

Changuang Yao^{1,2}, Hongyan Xie^{1,2} and Dongmei Cui^{1*}

¹ State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

² University of the Chinese Academy of Sciences, Changchun Branch, Changchun 130022, China.

* Author to whom correspondence should be addressed; E-mail: dmcui@ciac.ac.cn
Tel.: +86 (0) 431 85262773; Fax: +86 (0) 431 85262774.

SFig. 1 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of 2-PB.

SFig. 2 ¹³C NMR (100M, CDCl₃, 25 °C) spectrum of 2-PB.

SFig. 3 ¹H NMR spectrum of complex **2a**.

SFig. 4 ¹H NMR spectrum of complex **3a**.

SFig. 5 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entries 2)

SFig. 6 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 4)

SFig. 7 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 10)

SFig. 8 ¹³C NMR (100M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 10)

SFig. 9 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 11)

SFig. 10 ¹³C NMR (100M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 11)

SFig. 11 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 12)

SFig. 12 ¹³C NMR (100M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 12)

SFig. 13 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 13)

SFig. 14 ^1H NMR (400M, CDCl_3 , 25 °C) spectrum of P(2-PB). (Table 1, entry 14)

SFig. 15 GPC traces of P(2-PB)s (Table 1, entries 1, 5-9)

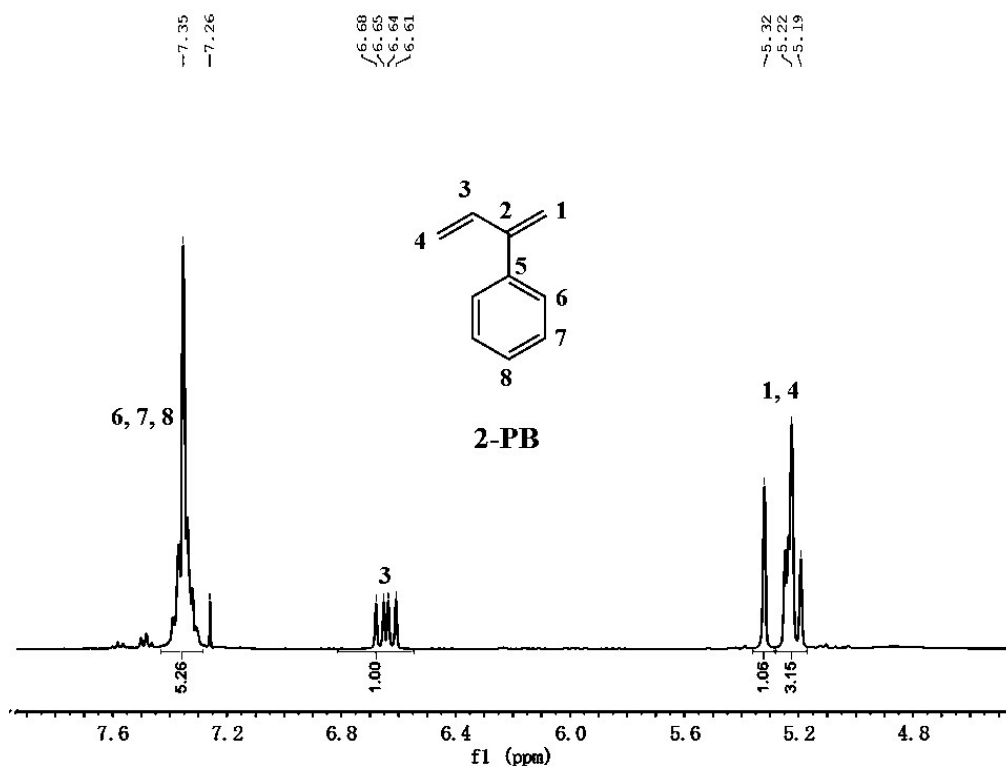
STable 1. Polymerization of 2-PB with $\text{Lu}/[(\text{Ph}_3\text{C})][(\text{B}(\text{C}_6\text{F}_5)_4)]$: conversion vs time.

($[\text{Lu}]_0 = 5.0 \mu\text{mol/mL}$, $[\text{2-PB}]_0/[\text{Lu}]_0 = 200$, Chlorobenzene, 25 °C).

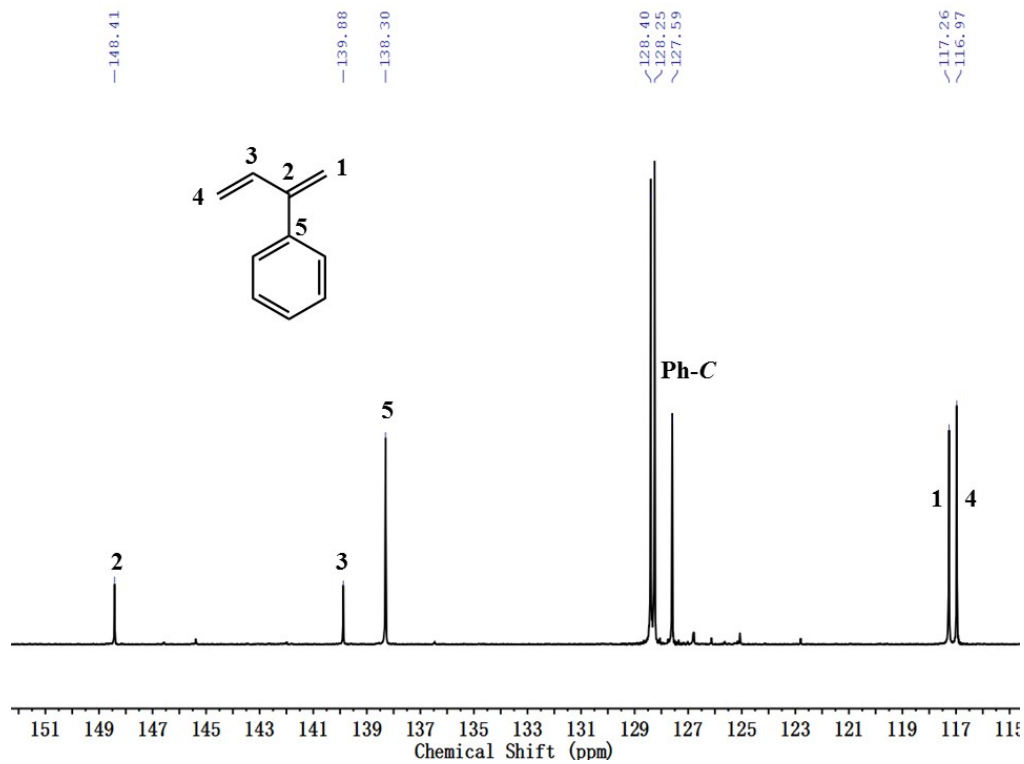
SFig. 16 Polymerization of 2-PB with $\text{Lu}/[(\text{Ph}_3\text{C})][(\text{B}(\text{C}_6\text{F}_5)_4)]$: conversion vs time.

($[\text{Lu}]_0 = 5.0 \mu\text{mol/mL}$, $[\text{2PB}]_0/[\text{Lu}]_0 = 200$, Chlorobenzene, 25 °C).

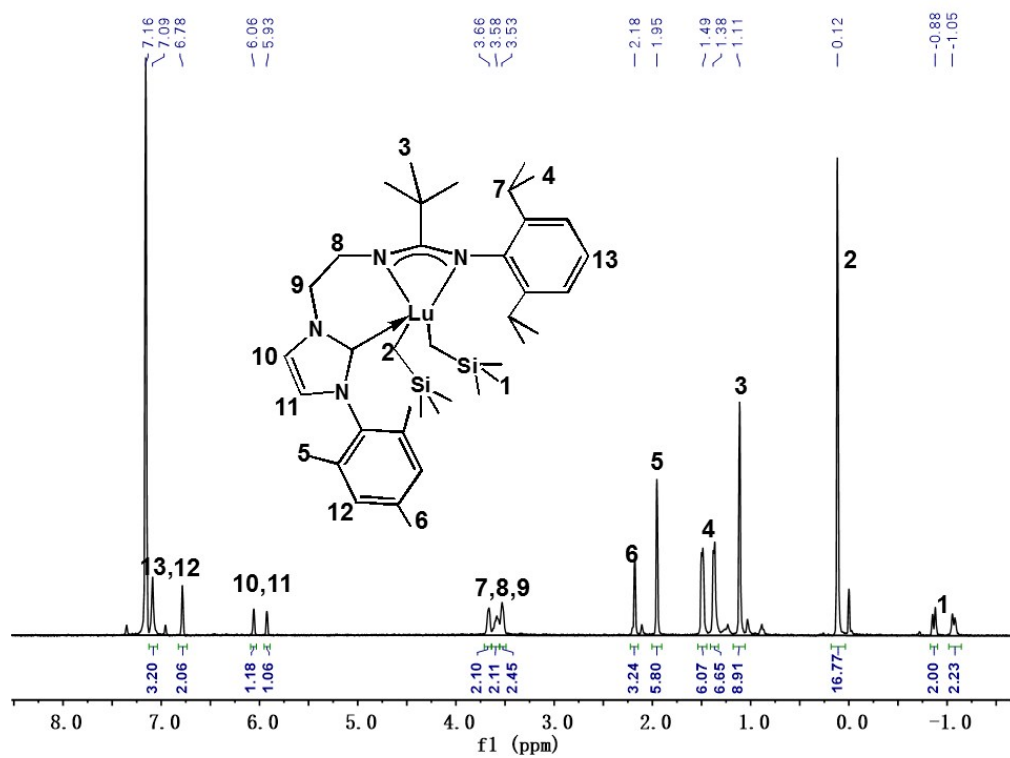
SFig. 17 Thermogram of P(2-PB). (Table 1, entry 12)



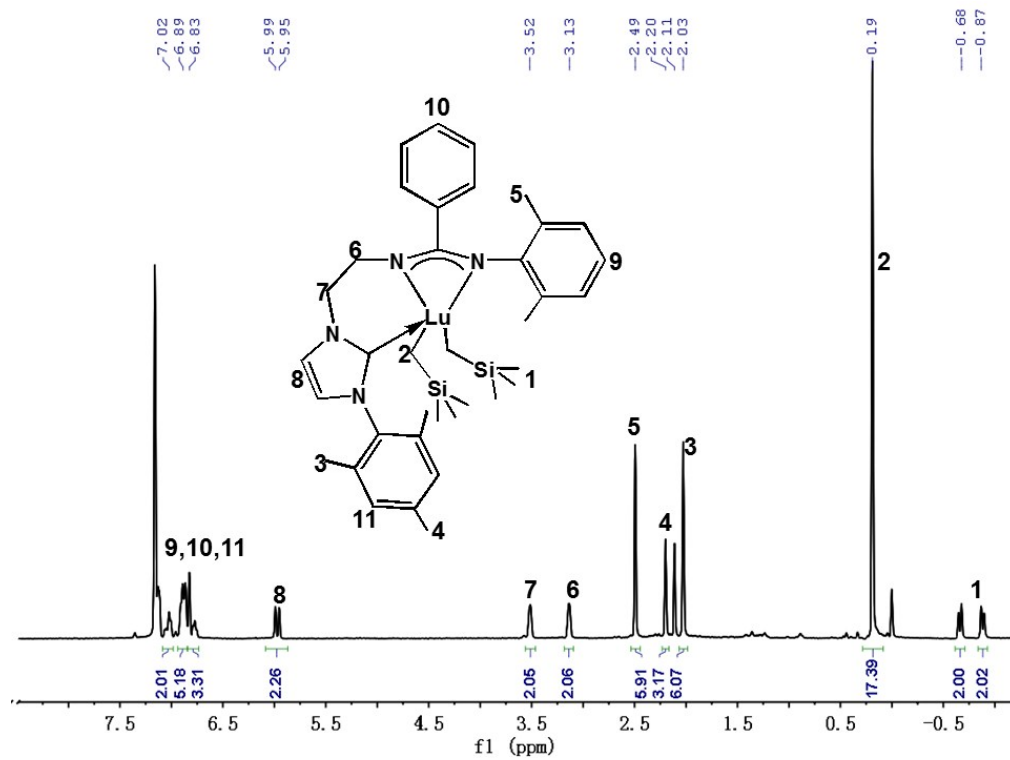
SFig. 1 ^1H NMR (400M, CDCl_3 , 25 °C) spectrum of 2-PB.



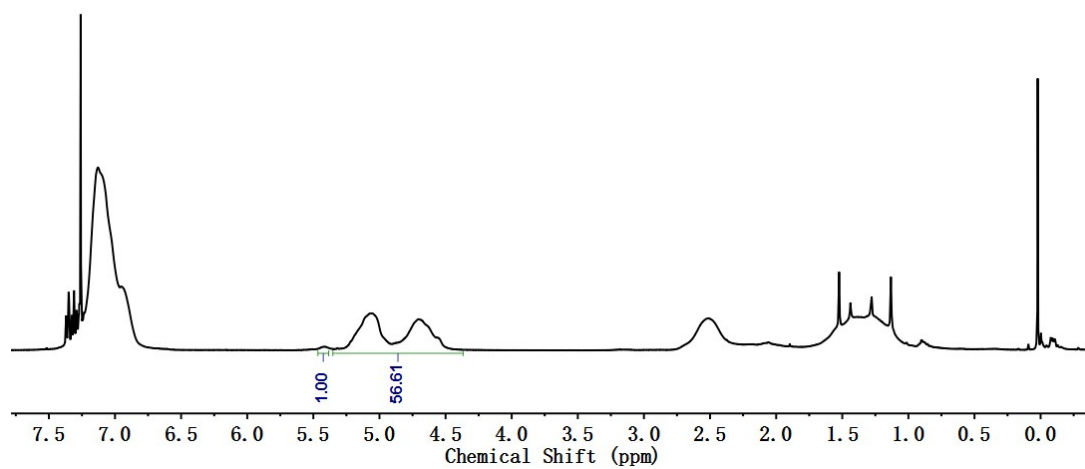
SFig. 2 ^{13}C NMR (100M, CDCl_3 , 25 °C) spectrum of 2-PB.



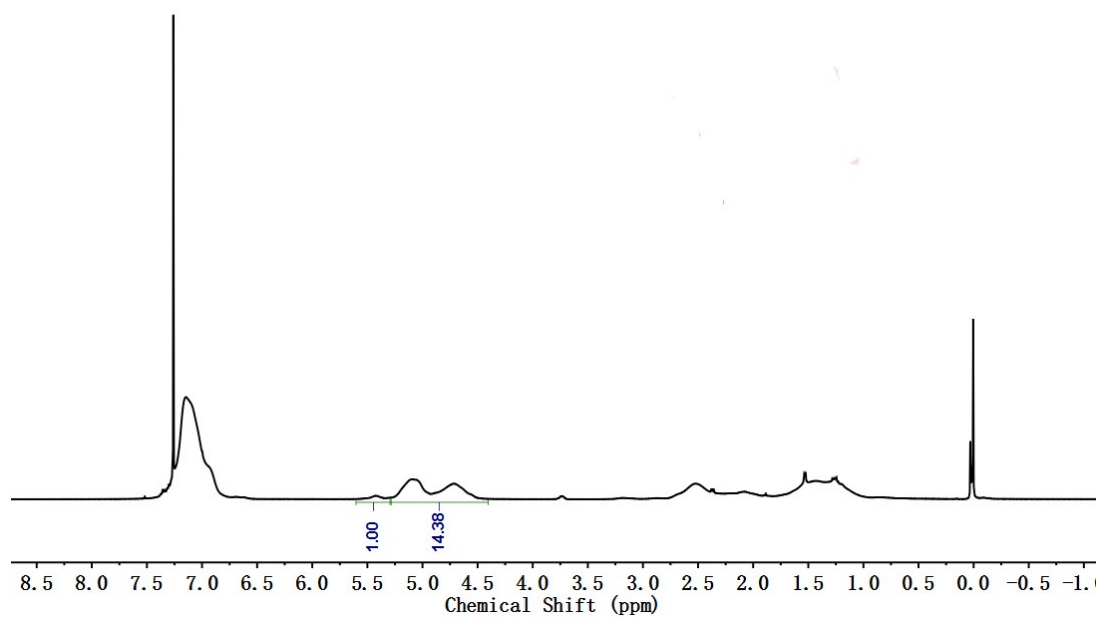
SFig. 3 ^1H NMR spectrum of complex **2a**.



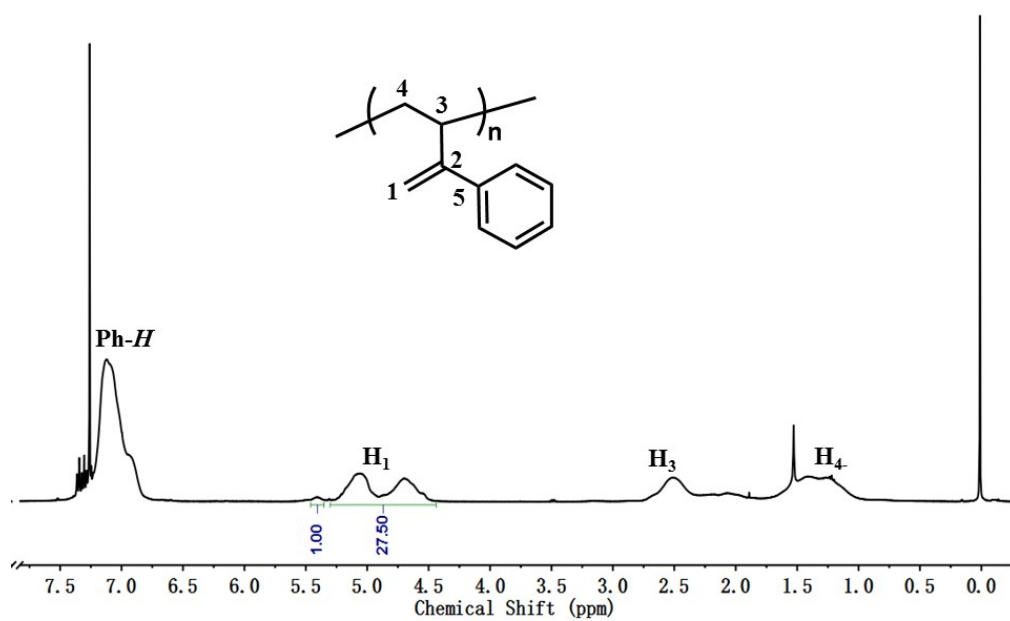
SFig. 4 ¹H NMR spectrum of complex 3a.



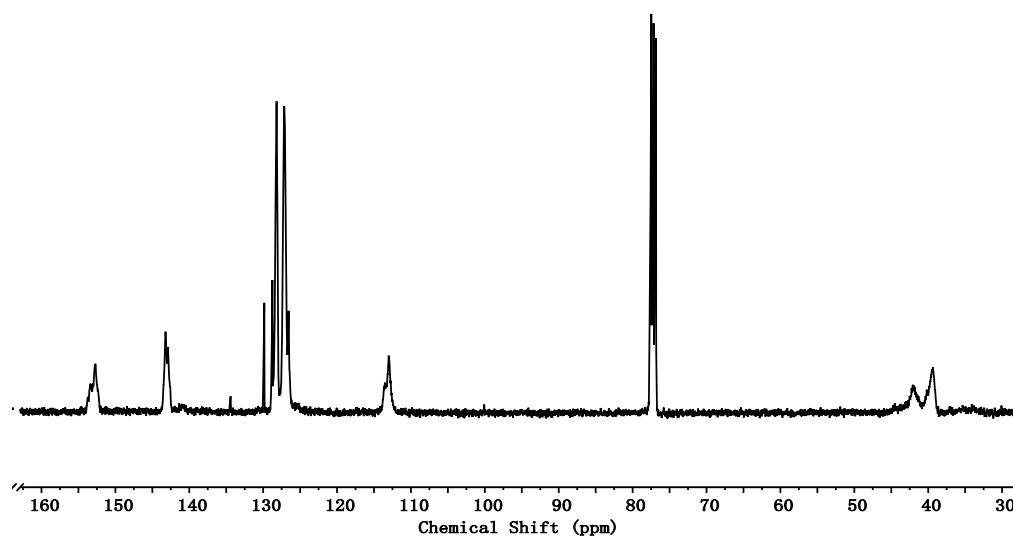
SFig. 5 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 2)



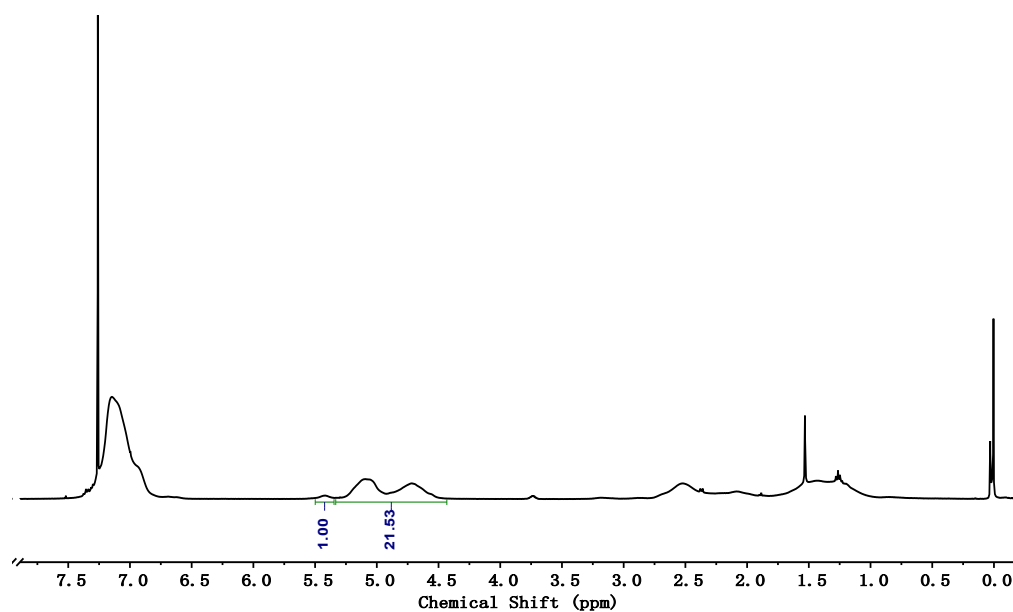
SFig. 6 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 4)



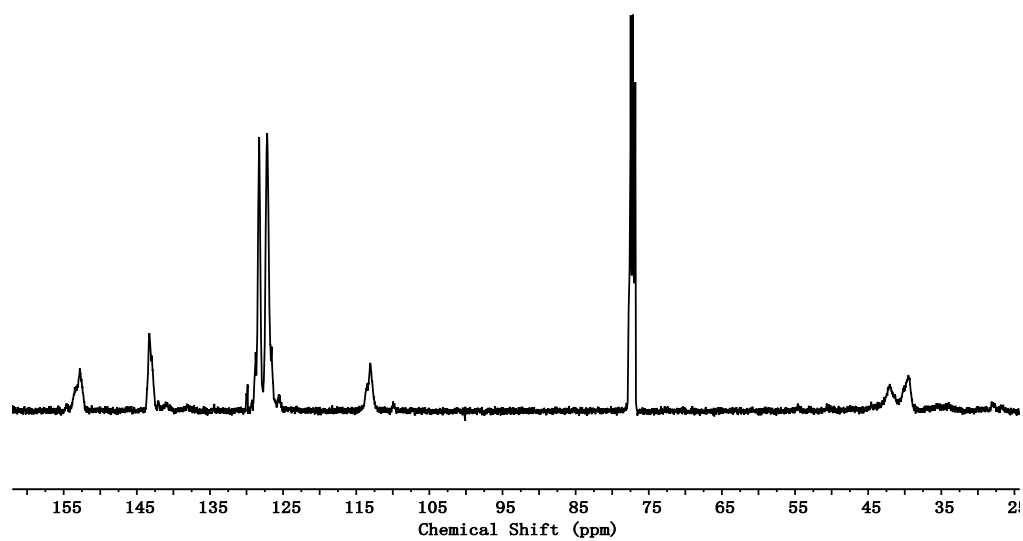
SFig. 7 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB). (Table 1, entry 10)



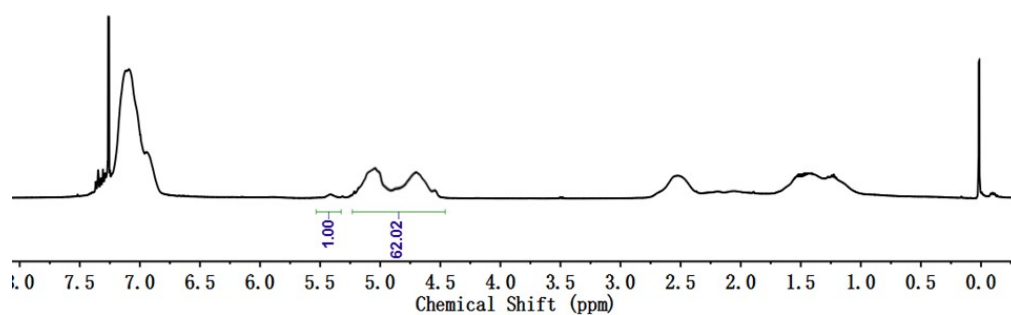
SFig. 8 ¹³C NMR (100M, CDCl₃, 25 °C) spectrum of P(2-PB).(Table 1, entry 10)



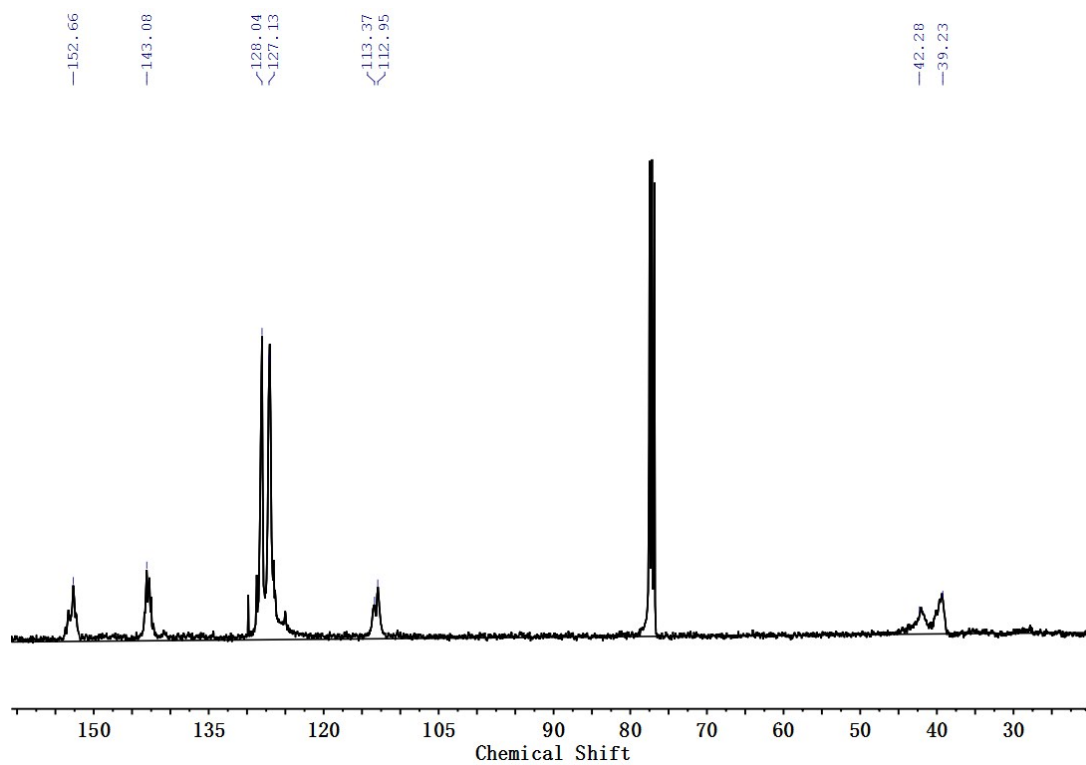
SFig. 9 ¹H NMR (400M, CDCl₃, 25 °C) spectrum of P(2-PB).(Table 1, entry 11)



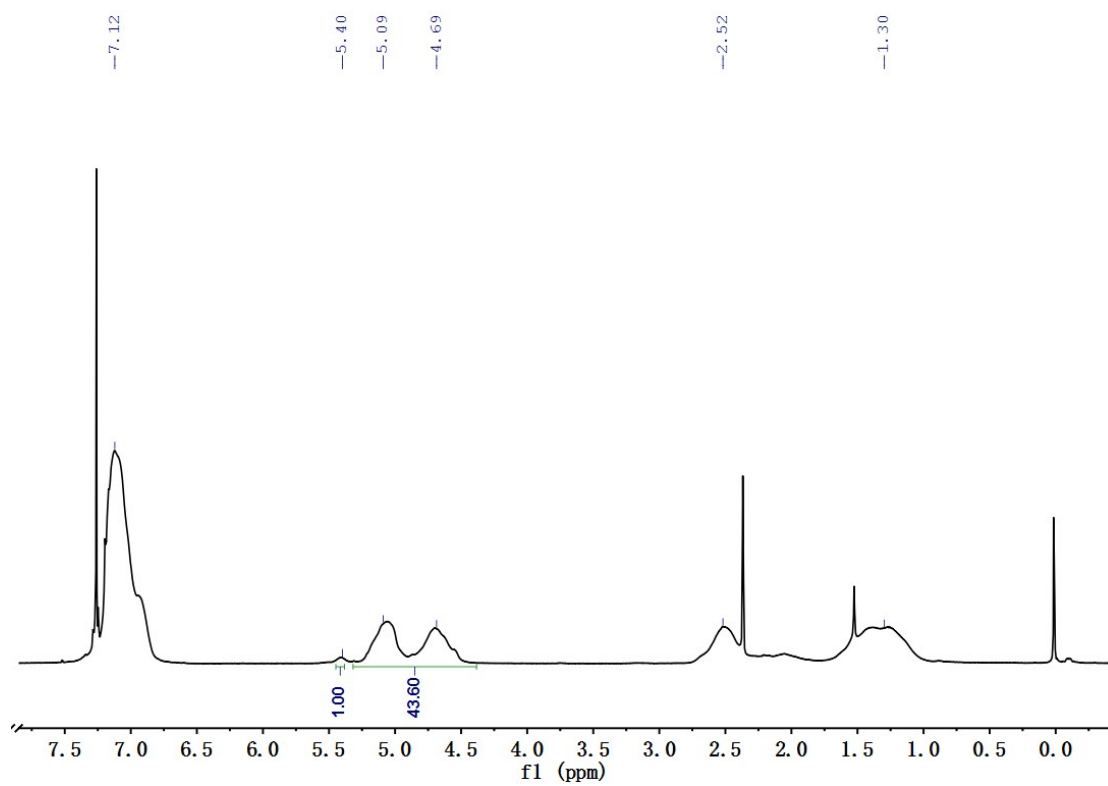
SFig. 10 ^{13}C NMR (100M, CDCl_3 , 25 °C) spectrum of P(2-PB).(Table 1, entry 11)



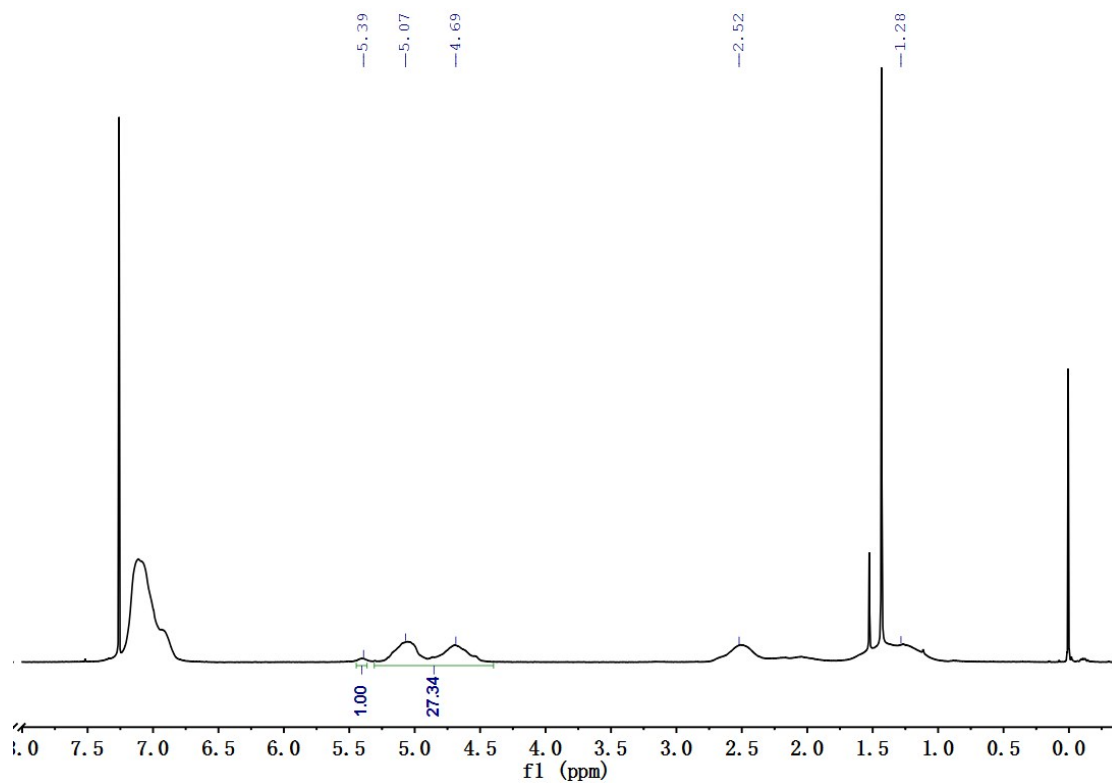
SFig. 11 ^1H NMR (400M, CDCl_3 , 25 °C) spectrum of P(2-PB).(Table 1, entry 12)



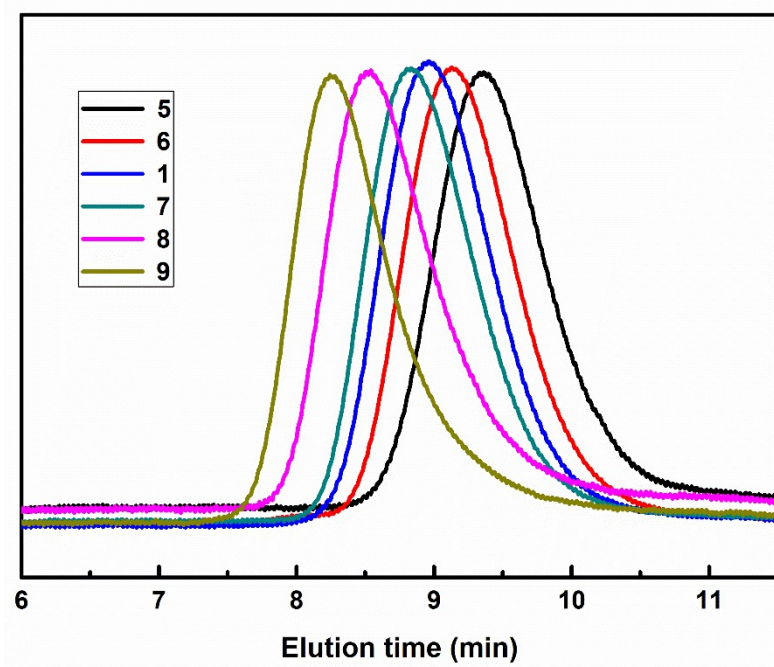
SFig. 12 ^{13}C NMR (100M, CDCl_3 , 25 $^\circ\text{C}$) spectrum of P(2-PB).(Table 1, entry 12)



SFig. 13 ^1H NMR (400M, CDCl_3 , 25 $^\circ\text{C}$) spectrum of P(2-PB).(Table 1, entry 13)



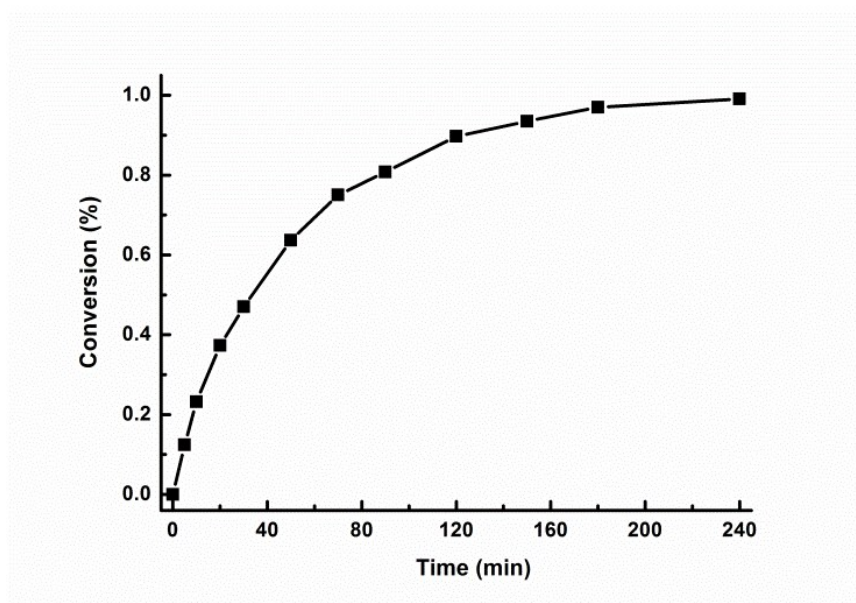
SFig. 14 ^1H NMR (400M, CDCl_3 , 25 $^\circ\text{C}$) spectrum of P(2-PB). (Table 1, entry 14)



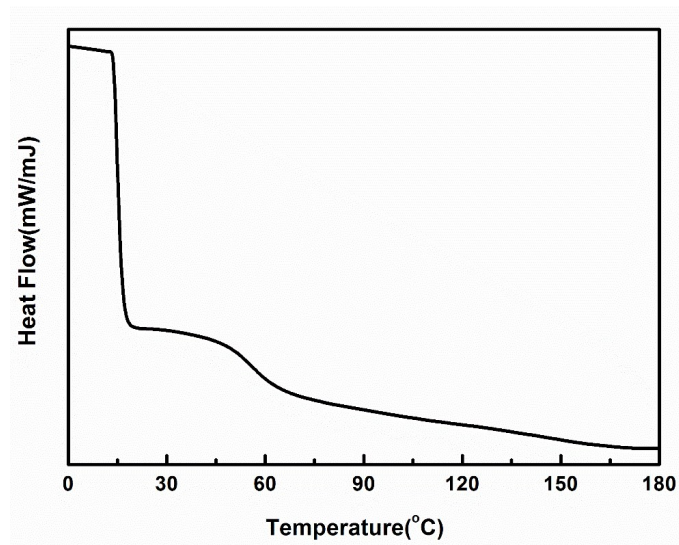
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Time (min)	Conversion (%)
0	0
5	12.4
10	23.2
20	37.3
30	47.0
50	63.7
70	75.0
90	80.8
120	89.7
150	93.5
180	97.0
240	99.1



SFig. 16 Polymerization of 2-PB with $\text{Lu}/[(\text{Ph}_3\text{C})][(\text{B}(\text{C}_6\text{F}_5)_4)]$: conversion vs time. ($[\text{Lu}]_0 = 5.0 \mu\text{mol/mL}$, $[\text{2-PB}]_0/[\text{Lu}]_0 = 200$, Chlorobenzene, $25 \text{ }^\circ\text{C}$).



SFig. 17 Thermogram of P(2-PB). (Table 1, entry 12)