Supporting information

Regio- and stereo-selective polymerization of 1,3-butadiene catalyzed phosphorus-nitrogen PN^3-pincer cobalt(II) complexes

Dirong Gong [a,b], Xuequan Zhang[c], Kuo-Wei Huang[a*]

[a] *King Abdullah University of Science and Technology, Division of Physical Sciences and Engineering* and *KAUST Catalysis Center, Thuwal 23955-6900, Saudi Arabia.*

[b] *Department of Polymer Science and Engineering, Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, P. R. China*

[c] *Key Laboratory of Synthetic Rubber, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, P. R. China.*

hkw@kaust.edu.sa

Content list:

Table S1 Crystal data and structure refinements of complexes **$CoCl_2$-H, $CoCl_2$-Me, $CoBr_2$-^{i}Pr** and **CoI_2-Me**

	$CoCl_2$-H	**$CoCl_2$-Me**	**$CoBr_2$-^{i}Pr**	**CoI_2-Me**
Formula	$C_{16}H_{24}Cl_2CoN_4P$	$C_{18}H_{29}Cl_2CoN_4P$	$C_{22}H_{37}Br_2CoN_4P$	$C_{18}H_{29}I_2CoN_4P$
Molecular weight	433.20	462.26	607.27	645.16
Crystal system	triclinic	triclinic	orthorhombic	triclinic
Space group	P21/n	P21/C	P212121	P21/C
a (Å)	12.4579(4)	16.2575(8)	11.5226(7)	16.0679(6)
b (Å)	12.4065(5)	9.2445(4)	12.0510(6)	8.9042(4)
c (Å)	14.3704(6)	15.8382(6)	19.2018(9)	17.2884(5)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	111.364(4)	107.243(4)	90.00	103.574(3)
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	2068.45(14)	2273.38(17)	2666.3(2)	2404.39(16)
Z	4	4	4	4
D_{calcd} (Mg/m^3)	1.398	1.351	1.513	1.520
Absorp coeff (mm^{-1})	1.171	1.070	3.717	3.358
F(000)	900	964	1236	857
Crystal size (mm)	0.23×0.21×0.16	0.25×0.15×0.12	0.35×0.32×0.20	0.23×0.21×0.11
θ Range (deg)	3.04 to 29.52	3.07 to 29.50	2.71 to 28.82	3.01 to 29.04
No. of reflns collected	45703	49833	10252	10648
No. of indep reflns	5453 (R_{int}= 0.0381)	3998 (R_{int}= 0.1107)	5164 (R_{int}= 0.038)	4981 (R_{int}= 0.0339)
No. of data/ restraint/params	5453/0/223	3998/0/243	5164/0/281	4981/0/243
GOF on F^2	1.049	1.162	1.006	1.056
R_1(I>2sigma(I))	0.0418	0.0425	0.04	0.0549
wR_2	0.0929	0.2937	0.0991	0.0879

Table S2 The selected bond length (Å) and angles (°) for complexes **$CoCl_2$-H, $CoCl_2$-Me, $CoBr_2$-^{i}Pr** and **CoI_2-Me**

X = Cl, Br or I	**$CoCl_2$-H**	**$CoCl_2$-Me**	**$CoBr_2$-^{i}Pr**	**CoI_2-Me**
Bond distance (Å)				
Co1-N1	2.096 6(15)	2.112(8)	2.101(4)	2.138(3)
Co1-N4	2.14 17(16)	2.104(10)	2.170(4)	2.098(4)
Co1-X2	2.3034(5)	2.313(3)	2.4627(9)	2.6818(6)
Co1-X1	2.3044(5)	2.339(3)	2.4207(9)	2.6519(7)
Co1-P	2.5034(5)	2.468(3)	2.5058(15)	2.4878(13)
Bond angle (°)				
N1-Co1-N4	75.68(6)	74.7(3)	75.24(16)	74.75(13)
N1-Co1-X1	122.50(5)	99.3(2)	97.66(12)	155.41(9)
N4-Co1-X2	94.38(5)	93.3(6)	89.94(12)	102.91(9)
N1-Co1-X1	127.82(4)	148.6(3)	152.08(12)	99.92(9)
N4-Co1-X1	92.44(5)	99.2(3)	100.95(11)	93.21(14)
X2-Co1-X1	108.79(2)	111.494(11)	110.08(4)	104.66(2)
N1-Co1-P	78. 97(4)	77.8(2)	78.27(11)	76.97(9)
N4-Co1-P	154.15(4)	149.4(3)	148.89(12	146.28(12)
X2-Co1-P	102.75(2)	103.84(12)	109.63(4)	95.23(3)
X1-Co1-P	100.004(19)	97.29(11)	94.83(4)	109.52(3)

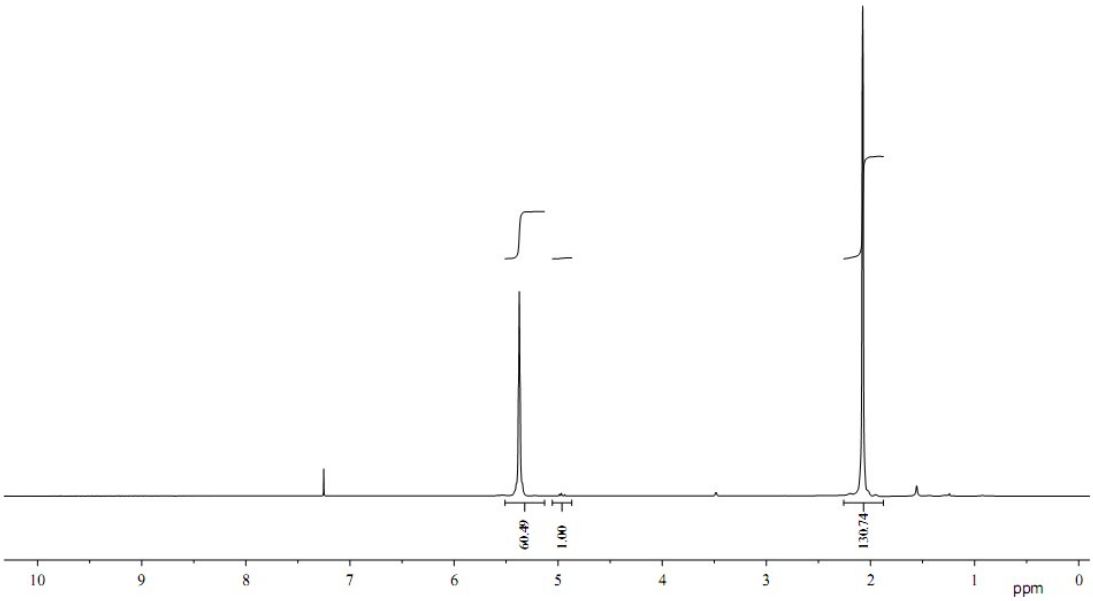

Fig.S1 The ^{1}H NMR of obtained *cis*-1,4 polybutadiene (entry 1, cis-1,4 content: 98.4%)

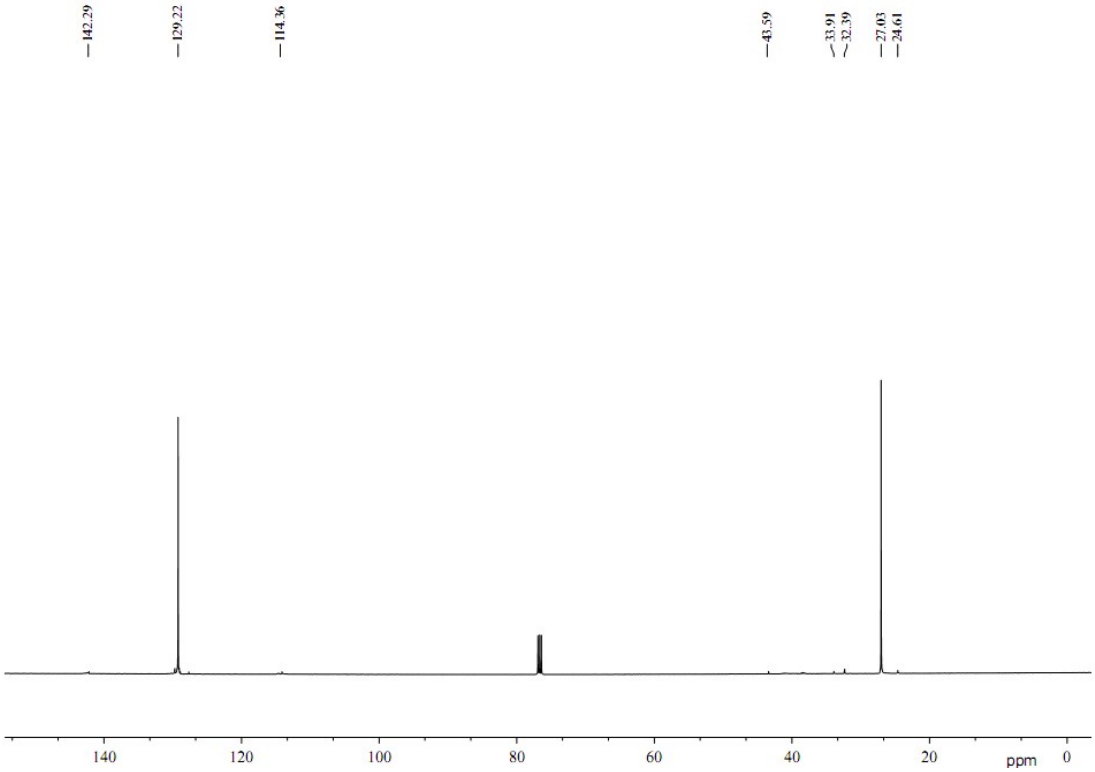

Fig.S2 The ^{13}C NMR of obtained *cis*-1,4 polybutadiene (entry 1, *cis*-1,4 content: 98.4%)

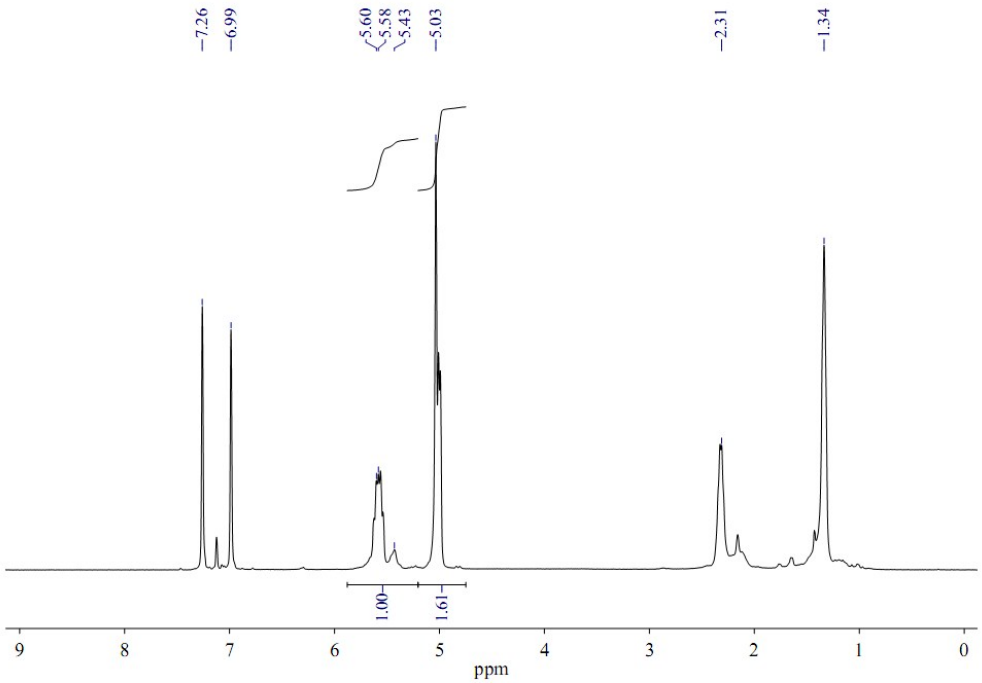

Fig.S3 The ^{1}H NMR of obtained 1,2-polybutadiene (1,2 content: 89.9%)

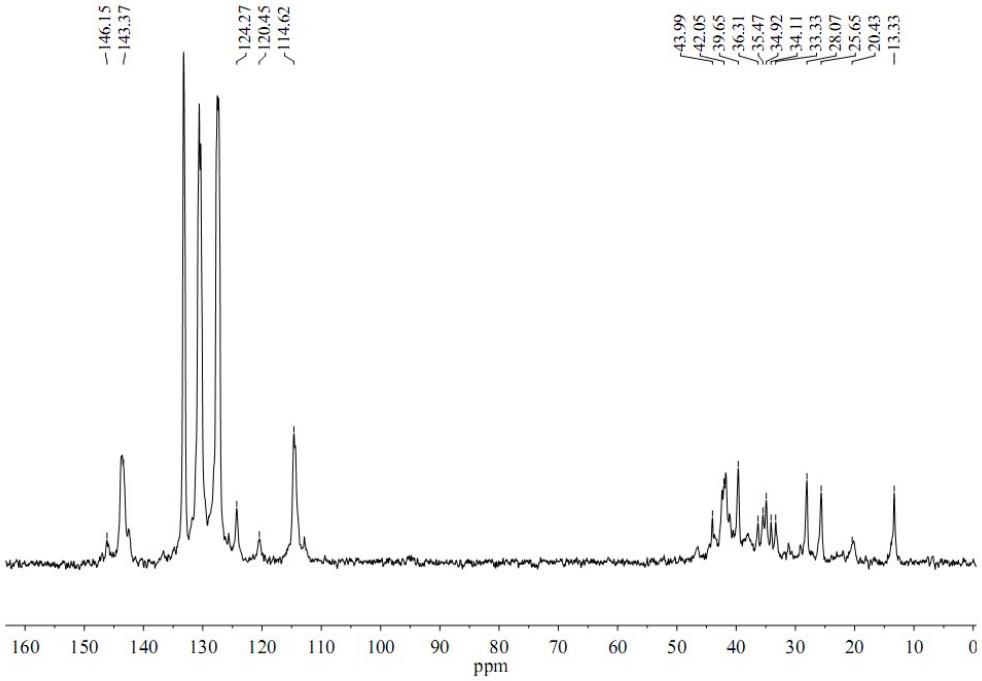

Fig.S4 The ^{13}C NMR of obtained 1,2-polybutadiene (1,2 content: 89.9%)