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Supporting Information

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Cationic Rare Earth Metal Alkyls bearing a Bis-(phosphinophenyl)amido (PNP) Ancillary Ligand. An Excellent Catalyst System for Living *cis*-1,4-Polymerization and Copolymerization of Isoprene and Butadiene

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Experimental Section

General Procedure and Materials. All manipulations were performed under a dry and oxygen-free nitrogen or argon atmosphere using Schlenk techniques or an Mbraun glovebox. Argon and nitrogen were purified by being passed through a Dryclean column (4 A molecule sieves, Nikka Seiko Co.) and a Gasclean GC-RX column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4 A) catalyst unit. The concentration of the oxygen and moisture in the glovebox was always kept below 0.1 ppm (monitored by an Mbraun O_2/H_2O Combi-Analyzer). THF, Et_2O, and hexane were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips, and then stored in the glovebox. Monochlorobenzene was distilled from CaH_2, and degassed by the freeze-pump-thaw method. Isoprene and styrene (Junsei Chemical Co., Ltd.) was dried by stirring with CaH_2 for 48 hours, and distilled under reduced pressure before use. Butadiene (>99%) (Takachiho Chemical Industrial Co. Ltd.) was dried by passing through the toluene solution of $AlEt_3$, and a Dryclean column (4 A molecule sieves, Nikka Seiko Co.) and a Gasclean GC-RX column (Nikka Seiko Co.). $LnCl_3$ (Ln = Y, Sc, Lu) was purchased from Strem Chemical, Inc., $LiCH_2SiMe_3$, $KPPh_2$ (0.5 mol/l solution in THF) were bought from Aldrich. 2-fluoroaniline and 2-bromofluorobenzene were obtained from Tokyo Chemical Industry Co., Ltd.. Sodium *tert*-butoxide, $Pd(OAc)_2$, and 1,4-dioxane were obtained from Wako Pure Chemical Industries, Ltd. *rac*-BINAP was purchased from Kanto Kagaku Co., Ltd. $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were purchased from Toschchem Corporation and used without purification. The deuterated solvents were obtained from Cambridge Isotope and dried by sodium chips. $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Y, Lu)[1] and bis(2-diphenylphosphinophenyl)amine ($PNP^{Ph}H$) ligand[2] were prepared according to literature procedures. ^1H and ^{13}C NMR spectra of polymers were recorded using TMS as internal standard on a JNM EX-400 in $CDCl_3$ at room temperature. The NMR spectra of air and moisture sensitive compounds were recorded by using of J. Young valve NMR tube (Wilmad 528-JY) on a JNM EX-400 in C_6D_6. The chemical shifts for ^{31}P NMR spectra were recorded based on an external 85% H_3PO_4 standard. The weight-average molecule weight (M_w), the number-average molecular weight (M_n), and the molecular weight distribution (M_w/M_n) of the polymers were measured by means of gel permeation chromatography on TOSOH HLC-8220 GPC (Column: Super HZM-H×3) at 40 °C using THF as eluent (the flowing rate is 0.35 mL/min) against polystyrene standards. DSC was performed on Perkin Elmer Pyrid DSC at a heating rate of 10 °C/min under N_2 atmosphere.

Synthesis of $[(PNP^{Ph})Sc(CH_2SiMe_3)_2]$ (**1**). A THF solution (20 mL) of bis(2-diphenylphosphinophenyl)amine ($PNP^{Ph}H$) (0.506 g, 0.941 mmol) was slowly added into a THF solution (5 mL) of $[Sc(CH_2SiMe_3)_3(THF)_2]$ (0.424 g, 0.941 mmol) with good stirring in 20 min, to give a yellow solution. After being stirred for 10 minutes, all volatiles were removed in vacuum, and the residue was dried under reduced pressure for 3 h. The resulting yellow powder was washed with cold hexane and dried up. Yield: 0.657 g (92.0%) of $[(PNP^{Ph})Sc(CH_2SiMe_3)_2]$. Anal. Calcd for $C_{44}H_{50}NP_2ScSi_2$: C, 66.91; H, 6.67; N, 1.85. Found: C, 67.22; H, 6.99; N, 1.48.

^{1}H NMR (400 MHz, RT, C_6D_6): d 7.60 (m, 8H, Ar), 7.05–6.90 (m, 18H, Ar), 6.53 (t, *J* = 7 Hz, 2H, Ar), 0.11(s, 18H, $CH_2Si\mathit{Me}_3$), -0.16 (s, 4H, $C\mathit{H}_2SiMe_3$). ^{13}C NMR (100 MHz, RT, C_6D_6): d 159.94 (t, *J* = 12 Hz, Ar), 134.16 (s, Ar), 133.90 (br, Ar), 132.82 (s, Ar), 130.91 (t, *J* = 11 Hz, Ar), 130.16 (s, Ar), 128.83 (dd, *J* = 5, 4 Hz, Ar), 120.74 (d, *J* = 2 Hz, Ar), 120.26 (dd, *J* = 17, 16 Hz, Ar), 119.89 (d, *J* = 2 Hz, Ar), 55.18 (s, $\mathit{C}H_2SiMe_3$), 3.95 (s, $CH_2Si\mathit{Me}_3$). ^{31}P NMR (160 MHz, RT, C_6D_6): d –8.28 (s, PPh_2).

^{1}H NMR (400 MHz, RT, C_4D_8O): δ 7.34-7.20 (m, 20H, Ar), 7.10 (t, *J* = 15 Hz, 2H, Ar), 6.95 (t, *J* = 13 Hz, 2H, Ar), 6.68 (t, *J* = 13 Hz, 2H, Ar), 6.63 (t, *J* = 15 Hz, 2H, Ar), 0.04 (s, 4H, $C\mathit{H}_2SiMe_3$), -0.21 (s, 18H, $CH_2Si\mathit{Me}_3$). ^{13}C NMR (100 MHz, RT, C_4D_8O): d 159.01 (d, *J* = 25 Hz, Ar), 135.32 (s, Ar), 135.13 (d, *J* = 11 Hz, Ar), 134.29 (d, *J* = 15 Hz Ar), 131.84 (s, Ar), 129.48 (s, Ar), 128.83 (d, *J* = 8 Hz, Ar), 124.09 (d, *J* = 22 Hz, Ar), 121.05 (s, Ar), 120.23 (s, Ar), 46.13 (s, $\mathit{C}H_2SiMe_3$), 4.19 (s, $CH_2Si\mathit{Me}_3$). ^{31}P NMR (160 MHz, RT, C_4D_8O): d –11.61 (s, PPh_2).

Synthesis of [(PNP^{Ph})Y(CH$_2$SiMe$_3$)$_2$(THF)] (**2**). A THF solution (20 mL) of bis(2-diphenylphosphinophenyl)amine ($PNP^{Ph}H$) (1.554 g, 2.891 mmol) was added slowly into a THF solution (5 mL) of [$Y(CH_2SiMe_3)_3(THF)_2$] (1.430 g, 2.891 mmol) with good stirring in 30 min, to give a yellow solution. After being stirred for 10 minutes, all volatiles were removed in vacuum, and the residue yellow solid was dried at reduced pressure for 3 h. The resulting yellow powder was washed with cold hexane, and then dried up. 2.257 g (89.5%) of [(PNP^{Ph})$Y(CH_2SiMe_3)_2(THF)$] was obtained. Anal. Calcd for $C_{48}H_{58}NOP_2Si_2Y$: C, 66.11; H, 6.70; N, 1.61. Found: C, 65.88; H, 6.91; N, 1.40.

^{1}H NMR (400 MHz, RT, C_6D_6): d 7.49 (m, 8H, Ar), 7.07–6.96 (m, 18H, Ar), 6.56 (t, *J* = 7 Hz, 2H, Ar), 3.60 (m, 4H, a–THF), 1.17 (m, 4H, ß–THF), 0.28(s, 18H, $CH_2Si\mathit{Me}_3$), –0.03 (d, *J* = 3 Hz, 4H, $C\mathit{H}_2SiMe_3$). ^{13}C NMR (100 MHz, RT, C_6D_6): d 157.57 (d, *J* = 22 Hz, Ar), 135.16 (s, Ar), 134.01 (d, *J* = 12 Hz, Ar), 133.70 (d, 15 Hz, Ar), 131.69 (s, Ar), 129.03 (s, Ar), 128.44 (d, *J* = 8 Hz, Ar), 122.36 (d, *J* = 22 Hz, Ar), 120.44 (d, *J* = 5 Hz, Ar), 119.79 (d, *J* = 3 Hz, Ar), 69.78 (s, a–THF), 38.00 (dt, *J* = 33 Hz, $\mathit{C}H_2SiMe_3$), 25.02 (s, ß–THF), 4.88 (s, $CH_2Si\mathit{Me}_3$). ^{31}P NMR (160 MHz, RT, C_6D_6): d –11.60 (d, J_{Y-P} = 38 Hz, $\mathit{P}Ph_2$).

^{1}H NMR (400 MHz, RT, C_4D_8O): d 7.34–7.23 (m, 20H, Ar), 6.97 (t, *J* = 8 Hz, 2H, Ar), 6.85–6.77 (m, 4H, Ar), 6.55 (t, *J* = 15, 2H, Ar), 3.61 (m, 4H, a–THF), 1.72 (m, 4H, ß–THF), –0.19 (s, 18H, $CH_2Si\mathit{Me}_3$), –0.57 (d, *J* = 3 Hz, 4H, $C\mathit{H}_2SiMe_3$). ^{13}C NMR (100 MHz, RT, C_4D_8O): d 159.78 (d, *J* = 24 Hz, Ar), 135.90 (s, Ar), 135.76 (d, *J* = 6 Hz, Ar), 134.23 (d, 15 Hz, Ar), 131.92 (s, Ar), 129.28 (s, Ar), 128.76 (d, *J* = 8 Hz, Ar), 123.74 (d, *J* = 6 Hz, Ar), 119.46 (d, *J* = 3 Hz, Ar), 119.79 (d, *J* = 3 Hz, Ar), 68.06 (s, a–THF), 36.27 (dt, *J* = 37 Hz, $\mathit{C}H_2SiMe_3$), 26.28 (s, ß–THF), 4.64 (s, $CH_2Si\mathit{Me}_3$). ^{31}P NMR (160 MHz, RT, **C_4D_8O**): d –11.63 (d, J_{Y-P} = 31 Hz, $\mathit{P}Ph_2$)

Synthesis of [(PNP^{Ph})Lu(CH$_2$SiMe$_3$)$_2$(THF)] (**3**). A THF solution (20 mL) of bis(2-diphenylphosphinophenyl)amine ($PNP^{Ph}H$) (0.694 g, 1.291 mmol) was slowly added into a THF solution (5 mL) of [$Lu(CH_2SiMe_3)_3(THF)_2$] (0.750 g, 1.291 mmol) with good stirring in 20 min, to give a yellow solution. After being stirred for 10 minutes, all volatiles were removed in vacuum, and the residue was dried at reduced pressure for 3 h. The resulting yellow solid was washed with cold hexane, and then dried up. 1.104 g (89.2%) of [(PNP^{Ph})$Lu(CH_2SiMe_3)_2(THF)$] was obtained. A single crystal of [$PNP^{Ph}Lu(CH_2SiMe_3)_2(THF)$] (**3**) was obtained by recrystallization in toluene/hexane at -30 °C for 1 week. Anal. Calcd for $C_{48}H_{58}LuNOP_2Si_2$: C, 60.17; H, 6.10; N, 1.46. Found: C, 59.88; H, 6.29; N, 1.28.

^{1}H NMR (400 MHz, RT, C_6D_6): d 7.50 (m, 8H, Ar), 7.07–6.95 (m, 18H, Ar), 6.56 (t, *J* = 7 Hz, 2H, Ar), 3.61 (m, 4H, a–THF), 1.19 (m, 4H, ß–THF), 0.26 (s, 18H, $CH_2Si\mathit{Me}_3$), –0.20 (s, 4H, $C\mathit{H}_2SiMe_3$). ^{13}C NMR (100 MHz, RT, C_6D_6): d 158.48 (d, *J* = 22 Hz, Ar), 135.16 (s, Ar), 133.96 (d, *J* = 15 Hz, Ar), 133.74 (d, 15 Hz, Ar), 131.82 (s, Ar), 129.11 (s, Ar), 128.43 (d, *J* = 8 Hz, Ar), 122.09 (d, *J* = 25 Hz, Ar), 120.54 (t, *J* = 3 Hz, Ar), 119.79 (t, *J* = 2 Hz, Ar), 69.77 (s, a–THF), 44.03 (s, $\mathit{C}H_2SiMe_3$), 25.07 (s, ß–THF), 5.06 (s, $CH_2Si\mathit{Me}_3$). ^{31}P NMR (160 MHz, RT, C_6D_6): d –6.09 (s, $\mathit{P}Ph_2$).

^{1}H NMR (400 MHz, RT, C_4D_8O): d 7.32–7.20 (m, 20H, Ar), 7.06 (t, *J* = 16 Hz, 2H, Ar), 6.97 (t, *J* = 14 Hz, 2H, Ar), 6.81 (t, *J* = 13 Hz, 2H, Ar), 6.58 (t, *J* = 14 Hz, 2H, Ar), 3.61 (m, 4H, a–THF), 1.77 (m, 4H, ß–THF), –0.19 (s, 18H, $CH_2Si\mathit{Me}_3$), –0.76 (s, 4H, $C\mathit{H}_2SiMe_3$). ^{13}C NMR (100 MHz, RT, C_4D_8O): d 159.57 (s, Ar), 135.94 (s, Ar), 135.59 (d, *J* = 10 Hz, Ar), 134.24 (d, *J* = 15 Hz, Ar), 131.92 (s, Ar), 129.35 (s, Ar), 128.80 (d, *J* = 8 Hz, Ar), 123.37 (d, *J* = 20 Hz, Ar), 121.65 (d, *J* = 6Hz, Ar), 119.79 (d, *J* = 3 Hz, Ar), 68.06 (s, a-THF), 41.54 (t, *J* = 8 Hz, $C\mathit{H}_2SiMe_3$), 26.31 (s, ß-THF), 4.84 (s, $CH_2Si\mathit{Me}_3$). ^{31}P NMR (160 MHz, RT, C_4D_8O): d –13.51 (s, $P\mathit{Ph}_2$).

Isolation of the cationic Scandium alkyl complex [(PNP^{Ph})Sc(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (**4**). A THF solution (10 mL) of [PhMe$_2$NH][B(C$_6$F$_5$)$_4$] (0.234 g, 0.298 mmol) was slowly added into a THF solution (5 mL) of [(PNP^{Ph})Sc(CH$_2$SiMe$_3$)$_2$] (**1**) (0.225 g, 0.298 mmol) with rapid stirring in 10 min, to give a yellow solution. After being stirred for 10 min, all volatiles were removed in vacuum, and the residue was dried under reduced pressure for 2 h. The resulting yellow solid was washed with cold hexane/THF(10:1), and then dried up to give 0.276 g (62%) of [(PNP^{Ph})Sc(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (**4**). Anal. Calcd for $C_{72}H_{55}BF_{20}NO_2P_2SiSc$: C, 57.96; H, 3.72; N, 0.94. Found: C, 58.42; H, 4.06; N, 1.16.

^{1}H NMR (400 MHz, RT, C_4D_8O): d 7.45–6.54 (m, 28H, Ar), 3.61 (m, THF), 1.72 (m, THF), 0.44 (s, 2H, $C\mathit{H}_2SiMe_3$), –0.21 (s, 9H, $CH_2Si\mathit{Me}_3$). ^{13}C NMR (100 MHz, RT, C_4D_8O): d 159.36 (s, Ar), 150.12 (s, Ar), 147.67 (s, Ar), 140.08 (t, *J* = 14 Hz, Ar), 138.12 (t, *J* = 14 Hz, Ar), 137.63 (t, *J* = 14 Hz, Ar), 136.05 (s, Ar), 135.62 (t, *J* = 14 Hz, Ar), 133.92 (t, *J* = 7 Hz, Ar), 133.50 (s, Ar), 131.94 (t, *J* = 10 Hz, Ar), 131.11 (s, Ar), 129.97 (t, *J* = 5 Hz, Ar), 129.80 (t, *J* = 5 Hz, Ar), 122.62 (s, Ar), 121.70 (s, Ar), 121.11 (t, *J* = 4 Hz, Ar), 68.162 (s, THF), 52.88 (s, $C\mathit{H}_2SiMe_3$), 25.78 (s, THF), 3.87 (s, $-CH_2Si\mathit{Me}_3$). ^{31}P NMR (160 MHz, RT, C_4D_8O): d –8.14 (s, PPh_2).

Isolation of the cationic yttrium alkyl complex [(PNP^{Ph})Y(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (**5**). A THF solution (10 mL) of [PhMe$_2$NH][B(C$_6$F$_5$)$_4$] (0.290 g, 0.372 mmol) was slowly added into a THF solution (10 mL) of [(PNP^{Ph})Y(CH$_2$SiMe$_3$)$_2$(THF)] (**3**) (0.324 g, 0.372 mmol) with rapid stirring in 10 min, to give a yellow solution. After being stirred for 10 min, all volatiles were removed in vacuum, and the residue was dried under reduced pressure for 2 h. The resulting yellow solid was washed with cold hexane/THF (10:1), and then dried up to give 0.343 g (60%) of [(PNP^{Ph})Y(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (**5**). Anal. Calcd for $C_{72}H_{55}BF_{20}NO_2P_2SiY$: C, 56.30; H, 3.61; N, 0.92. Found: C, 56.04; H, 4.07; N, 0.55.

^{1}H NMR (400 MHz, RT, C_4D_8O): d 7.46–6.58 (m, 28H, Ar), 3.61 (m, THF), 1.77 (m, THF), –0.27 (s, 9H, $CH_2Si\mathit{Me}_3$), –0.34 (s, 2H, $C\mathit{H}_2SiMe_3$). ^{13}C NMR (100 MHz, RT, C_4D_8O): d 151.40 (s, Ar), 134.00 (, *J* = 7 Hz, Ar), 133.51 (s, Ar), 133.17 (s, Ar), 130.89 (s, Ar), 129.68 (t, *J* = 4 Hz, Ar), 129.21 (s, Ar), 122.86 (s, Ar), 120.95 (s, Ar), 116.84 (s, Ar), 113.05 (s, Ar), 68.10 (s, THF), 44.06 (s, $C\mathit{H}_2SiMe_3$), 26.31 (s, THF), 4.00 (s, $-CH_2Si\mathit{Me}_3$). ^{31}P NMR (160 MHz, RT, C_4D_8O): d –14.21 (d, $J_{Y\text{-}P}$ = 60 Hz, $P\mathit{Ph}_2$).

Isolation of the cationic lutetium alkyl complex [(PNP^{Ph})Lu(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (**6**). A THF solution (10 mL) of [PhMe$_2$NH][B(C$_6$F$_5$)$_4$] (0.111 g, 0.141 mmol) was slowly added into THF solution (5 mL) of [(PNP^{Ph})Lu(CH$_2$SiMe$_3$)$_2$(THF)] (**3**) (135 mg, 0.141 mmol) with rapid stirring in 10 min, to give a yellow solution. After being stirred for 10 min, all volatiles were removed in vacuum, and the residue was dried under reduced pressure for 2 h. The resulting yellow solid was washed with cold hexane, and then dried up to give 0.149 g (65%) of [(PNP^{Ph})Lu(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (**6**). A single crystal of [PNP^{Ph}Lu(CH$_2$SiMe$_3$)(THF)$_2$][B(C$_6$F$_5$)$_4$] (**6**) was obtained by recrystallization in chlorobenzene/hexane at -30 °C for 1 week. Anal. Calcd for $C_{72}H_{55}BF_{20}LuNO_2P_2Si$: C, 53.31; H, 3.42; N, 0.86. Found: C, 53.96; H, 3.56; N, 1.33.

^{1}H NMR (400 MHz, RT, C_4D_8O): d 7.44–6.58 (m, 28H, Ar), 3.61 (m, THF), 1.77 (m, THF), –0.23 (s, 9H, $CH_2Si\mathit{Me}_3$), –0.55 (s, 2H, $C\mathit{H}_2SiMe_3$). ^{13}C NMR (100 MHz, RT, C_4D_8O): d 163.00 (s, Ar), 151.40 (s, Ar), 134.90 (s, Ar), 134.01 (d, *J* = 7 Hz, Ar), 133.90 (s, Ar), 133.19 (s, Ar), 130.70 (s, Ar), 129.63 (s, Ar), 129.57 (d, *J* = 4 Hz, Ar), 129.21 (s, Ar), 123.34 (s, Ar),

121.17 (s, Ar), 116.84 (s, Ar), 113.05 (s, Ar), 68.10 (s, THF), 47.06 (s, *C*H_2SiMe$_3$), 26.31 (s, THF), 4.28 (s, –CH_2Si*Me*$_3$). ^{31}P NMR (160 MHz, RT, C_4D_8O): d –7.12 (s, PPh_2).

A typical procedure for polymerization of isoprene at room temperature (Table 1, run 7): In a glovebox, to a 100 mL flask, which contained a magnetic stirrer and was equipped with a dropping funnel, 8 mL of a C_6H_5Cl solution of [(PNP^{Ph})Y(CH_2SiMe_3)$_2$(THF)] (**2**) (0.025 mmol, 0.022 g) and 1.022 g of isoprene (15.0 mmol) were added successively. [$PhMe_2NH$][B(C_6F_5)$_4$] (0.025 mmol, 0.020 g) in 2 mL of C_6H_5Cl was added into the dropping funnel. The reaction apparatus was moved outside and placed in a water bath (at room temperature). The C_6H_5Cl solution of [$PhMe_2NH$][B(C_6F_5)$_4$] was dropped quickly into the flask from the dropping funnel under rapid stirring. After 20 min, the polymerization was terminated by injecting methanol. The reaction mixture was poured into a large quantity of methanol (200 mL) containing a small amount of hydrochloric acid and butylhydroxytoluene (BHT) as a stabilizing agent. The precipitated polymer was washed by methanol, and dried under vacuum at 60 °C to a constant weight to afford 1.021 g (100% yield) of polyisoprene with *cis*-1,4 content of 99.6%. ^{1}H NMR (400Hz, RT, $CDCl_3$): δ 5.12 (br s, 1H, =C*H*), 2.04 (br s, 4H, –CH_2–), 1.69 (br s, 3H, –CH_3). ^{13}C NMR (100Hz, RT, $CDCl_3$): δ 135.08 (s, –CH_2(Me)*C*=CH), 124.92 (s, –CH_2(Me)C=*C*HCH_2), 32.29 (s, –*C*H_2(Me)C=CH–), 26.50 (s, C=CH*C*H_2–), 23.53 (s, –CH_2(*Me*)C=CH) (See Figures S2 and S3).

A typical procedure for polymerization of isoprene at high temperature (Table 1, run 13): In a glovebox, to a 100 mL flask, which contained a magnetic stirrer and was equipped with a dropping funnel, 7 mL of a C_6H_5Cl solution of [$PhMe_2NH$][B(C_6F_5)$_4$] (0.025 mmol, 0.020 g) was added. [(PNP^{Ph})Y(CH_2SiMe_3)$_2$(THF)] (**2**) (0.025 mmol, 0.022 g) in 3 mL of C_6H_5Cl and 1.022 g of isoprene (15.0 mmol) were added into the dropping funnel in the glovebox successively. The reaction apparatus was moved outside and placed in a water bath (at 50 °C). After 10 min, the C_6H_5Cl solution of [(PNP^{Ph})Y(CH_2SiMe_3)$_2$(THF)] (**2**) and isoprene was dropped quickly into the flask from the dropping funnel and the mixture solution was stirred rapidly at 50 °C for 10 min. The polymerization was terminated by injecting methanol, and the reaction mixture was poured into a large quantity of methanol containing a small amount of hydrochloric acid and butylhydroxytoluene (BHT) as a stabilizer. The precipitated polymer was washed by methanol, and dried under vacuum at 60 °C to constant weight to afford 0.920 g (90% yield) of polyisoprene with *cis*-1,4 content of 98.7% (See Figures S4 and S5).

A typical procedure for polymerization of butadiene: In a glovebox, a toluene solution of Al^{i}Bu$_3$ (0.125 ml, 1 M, 1.25×10^{-4} mol, to purify butadiene) and 10 mL toluene were added into a glass pressure reactor. The reactor was taken out from the glovebox and sealed, and then butadiene (0.810 g, 1.5×10^{-2} mol) was added into the solution at –10 °C. The reactor was moved to a water bath (25 °C) and was stirred for 10 min. A toluene solution (2 mL) of **2** (22 mg, 2.5×10^{-5} mol), and a toluene solution (3 mL) of [Ph_3C][B(C_6F_5)$_4$] (23 mg, 2.5×10^{-5} mol) was successively added quickly by an injector. Rapid stirring of the polymerization mixture was maintained for 10 min. Polymerization was terminated by pouring the mixture into a large quantity of methanol (about 200 mL) containing small amount of hydrochloric acid (ca. 0.5 M) and butylhydroxyltoluene (BHT) as a stablizer. The precipitated polymer isolated by decantation, washed with methanol, then dried under vacuum at 60°C to constant weight to afford 0.807 g polymer (yield, ~100%), and analyzed by NMR spectroscopy (Figure S6 and S7), DSC (Figure S11), and GPC (Figure S15).

A typical procedure of copolymerization of isoprene and butadiene: In the glovebox, a toluene solution of Al^{i}Bu$_3$ (0.125 ml, 1 M, 1.25×10^{-4} mol, to purify butadiene) and 10 mL toluene were added into a glass pressure reactor. The reactor was taken out from the glovebox and sealed, and then butadiene (0.810 g, 1.5×10^{-2} mol) was added into the solution at – 10 °C, then, the reactor was moved to water bath (25 °C) and was stirred for 10 min. A toluene solution (2 mL) of **2** (22 mg, 2.5×10^{-5} mol), and a toluene solution (3 mL) of [Ph_3C][B(C_6F_5)$_4$] (23 mg, 2.5×10^{-5} mol) was successively added quickly by an injector. Rapid stirring of the polymerization mixture was maintained for 10 min. Then isoprene (0.511 g, 7.5×10^{-3} mol) was added by an injector. Rapid stirring of the reaction mixture was maintained for another 20 min. Polymerization was terminated

by pouring the mixture into a large quantity of methanol (about 200 mL) containing small amount of hydrochloric acid (ca. 0.5 M) and butylhydroxyltoluene (BHT) as a stablizer. The precipitated polymer isolated by decantation, washed with methanol, then dried under vacuum at 60°C to constant weight to afford 1.319 g polymer (yield, ~100%), and analyzed by NMR spectroscopy (Figure S8 and S9), DSC (Figure S12), and GPC (Figure S15).

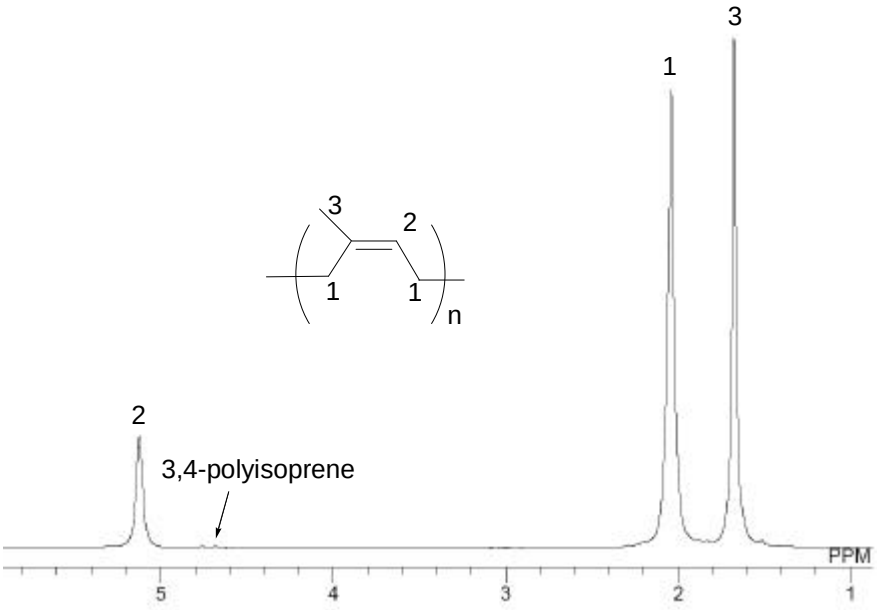

Figure S2. ^{1}H NMR spectrum of the 99.6% *cis*-1,4-polyisoprene in $CDCl_3$ at room temperature, scans: 100 times (run 12 in Table 1).

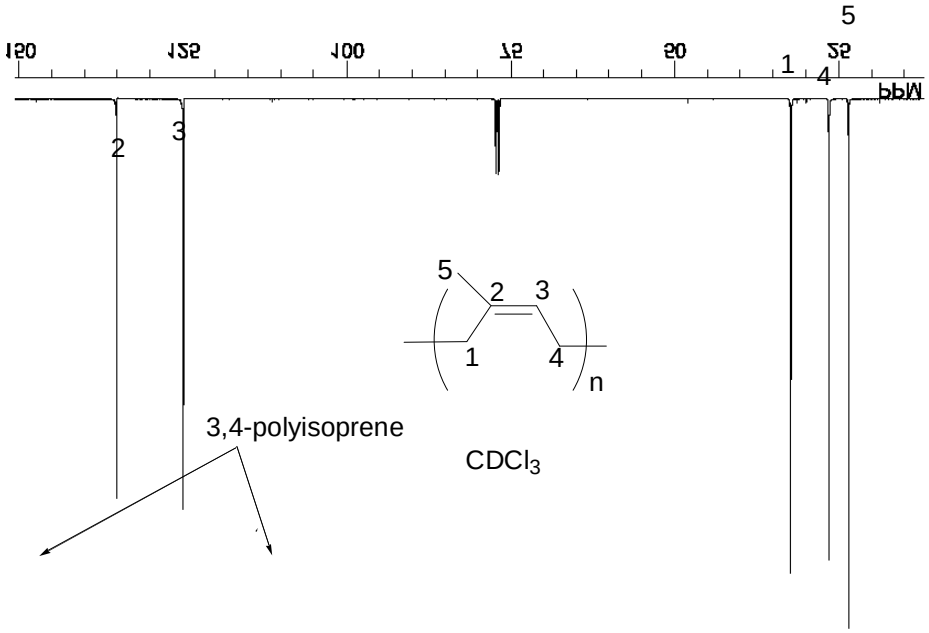

Figure S3. ^{13}C NMR spectrum of the 99.6% *cis*-1,4-polyisoprene in $CDCl_3$ at room temperature, scans: 12000 times (run 12 in Table 1).

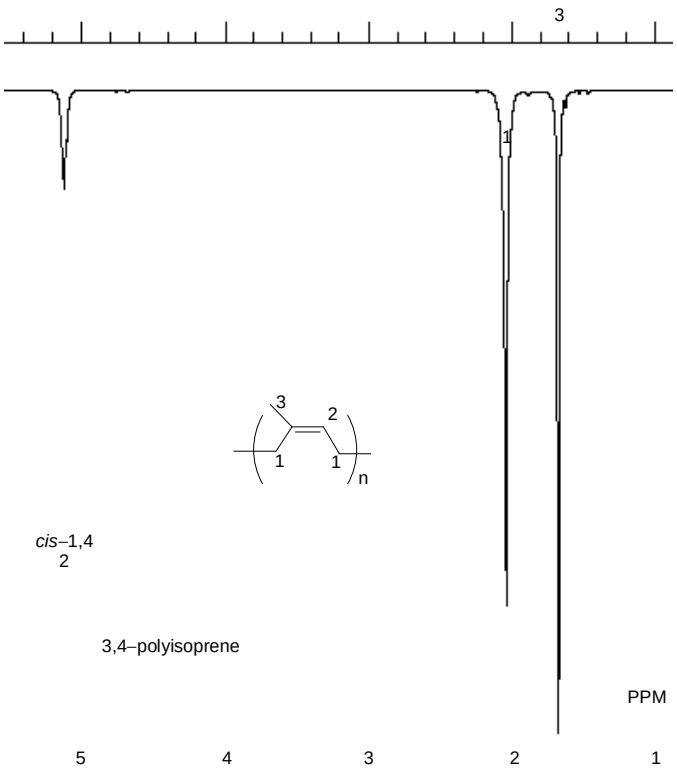

Figure S4. ^{1}H NMR spectrum of the 98.7% *cis*-1,4-polyisoprene in $CDCl_3$ at room temperature, scans: 100 times (run 13 in Table 1).

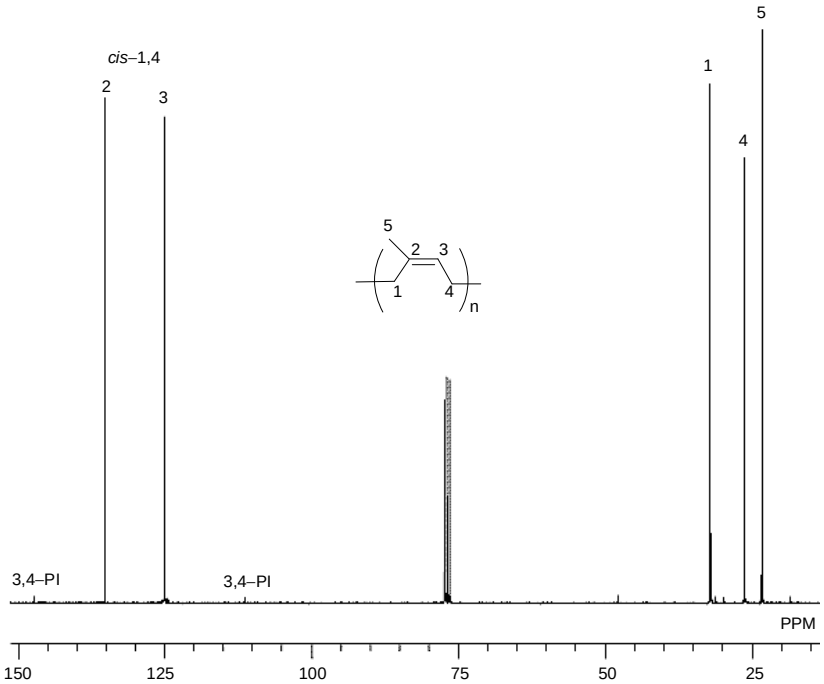

Figure S5. ^{13}C NMR spectrum of the 98.7% *cis*-1,4-polyisoprene in $CDCl_3$ at room temperature, scans: 12000 times (run 13 in Table 1).

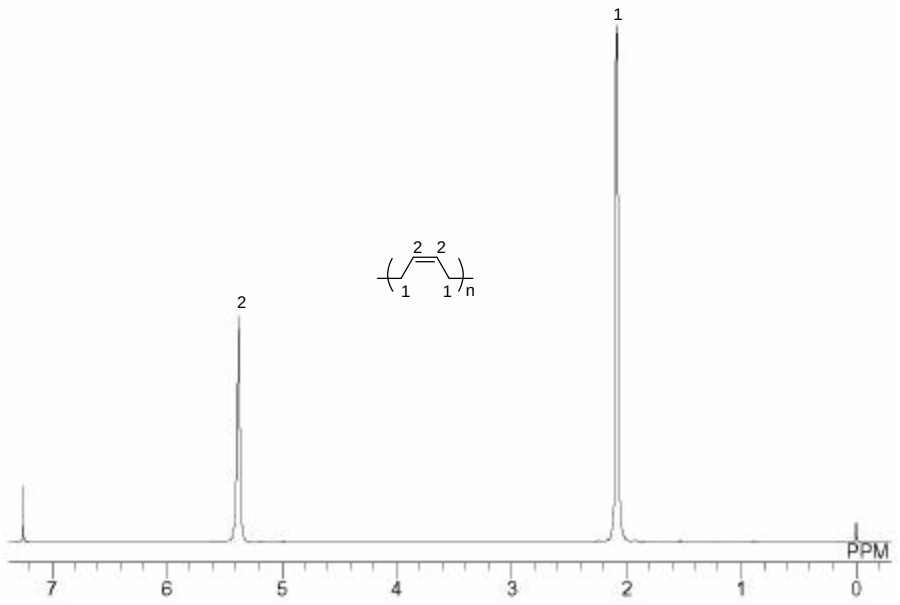

Figure S6. ^{1}H NMR spectrum of *cis*-1,4-polybutadiene (obtained at room temperature in $CDCl_3$)

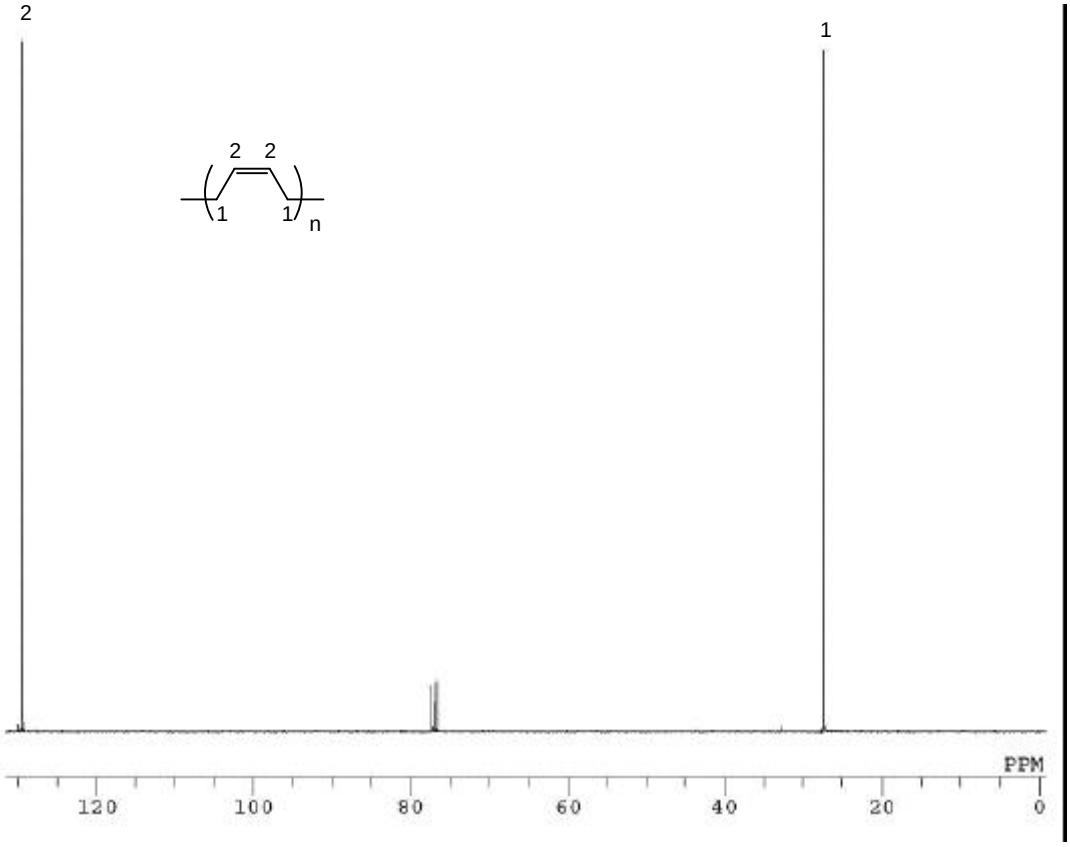

Figure S7. ^{13}C NMR spectrum of *cis*-1,4-polybutadiene (obtained at room temperature in $CDCl_3$)

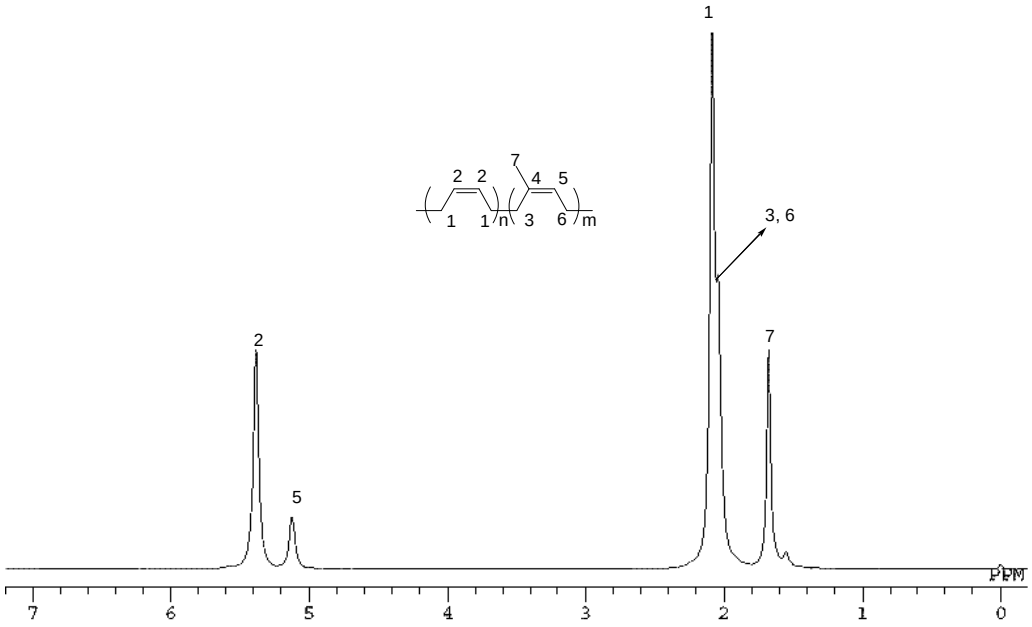

Figure S8. ^{1}H NMR spectrum of copolymer of isoprene and butadiene (obtained at room temperature in $CDCl_3$).

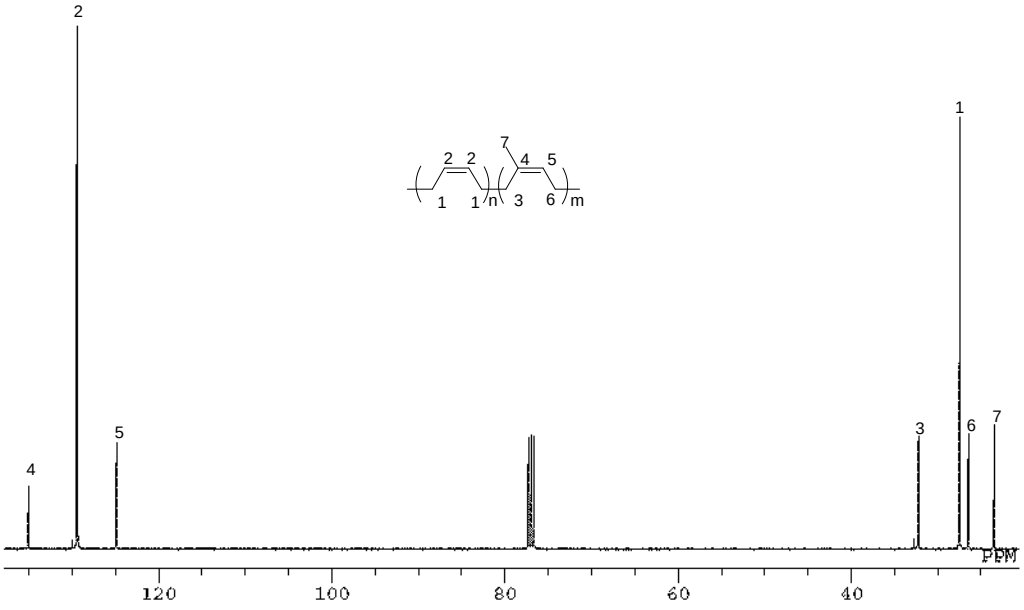

Figure S9. ^{13}C NMR spectrum of poly(butadiene-*b*-isoprene) (obtained at room temperature in $CDCl_3$).

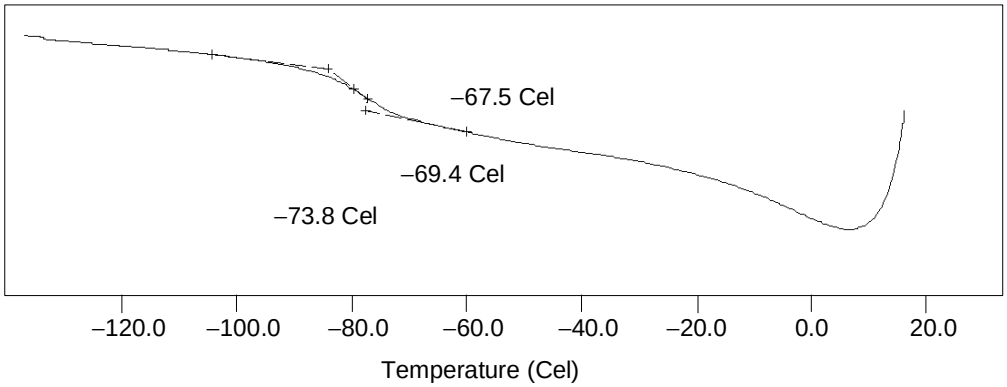

Figure S10. DSC curve of polyisoprene obtained at 0 °C (run 12, Table 1).

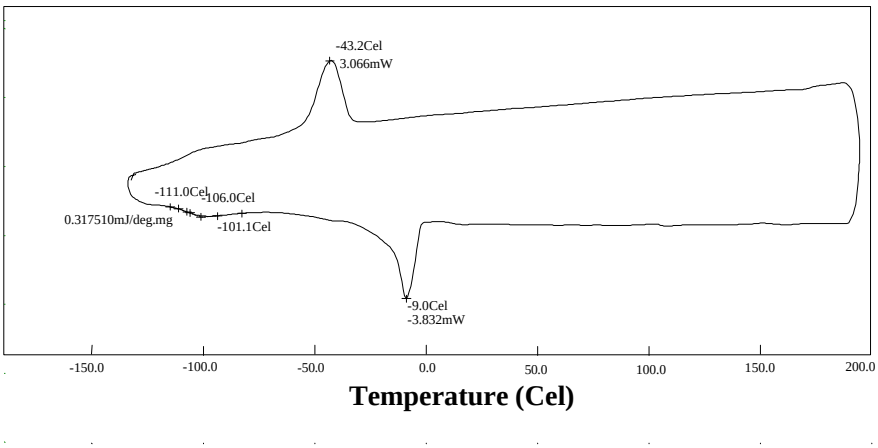

Figure S11. DSC chart of polybutadiene (Scheme 2).

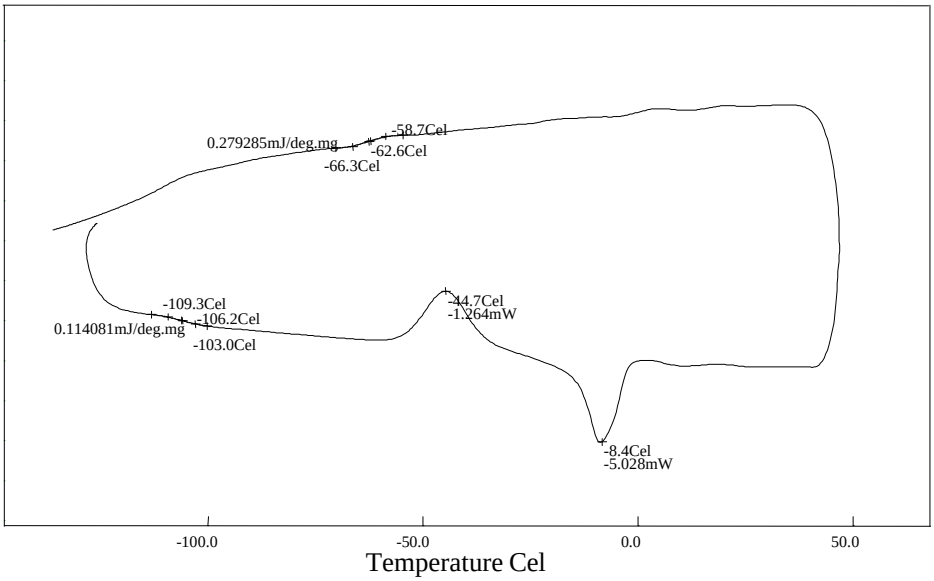

Figure S12. DSC chart of poly(butadiene-*b*-isoprene) (Scheme 2).

Figure S13. (a) Plots of M_n and M_w/M_n vs. conversion of isoprene (T_p = rt). (b) GPC profiles of polymers of runs 9 and 11.

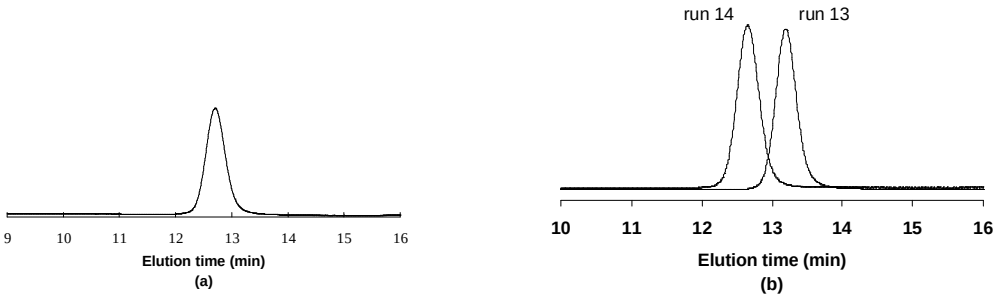

Figure S14. (a) GPC profile of a polymer obtained at 0 °C (run 12 in Table 1). (b) GPC profiles of polymers obtained at 50 °C (run 13 and run 14 in Table 1).

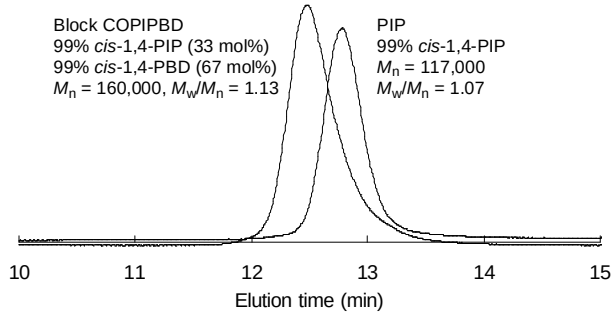

Figure S15. GPC profiles of the polymers obtained by sequentiall polymerization/copolymerization of butadiene and isoprene (Scheme 2).

X-ray Crystallographic Analysis. A crystal was sealed in the thin-wall glass capillary under a microscope in the glove box. Data collections were performed at –100 °C on a Bruker SMART APEX diffractometer with CCD area detector using graphite-monochromated Mo K_α radiation (λ= 0.71069 Å). The determination of crystal class and unit cell was carried out by SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structure was solved by using SHELXTL program. Refinement was performed on F^2 anisotropically by the full-matrix least-squares method for all the non-hydrogen atoms except crystal solvent. The crystal solvent was refined isotropically. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. The protons of toluene (crystal solvent) could not be placed at the calculated position due to disorder problem in complex **3**. CCDC 616257 (complex **3**) and 616258 (complex **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336033; or deposit@ccdc.cam.ac.uk).

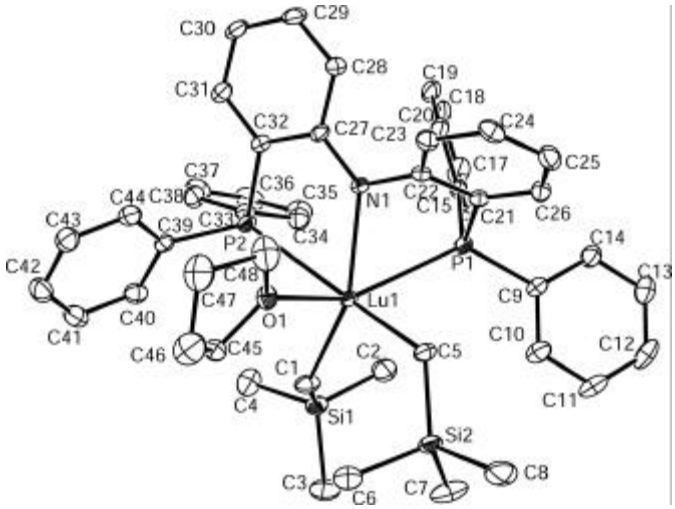

Figure S16. ORTEP structure of **3** (thermal ellipsoids at 30% level; hydrogen atoms and solvent molecule are omitted for clarity).

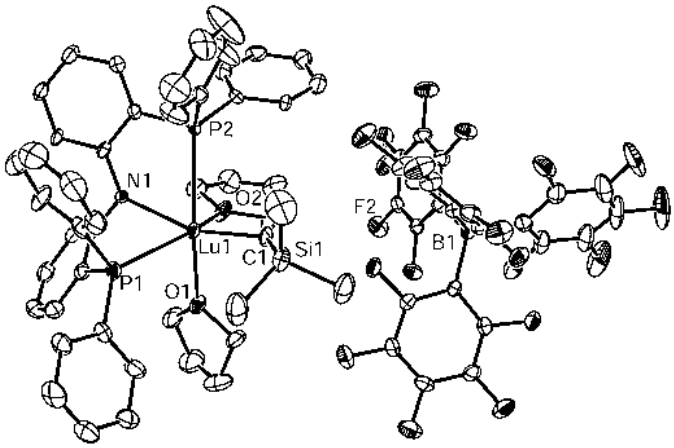

Figure S17. ORTEP structure of **6** (thermal ellipsoids at 30% level; hydrogen atoms and solvent molecule are omitted for clarity).

Description of Computations

For computational simplification, the THF-free Sc complex was selected for the present calculations. The geometry optimizations followed by analytic frequency calculations were performed with three-layer ONIOM((b3lyp/lanl2dz:hf/lanl2mb:uff) method[3] planted in Gaussion 03.[4] By using "Extrabasis" option, single *f*-polarization function (exponent of 0.27) was augmented for Sc, and one *d*-polarization function was augmented for P (exponent of 0.55) and Si (exponent of 0.45), respectively. The divisions of the layers are shown in Figure S18 (a), in which the reactive part of the cationic species (in red) was included in model system for high layer (B3LYP[5]) calculation. The atoms shown in black (Figure S18) were included in middle system for middle level (HF) calculation, and the remained parts (in blue) included in real system were treated by universal force field (UFF) molecular mechanics method.[6] The model system, middle system and real system are shown in Figure S18 (b), (c) and (d), respectively. The monomer molecule was included in high layer for the calculations of coordination complexes. The molecular orbital analysis was based on the one-layer Hartree-Fock single-point calculation of optimized geometry. The basis set used for the single-point calculation is the same as that in the geometry optimization. No symmetry restriction was used during all the calculations. The optimized alkyl cationic species and coordination complexes were confirmed to be minima (no imaginary frequencies).

The selected bond lengths in optimized cationic Sc alkyl complex and its LUMO are shown in Figure S19. These bond lengths shown in Figure S19 (a) indicates that the tridentate coordination mode are retained in the cationic species and that there is agostic interaction between Sc and one CH_3 group (Si–CH_3 bond length of 1.92 Å). The LUMO (Figure S19 (b)) mainly contributed from Sc-3d_{xy} orbital indicates the accessible site beside the alkyl for the coordination of monomer. The optimized structures of isoprene–[PNPScCH$_2$SiMe$_3$]$^+$ π-complexes are shown in Figure S20 together with their complexation energies shown below the related structures. Attempts to locate a *trans*-1,4 coordination complex failed because of the sterics of the PNP^{Ph} ligand.

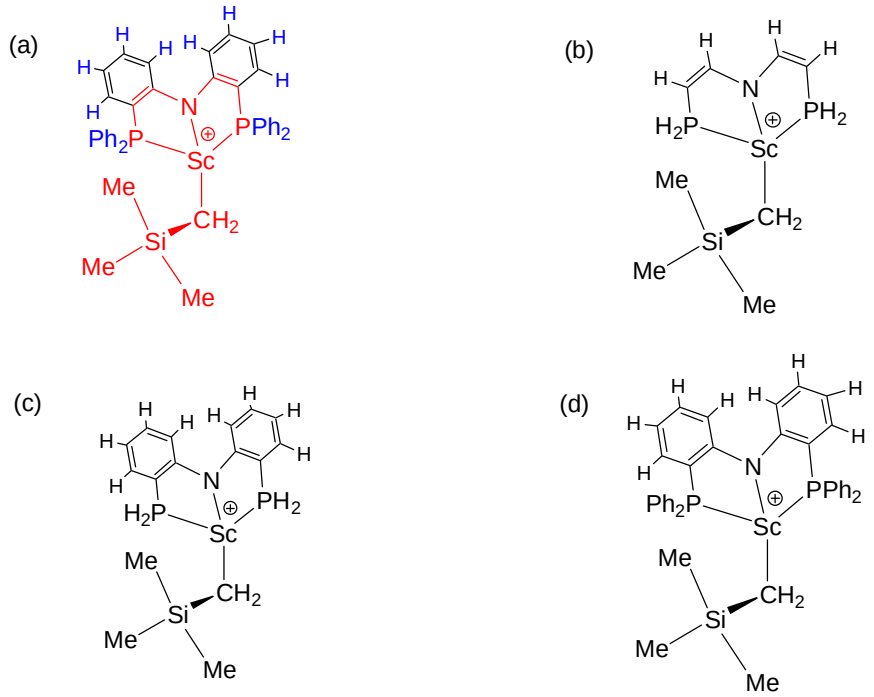

Figure S18. (a) The divisions of layers in Sc alkyl cationic species: red part for high layer, black-part for middle layer and the blue part for low layer; (b) model system; (c) middle system; (d) real system.

Figure S19. (a) Optimized cationic Sc alkyl species (bond length in Å). (b) LUMO of cationic Sc alkyl species.

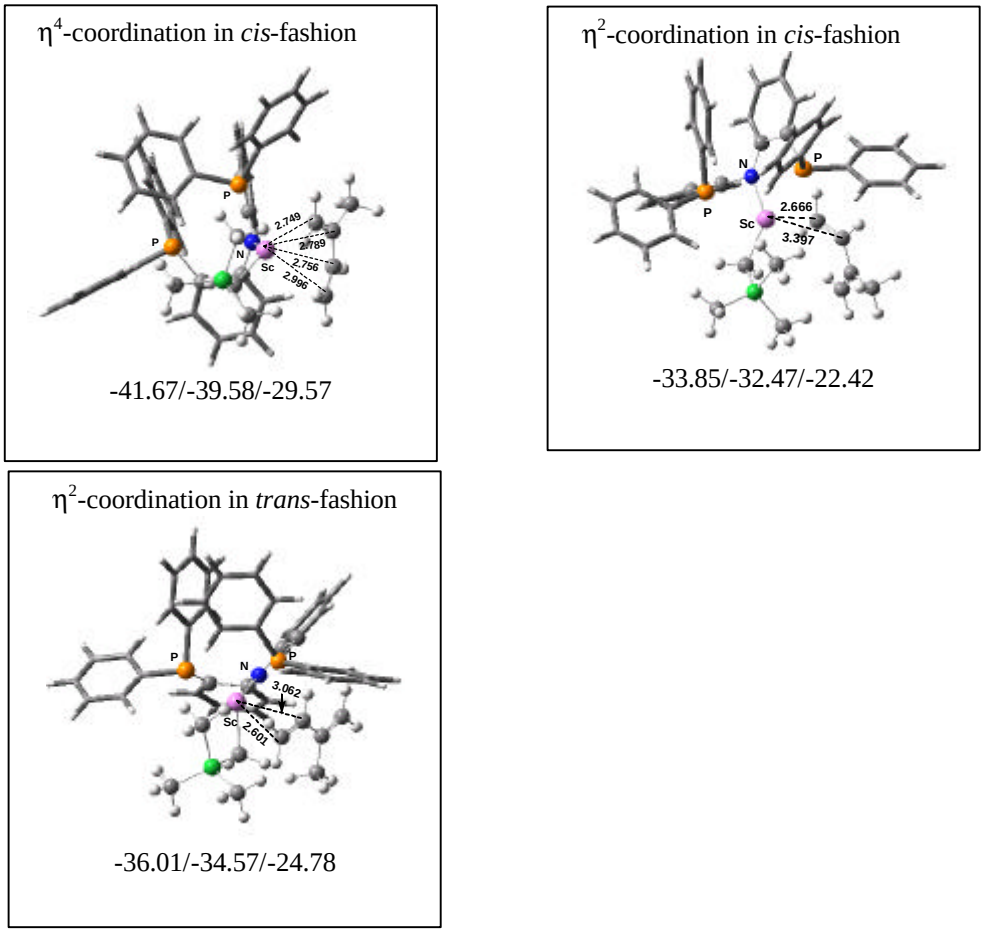

Figure S20. Isoprene–[PNPScCH$_2$SiMe$_3$]$^+$ π–complexes and their complexation energies (? E/? H/? G in kcal/mol) relative to separate reactants.

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Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03, Revision C.02*; Gaussian, Inc.: Pittsburgh, PA, 2004.

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