Supporting Information

Generation of cationic indenyl silylamide gadolinium and scandium complexes $[(Ind)Ln\{N(SiMe_3)_2\}]^+[B(C_6F_5)_4]^-$ and their reactivity for 1,3-butadiene polymerization

Olivier Tardif * and Kaita Shojiro

Elastomer Precision Polymerization Laboratory, RIKEN (The Institute of Physical and Chemical Research), Hirosawa 2-1, Wako, Saitama 351-0198, Japan

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Experimental Details

General Methods. All reactions were carried out under a dry and oxygen free argon atmosphere using Schlenk techniques and an Mbraun glove box. The argon was purified by being passed trough a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean CC-XR column (Nikka Seiko Co.). The nitrogen in the glove box was constantly circulated trough a copper/molecular sieves (4A) catalyst unit. The oxygen and moisture concentrations in the glove box atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 0.1 ppm. Samples for NMR spectroscopic measurements were prepared in the glove box by use of J. Young valve NMR tubes. ^1H, ^{13}C NMR spectra were recorded on a JNM-EX 270 (FT, 270 MHz for ^1H; 68.4 MHz for ^{13}C) spectrometer. NMR spectra of the gadolinium complexes **1**–**3**, and **7** were not informative because of the influence of the paramagnetic Gd(III) ions. IR spectra were recorded on a Shimadzu IRprestige-21 spectrometer using nujol mulls between KBr disks. 1,3-Butadiene (99%+, Takachiho Chemical Industrial Co.) was purified prior use by passing through a Dryclean column and a Gasclean GC-XR column (Nikka Seiko Co.). Elemental analyses were performed by Chemical Analysis Team, D & S Center, RIKEN. Solvents were dried using Mbraun Solvent Purification System. Anhydrous $GdCl_3$ and $ScCl_3$ were purchased from STREM.

Indene was obtained from Merck, 2-R-IndH (R = Me, Ph), and $K\{N(SiMe_3)_2\}$ were bought from Aldrich. $[PhNMe_2H][B(C_6F_5)_4]$, and $[Ph_3C][B(C_6F_5)_4]$ were purchased from Tosoh Finechem, and used without purification. 2-R-IndLi (R = H, Me) and 2-Ph-IndLi(THF) were prepared from the corresponding indene and nBuLi in hexane and THF, respectively. $[Et_3NH][BPh_4]$ was prepared according to literature (D. M., Amorose, R. A. Lee, J. L., Petersen, *Organometallics*, **1991**, *10*, 2191).

Typical procedure for polymerization of butadiene. In a glove box, toluene (18.5 mL) was added to $(2\text{-Ph-Ind})_2Gd\{N(SiMe_3)_2\}$ (21 mg, 3.0×10^{-5} mol) in a 30 mL glass pressure reactor, and $[Ph_3C][B(C_6F_5)_4]$ (28 mg, 3.0×10^{-5} mol) was added as solid to the solution. The solution mixture was stirred at room temperature for about 5 min, and *i*-Bu_3Al in toluene (0.4 mL, 0.3 M, 12×10^{-5} mol) was added, and the solution mixture was stirred at room temperature for 30 min. The reactor was moved out from the glove box, and placed in a cold bath at –40 ºC for 3 min, before adding butadiene (0.54 g, 1.0×10^{-2} mol). After addition of butadiene, the reactor was moved to a water bath and rapid stirring of the reaction mixture at 20 ºC was maintained for 15 min. The polymerization reaction was terminated by pouring the mixture into a large quantity of methanol containing a small amount of hydrochloric acid (ca. 0.5 M) and butylhydroxytoluene (BHT). The precipitated polymer was isolated after decantation, washed by methanol, and dried under reduced pressure at 60 ºC to constant weight.

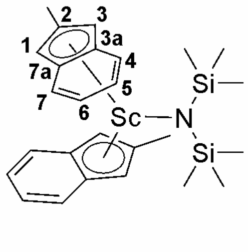
Polymer analysis. The microstructure of the polybutadiene was determined by IR spectroscopy (Shimadzu IRPrestige-21). Samples were prepared using 10 mg of polymer dissolved in 0.5 mL of CS_2 (S. Anzai, K. Irako, A. Onishi, J. Furukawa, Kyogo Kagaku Zasshi, 72, 1969, 2082). The weight-average molecular 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 gel permeation chromatography (GPC) [TOSOH HLC-8220 GPC; three columns of Super HZM-H; temperature, 40 ºC; eluent, THF;

flow rate, 0.35 mL/min; the columns were calibrated against 13 standard polystyrene samples (M_n = 5,480,000-500, $M_w/M_n < 1.15$)].

X-Ray Crystallographic Study.

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were sealed in thin-walled glass capillaries under a microscope in the glove box. Data collections were performed at 90 K on a Rigaku AFC-8 diffractometer with a Saturn 70 CCD area detector using confocal-mirror monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction was carried out using the program CrystalClear.[1] The structures were solved by using SHELXTL program.[2] Refinement for **2–7** was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

1) Rigaku/MSC Inc., (2005). CrystalClear SM ver. 1.3.36 Rigaku/MSC Inc., Texas, USA.
2) Sheldrick, G. M. *SHELXTL*, Version 6.1; Bruker AXS, Inc.; Madison, WI, 1999.



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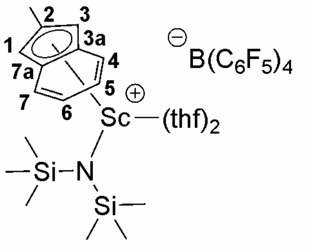

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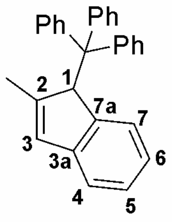


Sfigure 1. Nomenclature used for the NMR (^{1}H and ^{13}C) assignement of the indenyl ligand

Synthesis of (Ind)$_2$Gd{N(SiMe$_3$)$_2$} (1)

Anhydrous gadolinium chloride (0.791 g, 3 mmol) was suspended in 20 mL of THF. A THF solution (20 mL) of IndLi (0.745 g, 6.1 mmol) was slowly added, and the solution mixture was stirred at 65 °C for 14h. After removal of the solvent under reduce pressure, a toluene solution (20 mL) of K{N(SiMe$_3$)$_2$} (0.519 g, 2.6 mmol) was slowly added to the residue in 30 mL of toluene, and the solution mixture was stirred at room temperature for 16 h. Then the solvent was removed in vacuo, and the solid was filtered with hexane (60 mL). Upon concentration of the hexane solution under reduced pressure, a crystalline precipitate formed. This solid was isolated, dried under vacuum to give **1** as a yellow powder (0.729 g, 51% based on K{N(SiMe$_3$)$_2$}). (Found: C, 50.87; H, 5.52; N, 2.37. $C_{24}H_{32}Gd_1N_1Si_2$ requires C, 52.61; H, 5.89; N, 2.56%); ν_{max}(nujol)/cm^{-1} 2965(s), 2944(s), 2872(s) 2843(s), 1462(s), 1377(m), 1329(w), 1252(w), 1244(w), 1017(m), 866(w), 826(w), 768(m), 723(w), 600(w), 440(w).

Synthesis of (2-Me-Ind)$_2$Gd{N(SiMe$_3$)$_2$} (2)

Anhydrous gadolinium chloride (0.791 g, 3 mmol) was suspended in 20 mL of THF. A THF solution (20 mL) of (2-Me-Ind)Li (0.830 g, 6.1 mmol) was slowly added, and the solution mixture was stirred at 65 °C for 14h. After removal of the solvent under reduce pressure, a toluene solution (20 mL) of K{N(SiMe$_3$)$_2$} (0.519 g, 2.6 mmol) was slowly added to the residue in 30 mL of toluene, and the solution mixture was stirred at room temperature for 16 h. Then the solvent was removed in vacuo, and the solid was filtered with hexane (60 mL). After removal of the solvent under reduced pressure, the solid was filtered a second time with hexane (40 mL). Upon concentration of the hexane solution under reduced pressure, a crystalline precipitate formed. This solid was isolated, dried under vacuum to give **2** as a pale yellow powder (1.160 g, 78% based on K{N(SiMe$_3$)$_2$}). Single crystals suitable for X-ray analysis were grown in a concentrated solution of toluene at room temperature (Found: C, 52.68; H, 5.96; N, 2.15. $C_{26}H_{36}Gd_1N_1Si_2$ requires C, 54.22; H, 6.30; N, 2.43%); ν_{max}(nujol)/cm^{-1} 2953(s), 2922(vs), 2853(s), 1464(m), 1456(m), 1377(w), 1344(w), 1254(w), 1244(w), 1011(m), 868(w), 840(w), 826(w), 789(m), 741(w), 600(w), 440(w).

Synthesis of (2-Ph-Ind)$_2$Gd{N(SiMe$_3$)$_2$} (3)

Anhydrous gadolinium chloride (0.526 g, 2 mmol) was suspended in 20 mL of THF. A THF solution (20 mL) of (2-Ph-Ind)Li(THF) (1.081 g, 4.0 mmol) was slowly added, and the solution mixture was stirred at room temperature for 7 days. After removal of the solvent under reduced pressure, toluene (30 mL) was added to the residue and the suspension was treated with a toluene solution (20 mL) of K{N(SiMe$_3$)$_2$} (0.399 g, 2 mmol). After being stirred at room temperature for 16 h, the solvent was removed under reduced pressure, and the solid was filtered with hexane (100 mL). After evaporation of the hexane in vacuo, the residue was washed with a minimum of hexane, and was dried under vacuum. Recrystallization from a concentrated toluene solution gave bright yellow crystals of **3** (0.378 g, 27%). X-ray diffraction analysis was carried out on one of these crystals (Found: C, 61.09; H, 5.53; N, 1.81. $C_{36}H_{40}Gd_1N_1Si_2$ requires C, 61.76; H, 5.76; N, 2.00%).

Synthesis of (2-Me-Ind)$_2$Sc{N(SiMe$_3$)$_2$} (4)

Anhydrous scandium chloride (0.454 g, 3.0 mmol) was suspended in 30 mL of THF. A THF solution (20 mL) of (2-Me-Ind)Li (0.831 g, 6.1 mmol) was slowly added, and the solution mixture was stirred at room temperature for 16 h. After removal of the solvent under reduce pressure, a toluene solution (20 mL) of K{N(SiMe$_3$)$_2$} (0.559 g, 2.8 mmol) was added to the residue in toluene (30 mL), and the mixture was stirred at 60 ºC for 16 h. The solvent was removed in vacuo, and the solid was filtered with hexane (60 mL). The filtrate was concentrated under reduced pressure, and stored at −30 ºC to yield **4** as a yellow crystalline solid (0.987 mg, 76% based on K{N(SiMe$_3$)$_2$}). Single crystals suitable for X-ray analysis were grown in a concentrated solution of toluene at room temperature (Found: C, 66.64; H, 7.80; N, 2.83. $C_{26}H_{36}Sc_1N_1Si_2$ requires C, 67.35; H, 7.83; N, 3.02%); ^{1}H NMR (toluene-d$_8$, 22 ºC): δ −0.03 (18H, s, N(SiMe$_3$)$_2$), 2.26 (6H, s, Me), 5.55 (4H, s, H$_{1,3}$), 6.89 (4H, m, H$_{4,7}$ or H$_{5,6}$), 7.25 (4H, m, H$_{4,7}$ or H$_{5,6}$). ^{1}H NMR (THF-d$_8$, 22 ºC): δ −0.08 (18H, s, N(SiMe$_3$)$_2$), 2.40 (6H, s, Me), 5.70 (4H, s, H$_{1,3}$), 7.02 (4H, m, H$_{4,7}$ or H$_{5,6}$), 7.36 (4H, m, H$_{4,7}$ or H$_{5,6}$). ^{13}C NMR (toluene-d$_8$, 22 ºC): δ 4.1 (6C, s, N(SiMe$_3$)$_2$), 16.6 (2C, s, Me), 103.8 (4C, s, C$_{1,3}$), 122.3 (4C, s, C$_{4,7}$ or C$_{5,6}$), 123.4 (4C, s, C$_{4,7}$ or C$_{5,6}$), 129.1 (2C, s, C$_2$), 135.4 (4C, s, C$_{3a,7a}$). ^{13}C NMR (THF-d$_8$, 22 ºC): δ 4.4 (6C, s, N(SiMe$_3$)$_2$), 17.0 (2C, s, Me), 104.4 (4C, s, C$_{1,3}$), 122.9 (4C, s, C$_{4,7}$ or C$_{5,6}$), 124.1 (4C, s, C$_{4,7}$ or C$_{5,6}$), 129.8 (2C, s, C$_2$), 136.0 (4C, s, C$_{3a,7a}$). ν_{max}(nujol)/cm^{-1} 3067 (s), 2963 (s), 2943(s), 2895 (s), 1464 (s), 1377 (m), 1342 (w), 1258(w), 1244(w), 980(m), 866(m), 844(w), 814(m), 795 (m), 780(w), 741(w), 723(w), 670(w), 620(w), 610(w), 451(w).

Synthesis of [(2-Me-Ind)Sc{N(SiMe$_3$)$_2$}(PhNMe$_2$)]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (5)

Solid [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (0.259 g, 0.323 mmol) was added in small portions to a toluene solution (5 mL) of **4** (0.150 g, 0.323 mmol) under agitation, and the solution mixture was stirred at room temperature. After 45 min, the solvent was removed under vacuum to yield an oily product. The oil was layered with a small amount of hexane, and within few days, yellow crystalline solid had precipitated. X-ray diffraction analysis was carried out on one of these crystals. The solid was washed with hexane to give **5** (317 mg, 87 %) as a pale powder (Found: C, 50.74; H, 3.26; N, 2.27.

$C_{48}H_{38}Sc_1B_1F_{20}N_2Si_2$ requires C, 50.87; H, 3.38; N, 2.47%); ^{1}H NMR (C_6D_5Cl/Me_4Si, 22 ºC): δ –0.14 (18H, s, $N(SiMe_3)_2$), 1.95 (3H, s, Me), 2.26 (6H, s, NMe_2), 5.88 (2H, s, $H_{1,3}$), 6.66 (2H, m, aryl), 6.95 (2H, m, $H_{4,7}$ or $H_{5,6}$), 7.08 (2H, m, $H_{4,7}$ or $H_{5,6}$), 7.23 (1H, m, aryl), 7.34 (2H, m, aryl); ^{13}C NMR (C_6D_5Cl/Me_4Si, 22 ºC): δ 2.8 (6C, s, $N(SiMe_3)_2$), 16.3 (1C, s, Me), 47.4 (2C, s, NMe_2), 106.5, 118.1, 123.8, 125.2, 130.3, 130.6, 134.2, 134.7 (*aryl* and *Indenyl*), 136.9 (8C, br d, J_{C-F} = 246.6 Hz, *m*–C_6F_5), 137.8 (8C, br d, J_{C-F} = 245.4 Hz, *p*–C_6F_5), 142.0, 142.7(*aryl* and *Indenyl*), 149.0 (8C, br d, J_{C-F} = 241.7 Hz, *o*–C_6F_5); ^{1}H NMR (THF-d_8, 22 ºC): δ 0.27 (18H, s, $N(SiMe_3)_2$), 2.64 (3H, s, Me), 2.90 (6H, s, NMe_2), 6.60 (1H, m, aryl), 6.62 (2H, s, $H_{1,3}$), 6.69 (2H, m, aryl), 7.11 (2H, m, aryl), 7.25 (2H, m, $H_{4,7}$ or $H_{5,6}$), 7.75 (2H, m, $H_{4,7}$ or $H_{5,6}$) (The ^{1}H NMR spectrum of **5** in THF-d_8 displays an equimolar mixture of **6**-[d_8] and free $PhNMe_2$).

Synthesis of [(2-Me-Ind)Sc{N(SiMe₃)₂}(THF)₂]⁺[B(C₆F₅)₄]⁻ (6) and [(2-Me-Ind)Sc{N(SiMe₃)₂}(THF)₁.₂₅]⁺[B(C₆F₅)₄]⁻ (6')

[$PhNMe_2H$][$B(C_6F_5)_4$] (0.259 g, 0.323 mmol) in THF (5 mL) was added dropwise to a THF solution (5 mL) of **4** (0.150 g, 0.323 mmol) to give a pale yellow solution. After stirring the solution mixture at room temperature for 45 min, the solvent was removed under vacuum. The residue was washed with hexane and dried under reduced pressure several times to give a pale pink powder. The solid was dissolved in THF, and layered with hexane to precipitate colorless crystals of **6**. X-ray diffraction analysis was carried out on one of these crystals. After the solvent was decanted, the crystals were isolated, washed with hexane and dried under vacuum to give $[(2\text{-Me-Ind})Sc\{N(SiMe_3)_2\}(THF)_{1.25}]^+[B(C_6F_5)_4]^-$ (**6'**) (270 mg, 76%) as a white powder (The partial loss of THF in **6** to give **6'** under vacuum was confirmed by ^{1}H NMR spectroscopy in C_5D_5N) (Found: C, 49.85; H, 3.79; N, 1.26. $C_{44}H_{35}Sc_1B_1F_{20}N_1O_1Si_2$ requires C, 48.68; H, 3.25; N, 1.29%; $C_{48}H_{43}Sc_1B_1F_{20}N_1O_2Si_2$ requires C, 49.80; H, 3.74; N, 1.21%); ^{1}H NMR (THF-d_8, 22 ºC): δ 0.27 (18H, s,

$N(SiMe_3)_2$), 2.64 (3H, s, Me), 6.62 (2H, s, $H_{1,3}$), 7.25 (2H, m, $H_{4,7}$ or $H_{5,6}$), 7.75 (2H, m, $H_{4,7}$ or $H_{5,6}$). ^{1}H NMR (C_5D_5N, 22 ºC): δ 0.18 (18H, s, $N(SiMe_3)_2$), 1.60 (5H, m, THF), 2.59 (3H, s, Me), 3.64 (5H, m, THF), 6.87 (2H, s, $H_{1,3}$), 7.21 (2H, m, $H_{4,7}$ or $H_{5,6}$, partially hidden by pyridine signal), 7.84 (2H, m, $H_{4,7}$ or $H_{5,6}$). ^{13}C NMR (THF-d_8, 22 ºC): δ 4.7 (6C, s, $N(SiMe_3)_2$), 17.7 (1C, s, Me), 107.1 (2C, s, $C_{1,3}$), 123.6 (2C, s, $C_{4,7}$ or $C_{5,6}$), 125.1 (2C, s, $C_{4,7}$ or $C_{5,6}$), 131.3 (1C, s, C_2), 137.0 (8C, br d, $J_{C–F}$ = 242.9 Hz, *m*–C_6F_5), 139.0 (4C, br d, $J_{C–F}$ = 245.6 Hz, *p*–C_6F_5), 141.6 (2C, s, $C_{3a,7a}$), 149.0 (8C, br d, $J_{C–F}$ = 241.9 Hz, *o*–C_6F_5) (Signals arising from *ipso*–C_6F_5 carbons were not observed). ^{13}C NMR (C_5D_5N, 22 ºC): δ 5.0 (6C, s, $N(SiMe_3)_2$), 17.7 (1C, s, Me), 26.1 (s, THF), 68.0 (s, THF), 107.2 (2C, s, $C_{1,3}$), 124.8 (2C, s, $C_{4,7}$ or $C_{5,6}$, other signal for $C_{4,7}$ or $C_{5,6}$ is hidden by C_5D_5N ca. 124 ppm), 131.1 (1C, s, C_2), 136.9 (br d partially hidden by pyridine signal, $J_{C–F}$ = 242.9 Hz, 8C, *m*–C_6F_5), 138.9 (4C, br d, $J_{C–F}$ = 242.9 Hz, *p*–C_6F_5), 141.7 (2C, s, $C_{3a,7a}$), 149.0 (8C, br d, $J_{C–F}$ = 241.9 Hz, *o*–C_6F_5) (Signals arising from *ipso*–C_6F_5 carbon were not observed).

Synthesis of $[(2\text{-Me-Ind})Gd\{N(SiMe_3)_2\}(THF)_3]^+[B(C_6F_5)_4]^-$ (7)

A THF solution of $[HNEt_3][B(C_6H_5)_4]$ (0.110 g, 0.260 mmol) was added to a THF solution (5 mL) of **2** (0.150 g, 0.260 mmol), and the solution mixture was stirred 16 h at room temperature. Volatiles were removed in vacuum, and the residue was washed with hexane several times to give an oily product. Layering hexane above a concentrated THF solution of the oil gave colorless crystals of **7**. X-ray diffraction was carried out on one of these crystals. After removal of the solvent, the crystals were dried up under vacuum to give **7** (0.150 g, 59 %) as a white crystalline powder. (Found C, 61.36; H, 7.06; N, 1.42. $C_{44}H_{55}Gd_1B_1N_1O_1Si_2$ requires C, 63.05; H, 6.61; N, 1.67%; $C_{48}H_{63}Gd_1B_1N_1O_2Si_2$ requires C, 63.34; H, 6.98; N, 1.54%; $C_{52}H_{71}Gd_1B_1N_1O_3Si_2$ requires C, 63.58; H, 7.28; N, 1.43%).

NMR scale reaction of $(2\text{-Me-Ind})_2Sc\{N(SiMe_3)_2\}$ with $[PhNMe_2H][B(C_6F_5)_4]$ in THF-d_8; Generation of $[(2\text{-Me-Ind})Sc\{N(SiMe_3)_2\}(thf\text{-}d_8)_2]^+[B(C_6F_5)_4]^-$ (6-[d$_8$]). To a THF-d_8 solution (ca. 0.5 mL) of **4** (0.015 g, 32 μmol) under stirring, was added solid $[PhNMe_2H][B(C_6F_5)_4]$ (0.025 g, 31 μmol) by small portions. The solution mixture was transferred in a Teflon-valved NMR tube, and ^1H NMR spectrum was recorded at 22 ºC. After 45 min, clean and quantitative conversion of **4** to **6-[d$_8$]** was observed together with the releases of free *N*,*N*-dimethylaniline $PhNMe_2$ and free 2-Me-IndH. The NMR data for the in situ generated cationic species were identical to those obtained for the isolated cation **6** in THF-d_8.

NMR scale reaction of (2-Me-Ind)$_2$Sc{N(SiMe$_3$)$_2$} with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in THF-d$_8$; Generation of [(2-Me-Ind)Sc{N(SiMe$_3$)$_2$}(thf-d$_8$)$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (6-[d$_8$]). To a THF-d_8 solution (ca. 0.5mL) of **4** (0.015 g, 32 μmol) under stirring, was added solid $[Ph_3C][B(C_6F_5)_4]$ (0.029 g, 31 μmol) by small portions. The solution mixture was transferred in a Teflon-valved NMR tube, and ^1H NMR spectrum was recorded at 22 ºC After 45 min, clean conversion of **4** to **6-[d$_8$]** was observed. The spectrum also contains resonances that were identified as those of 1-trityl-2-methylindene (1-Ph_3C-2-Me-Ind). Other not identified isomers are likely formed as shown by the presence of another series of resonances with more complicated splitting patterns.

^{1}H NMR data for (1-Ph$_3$C-2-Me-Ind)

The indene formed in the reaction of **4** with $[Ph_3C][B(C_6F_5)_4]$ was isolated as a toluene soluble white solid, and identified as 1-Ph_3C-2-Me-Ind, based on the ^1H NMR data. 1-Ph_3C-2-Me-Ind is also formed in the reaction of (2-Ph-Ind)Li(THF) with $[Ph_3C][B(C_6F_5)_4]$ in THF-d_8 as shown by NMR.

(Found: C, 93.46; H, 6.54. $C_{29}H_{24}$ requires C, 93.51; H, 6.49%); ^1H NMR (THF-d_8, 22°C): δ 1.77 (3H, s, Me), 5.32 (1H, s, H_1), 6.14 (1H, s, H_3), 6.68 (1H, m, $H_{4\text{-}7}$), 6.83 (2H, m, $H_{4\text{-}7}$), 6.93 (1H, m, $H_{4\text{-}7}$), 7.00–7.15 (9H, m, Ph_3C), 7.40 (6H, br s, Ph_3C). ^1H NMR (toluene-d_8, 22°C): δ 1.72 (3H, s, Me), 4.76 (1H, s, H_1), 6.05 (1H, s, H_3), 6.70–7.10 (13H, m, Ph_3C (9H) and $H_{4\text{-}7}$ (4H) overlap with toluene-d_8 aromatic signals), 7.32 (6H, br s, Ph_3C).

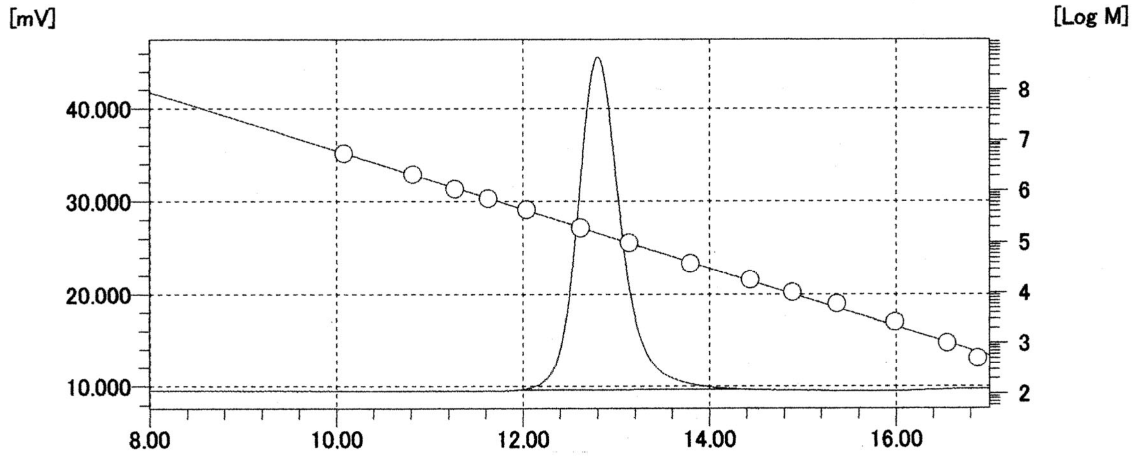


chart B

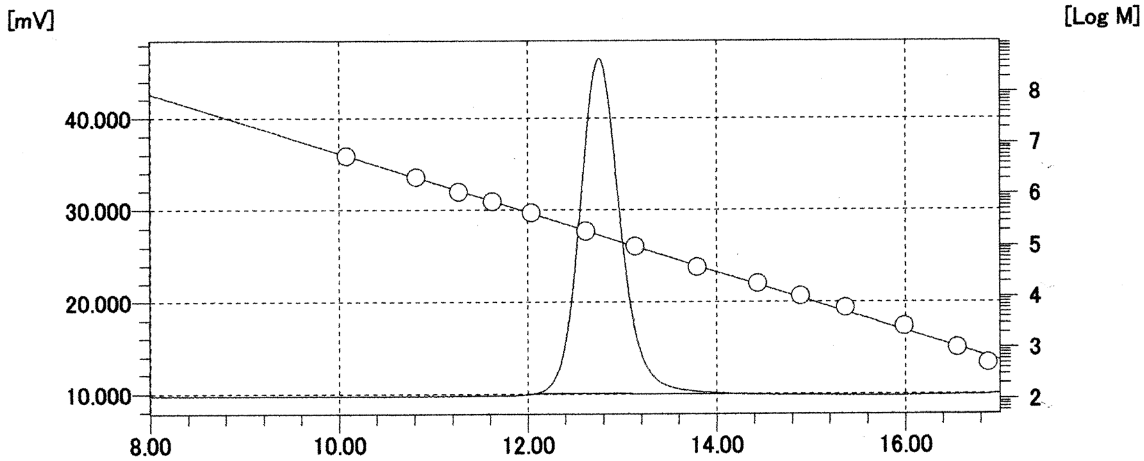
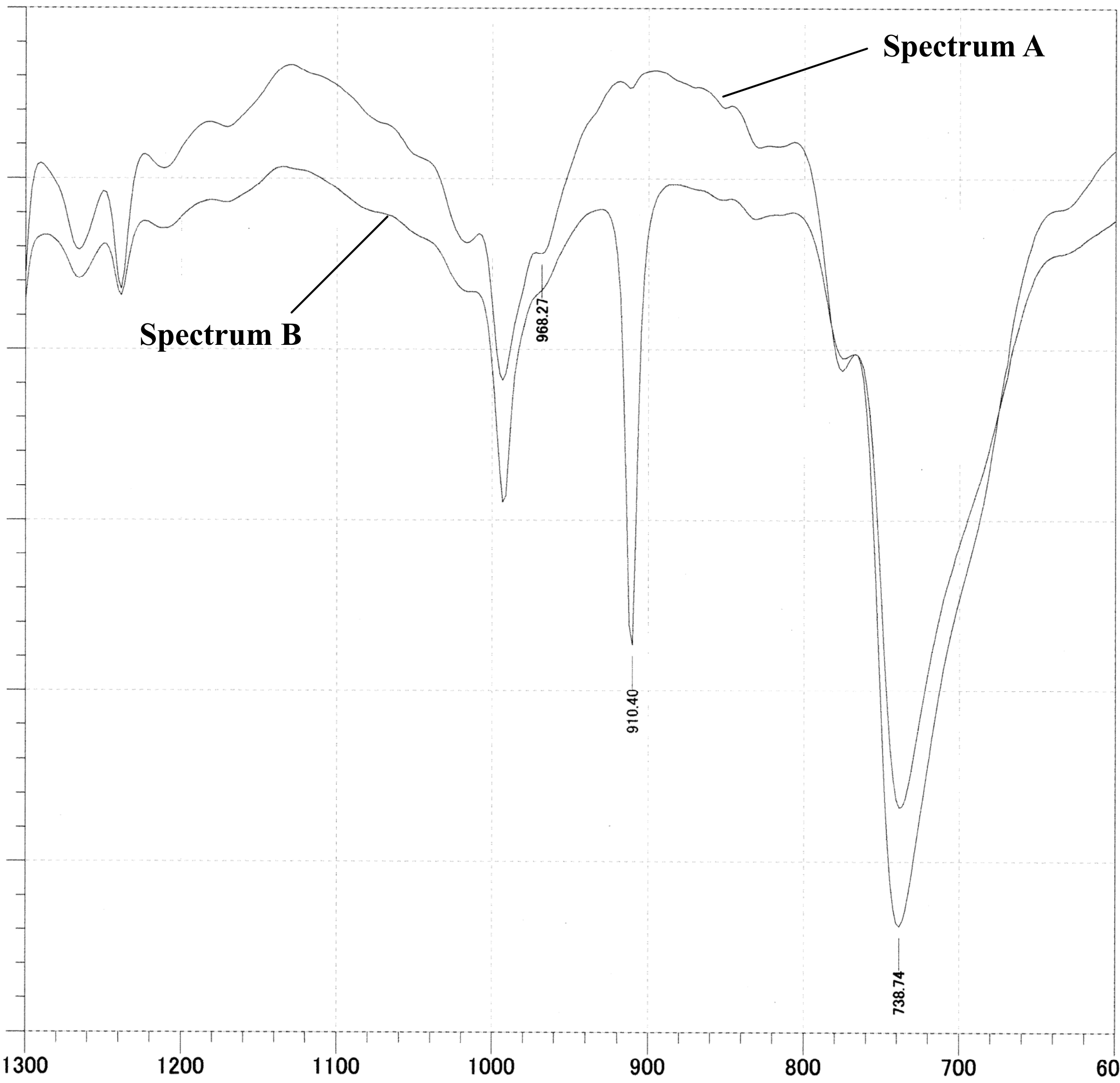
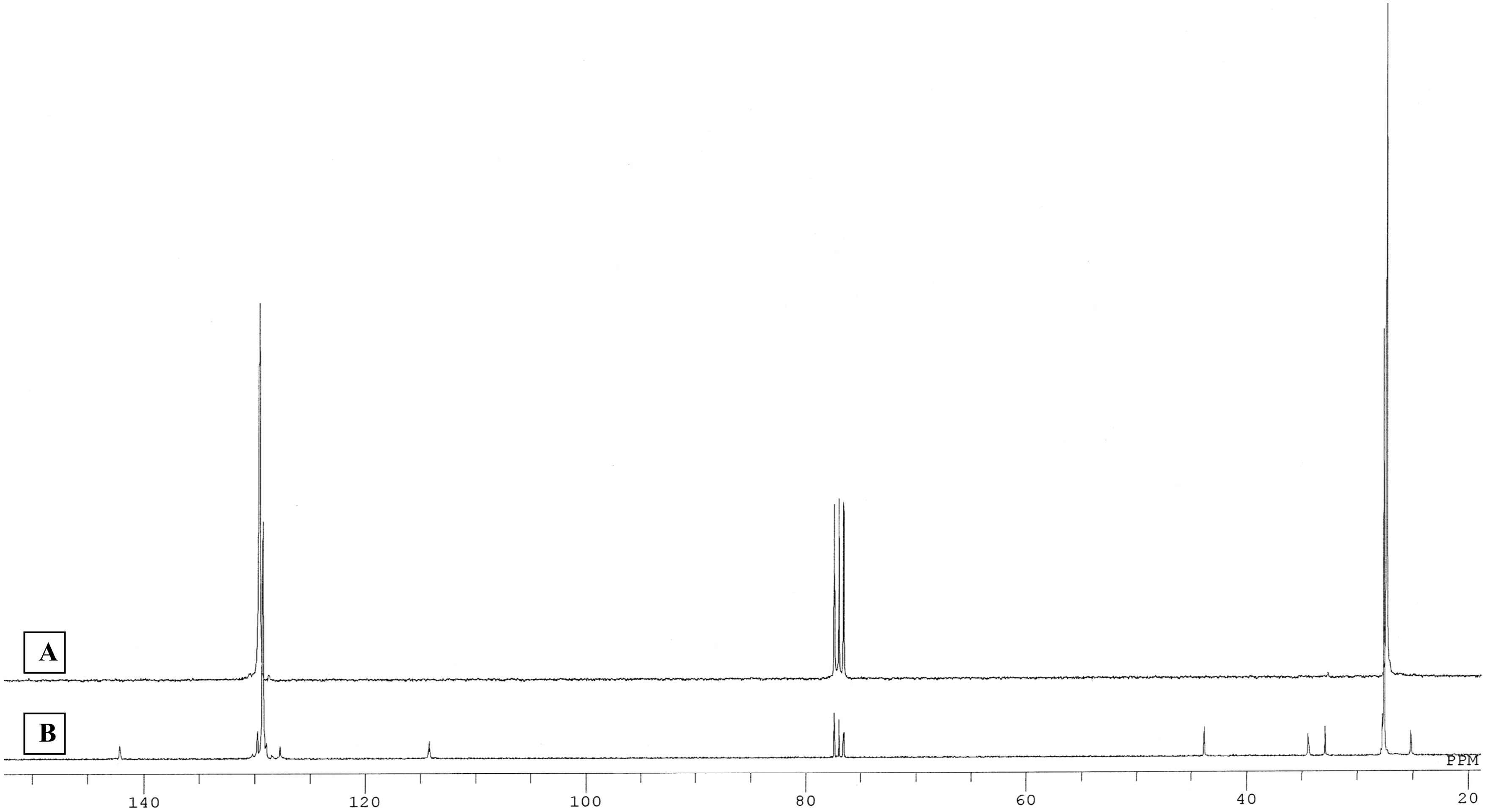


chart A

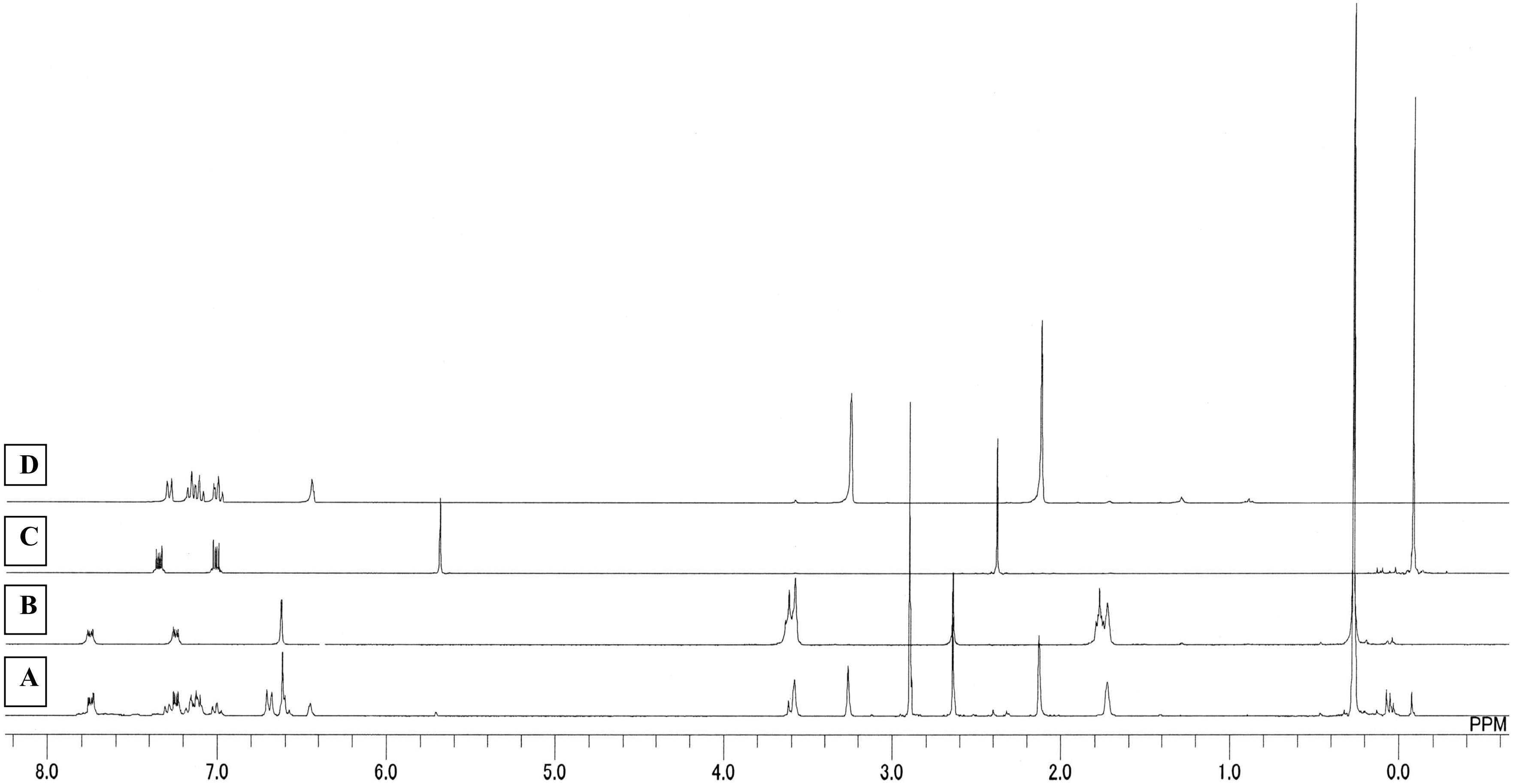
Sfigure 2. GPC charts of polybutadiene products (**chart A**: Table 1, run8; c**hart B**: Table 1, run 9)



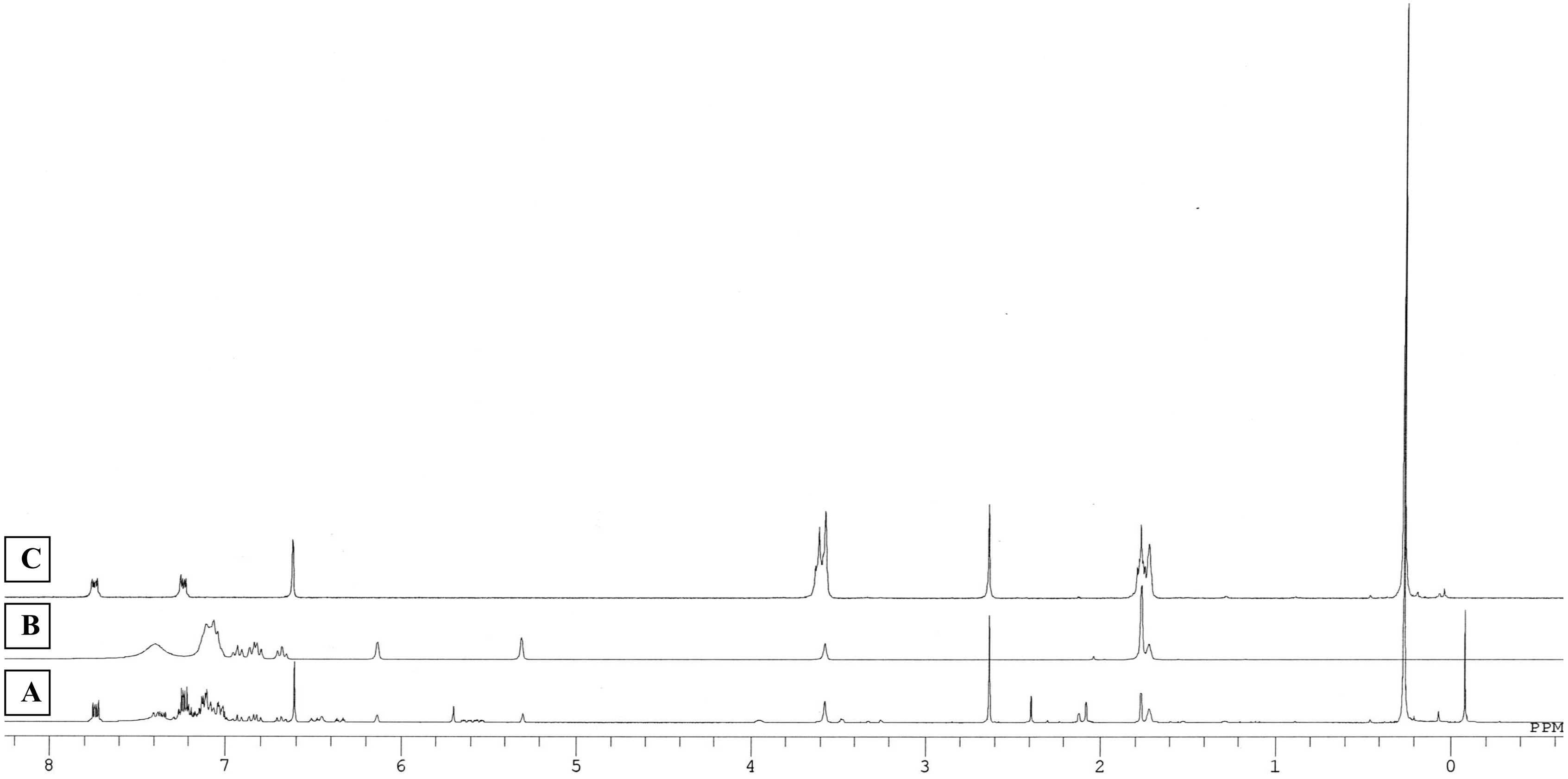
Sfigure 3. Superimposed IR spectra of polybutadiene products in CS_2 (**A**: 1,4-*cis* > 99%, Table 1, run 8; **B**: 1,4-*cis* = 87.6%, Table 1, run 10)



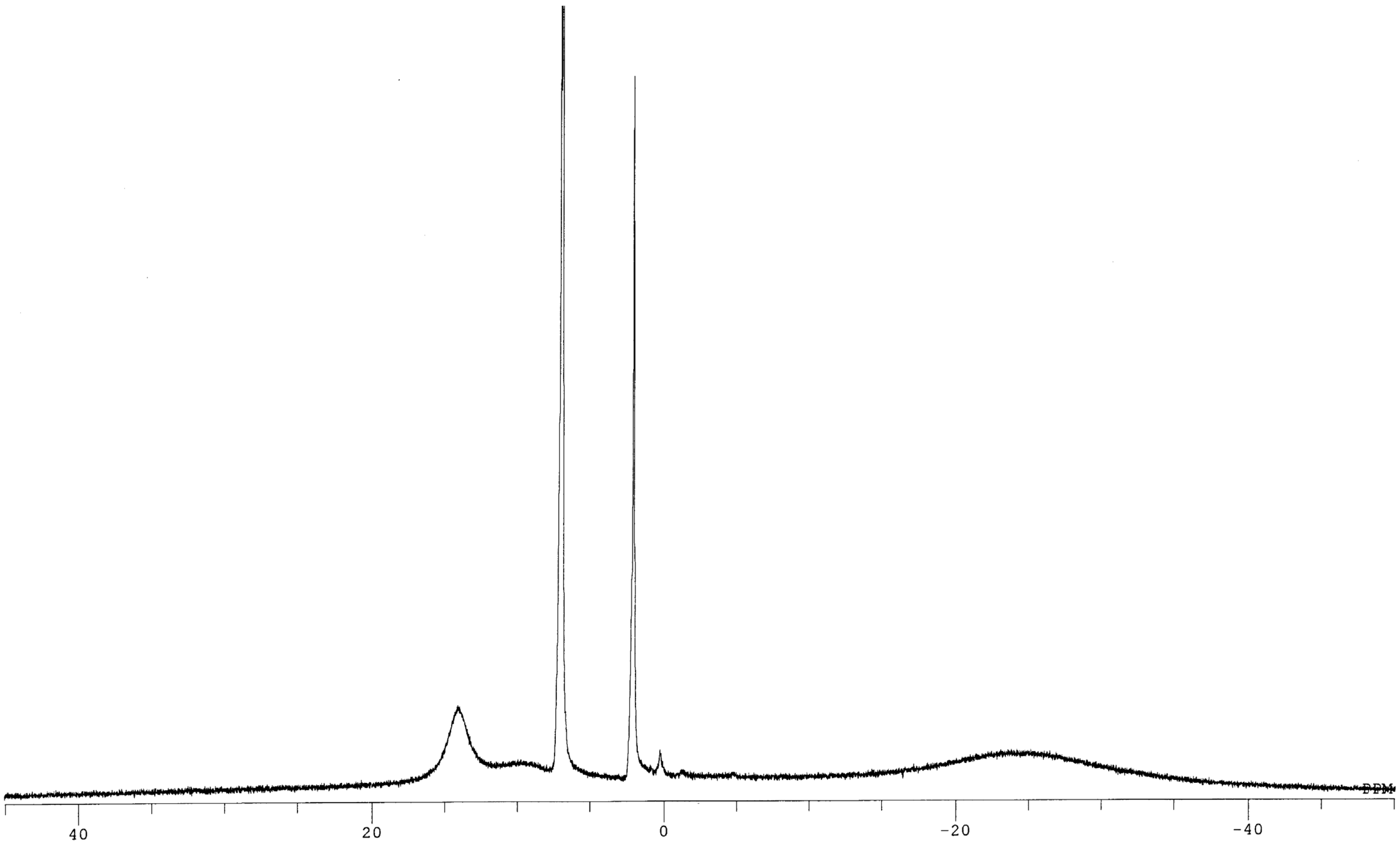
Sfigure 4. ^{13}C NMR spectra in $CDCl_3$ of polybutadienes (**A**: 1,4-*cis* > 99%, Table 1, run 8; **B**: 1,4-*cis* = 87.6%, Table 1, run 10)



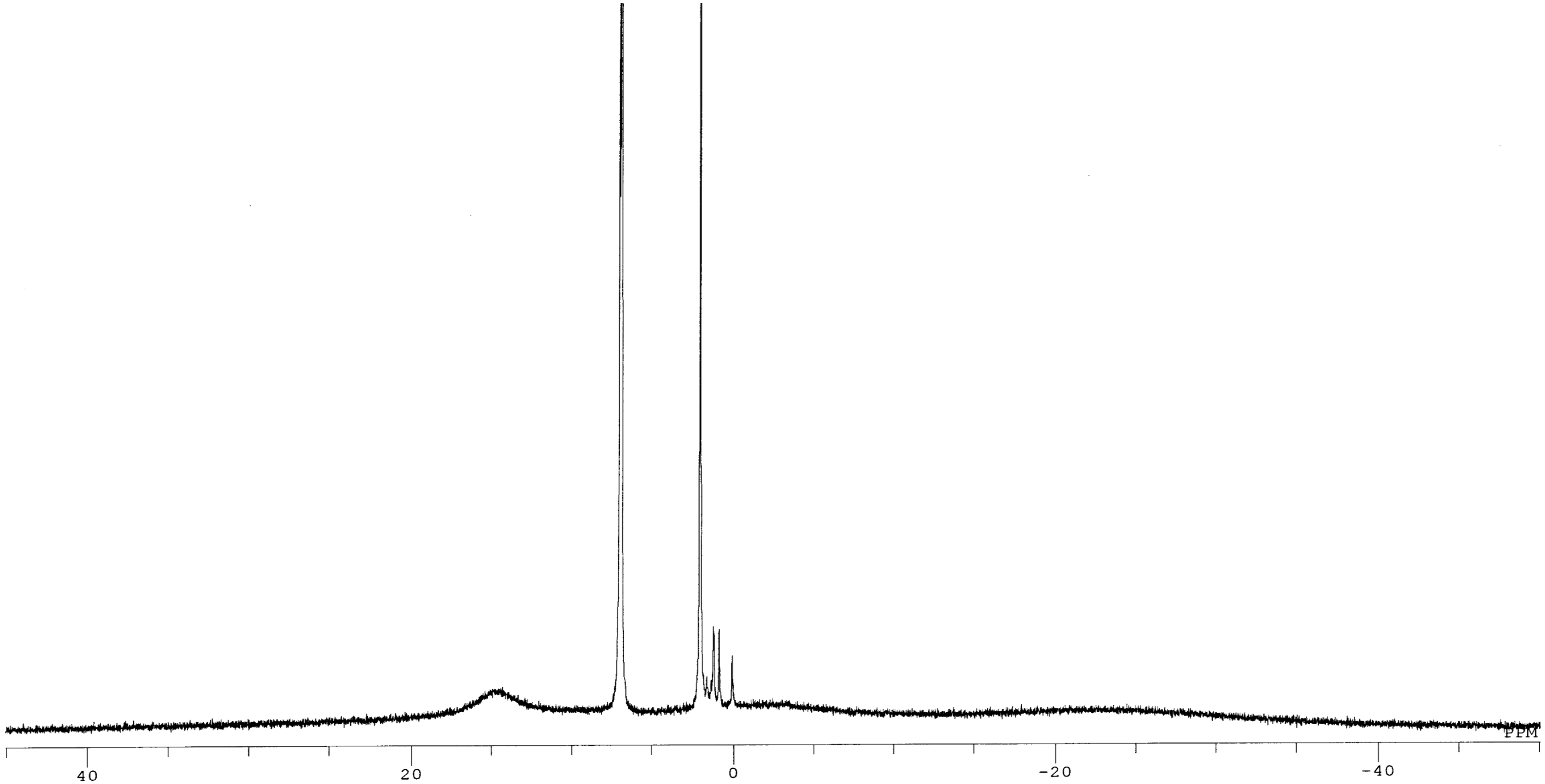
Sfigure 5. Monitoring the reaction of (2-Me-Ind)$_2$ScN{(SiMe$_3$)$_2$} (**4**) and [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] by ^{1}H NMR spectroscopy in THF-*d*$_8$: (**A**) in situ reaction of **4** with [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] after 45 min; (**B**) isolated cation complex **6**; (**C**) neutral complex **4**; (**D**) 2-Me-IndH.



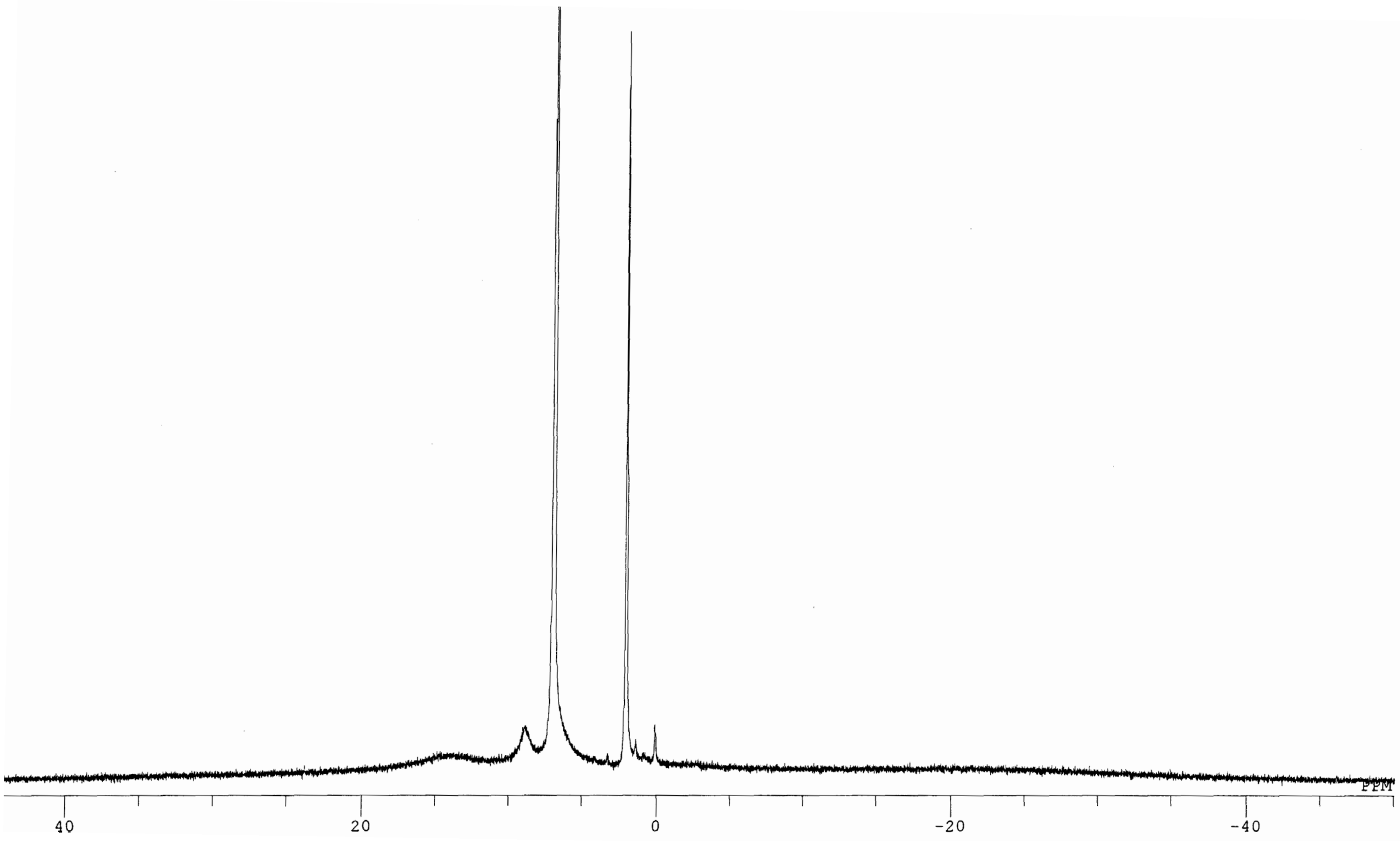
Sfigure 6. Monitoring the reaction of (2-Me-Ind)$_2$ScN{(SiMe$_3$)$_2$} (**4**) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] by ^{1}H NMR spectroscopy in THF-*d*$_8$: (**A**) in situ reaction of **4** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] after 45 min (a small excess of **4** was used); (**B**) isolated indene 1-Ph$_3$C-2-Me-Ind ; (**C**) isolated cation complex **6**



Sfigure 7. ^{1}H NMR spectrum of $(Ind)_2Gd\{N(SiMe_3)_2\}$ (**1**) in toluene-d_8 at 22 ºC



Sfigure 8. ^{1}H NMR spectrum of $(2\text{-Me-Ind})_2\text{Gd}\{\text{N}(\text{SiMe}_3)_2\}$ (**2**) in toluene-d_8 at 22 ºC



Sfigure 9. ^{1}H NMR spectrum of (2-Ph-Ind)$_2$Gd{N(SiMe$_3$)$_2$} (**3**) in toluene-d$_8$ at 22 ºC