

## Cationic scandium aminobenzyl complexes. synthesis, structure, and unprecedented catalysis of copolymerization of 1-hexene and dicyclopentadiene

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### Experimental Section:

**General Methods.** All manipulations of air and moisture-sensitive compounds were performed under an argon atmosphere by use of standard Schlenk techniques or nitrogen atmosphere in an Mbraun glovebox. Argon (Takachiho Chemical Industrial Co., Ltd.) was purified by being passed through a Dryclean column (4 A molecular sieves, Nikka Seiko Co.) and a Gasclean CC-XR column (Nikka Seiko Co.). Anhydrous THF, hexane, benzene, and toluene were purified by use of a SPS-800 solvent purification system (Mbraun), and dried over fresh Na chips in the glovebox. Dicyclopentadiene (DCPD) was purchased from Aldrich, dried over sodium, vacuum-transferred, and degassed by two freeze-pump-thaw cycles. 1-Hexene was purchased from TCI, dried over sodium, vacuum-transferred, and degassed by two freeze-pump-thaw cycles.  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ , and  $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$  were purchased from Tosoh Finechem Corporation and used without purification.  $\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  and  $\text{LiCH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o$  were prepared according to literature methods.<sup>1</sup>  $\text{C}_5\text{Me}_4\text{H}(\text{SiMe}_3)$ ,  $\text{C}_5\text{Me}_5\text{H}$ , and  $\text{C}_5\text{Me}_4\text{H}_2$  were purchased from Aldrich, and used as received. Deuterated solvents chlorobenzene- $d_5$  (99 atom% D) and benzene- $d_6$  (99.6 atom% D), and chloroform- $d_1$  (99.8 atom% D) were obtained from Cambridge Isotope.

Samples of rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes (Wilmad 528-JY). NMR ( $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{19}\text{F}$ ,  $^{29}\text{Si}$ ) spectra were recorded on a JNM-EX 400 (FT, 400 Hz) or a JNM-Alpha 600 spectrometer. Elemental analyses were performed on a MICRO CORDER JM10 apparatus (J-SCIENCE LAB Co.). The NMR data of copolymers were obtained on a JEOL JNM-EX 270 (FT, 300 MHz for  $^1\text{H}$ ; 75.5 MHz for  $^{13}\text{C}\{^1\text{H}\}$ ) spectrometer at 50 °C with chloroform- $d_1$  as solvent. The molecular weight and the molecular weight distribution of the polymer samples were determined at 40 °C by gel permeation chromatography on a TOSOH HLC-8220 GPC. THF was employed as an eluent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). The DSC measurements were performed on a Perkin-Elmer Pyris Diamond Differential Scanning Calorimeter at a rate of 20 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 350 °C, cooling to -100 °C, and then recording the second DSC scan.

**$\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$ .** Anhydrous scandium chloride (4.539 g, 30 mmol) was suspended in 20 mL of THF. A THF solution (40 mL) of  $\text{LiCH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o$  (12.702 g, 90 mmol) was slowly added at room temperature. After being stirred for 30 min, the solvent was removed under reduced pressure. The residue was dissolved in 80 mL of toluene and filtered to remove the lithium salt. The filtrate was concentrated and cooled down to -30 °C to give  $\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  as yellow cubic crystals (10.447 g, 78%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 22 °C): 1.64 (s, 6H,  $\text{CH}_2$ ), 2.27 (s, 18H,  $\text{NMe}_2$ ), 6.76–6.79 (m, 6H, aryl), 6.39–7.00 (m, 6H, aryl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 22 °C): 45.6 ( $\text{NMe}_2$ ), 48.9 ( $\text{CH}_2$ ), 118.3, 120.3, 127.0, 129.7, 143.4, 143.7 (aromatics).

**$(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2$  (**1a**).** In a glovebox, a THF solution (10 mL) of  $\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (1.543 g, 3.448 mmol) was added to a THF solution (5 mL) of  $\text{C}_5\text{Me}_4\text{H}(\text{SiMe}_3)$  (670 mg, 3.448 mmol) in a Schlenk tube with a Teflon cock. This tube was taken outside and was heated at 70 °C for 12 h. The solvent was removed under reduced pressure. The residue was washed with ether and dissolved in toluene. The solution was concentrated and was cooled down to -30 °C to give yellow prism crystals of **1a** (1.450 g, 83% yield). Recrystallization from a benzene solution gave single crystals suitable for X-ray analysis.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C): 0.36 (s, 9H,  $\text{SiMe}_3$ ), 1.54 (s, 4H,  $\text{CH}_2$ ), 1.72 (s, 6H,  $\text{C}_5\text{Me}_4$ ), 1.79 (s, 6H,  $\text{C}_5\text{Me}_4$ ), 2.37 (s, 12H,  $\text{NMe}_2$ ), 6.74 (d,  $J = 7.3$  Hz, 2H, aryl), 6.81 (t,  $J = 7.4$  Hz, 2H, aryl), 7.02 (t,  $J = 7.4$  Hz, 2H, aryl), 7.13 (d,  $J = 7.3$  Hz, 2H, aryl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C): 3.1 ( $\text{SiMe}_3$ ), 12.2, 14.9 ( $\text{C}_5\text{Me}_4$ ), 46.5 (br,  $\text{NMe}_2$ ), 47.4 ( $\text{CH}_2$ ), 116.2, 117.1, 121.1, 125.0, 126.5, 128.6, 130.7, 145.6, 147.9 (aromatics and Cp ring carbons). Anal. Calcd. for  $\text{C}_{30}\text{H}_{45}\text{SiScN}_2$ : C 71.11; H 8.95; N 5.53. Found: C 71.34; H 8.82; N 5.23.

**$(\text{C}_5\text{Me}_5)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2$  (**1b**).** In a glovebox, a THF solution (10 mL) of  $\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$  (1.543 g, 3.448 mmol) was added to a THF solution (5 mL) of  $\text{C}_5\text{Me}_5\text{H}$  (470 mg, 3.448 mmol) in a Schlenk tube with Teflon cock. This tube was taken outside and was heated at 70 °C for 12 h. The solvent was removed under reduced pressure. The residue was washed with ether and dissolved in toluene. The solution was concentrated and was cooled down to -30 °C to give yellow prism crystals of **1b** (1.280 g, 83% yield). Recrystallization from a benzene solution gave single crystals suitable for X-ray analysis.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 60 °C): 1.47 (s, 4H,  $\text{CH}_2$ ), 1.73 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 2.35 (s, 12H,  $\text{NMe}_2$ ), 6.71–6.83 (m, 4H, aryl), 6.99 (t,  $J = 7.4$  Hz, 2H, aryl), 7.13 (d,  $J = 7.3$  Hz, 2H, aryl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 60 °C): 11.8 (CpMe), 45.5 (br,  $\text{NMe}_2$ ), 47.3 ( $\text{CH}_2$ ), 117.1,

119.6, 120.9, 126.5, 130.7, 145.7, 147.7 (aromatics and Cp ring carbons). Anal. Calcd. for C<sub>28</sub>H<sub>39</sub>ScN<sub>2</sub>: C 74.97; H 8.76; N 6.24. Found: C 74.89; H 8.67; N 6.19.

(C<sub>5</sub>Me<sub>4</sub>H)Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)<sub>2</sub> (**1c**). In a glovebox, a THF solution (10 mL) of Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)<sub>3</sub> (447 mg, 1.000 mmol) was added to a THF solution (5 mL) of C<sub>5</sub>Me<sub>4</sub>H<sub>2</sub> (122 mg, 1.000 mmol) in a Schlenk tube with Teflon cock. This tube was taken outside and heated at 70 °C for 5 h. The solvent was removed under reduced pressure. The residue was washed with hexane and dissolved in toluene. The solution was concentrated and a small amount of ether was added to precipitate orange microcrystals of **1c** (370 mg, 85% yield). Layering diethyl ether on a concentrated toluene solution of **1c** gave single crystals suitable for X-ray analysis. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): 1.42 (s, 4H, CH<sub>2</sub>), 1.56 (brs, 6H, C<sub>5</sub>Me<sub>4</sub>H), 2.05 (s, 6H, C<sub>5</sub>Me<sub>4</sub>H), 2.32 (s, 12H, NMe<sub>2</sub>), 5.11 (s, 1H, C<sub>5</sub>Me<sub>4</sub>H), 6.73 (dd, *J* = 8.0, 0.7 Hz, 2H, aryl), 6.82 (dt, *J* = 7.5, 1.2 Hz, 2H, aryl), 7.02 (dt, *J* = 7.4, 1.2 Hz, 2H, aryl), 7.10 (dd, *J* = 7.5, 1.2 Hz, 2H, aryl). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C): 11.4 (br, C<sub>5</sub>Me<sub>4</sub>), 14.3 (C<sub>5</sub>Me<sub>4</sub>), 45.5 (CH<sub>2</sub>), 47.5 (br, NMe<sub>2</sub>), 113.0, 117.2, 120.0, 120.6, 121.0, 126.6, 130.5, 145.0, 147.1 (aromatics and Cp ring carbons). Anal. Calcd. for C<sub>27</sub>H<sub>37</sub>ScN<sub>2</sub>: C 74.63; H 8.58; N 6.45. Found: C 74.87; H 8.66; N 6.75.

(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)(κ<sup>2</sup>F-C<sub>6</sub>F<sub>5</sub>)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**2a**). A mixture of (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)<sub>2</sub> (0.025 g, 0.050 mmol) and [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.040 g, 0.050 mmol) in 10 mL toluene was stirred for 30 min. After the solvent was removed in vacuum, the resulting colorless residue was washed with hexane. Drying under vacuum gave **2a** as colorless microcrystals (0.051 g, 96 %). Attempts to recrystallize **2a** from C<sub>6</sub>H<sub>5</sub>Cl/hexane did not give a single crystal. However, layering hexane on a reaction mixture of (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)<sub>2</sub> and [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in C<sub>6</sub>H<sub>5</sub>Cl (concentrated to ca. 1 mL) at 25 °C afforded colorless single crystals of **2a** suitable for X-ray analysis. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>Cl, 25 °C, TMS): δ = 0.23 (s, 9H, C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>), 1.69 (s, 6H, NMe<sub>2</sub>), 1.93 (s, 6H, C<sub>5</sub>Me<sub>4</sub>), 2.34 (s, 6H, C<sub>5</sub>Me<sub>4</sub>), 2.47 (s, 2H, CH<sub>2</sub>), 6.57-6.68 (m, 2H, aryl), 6.71 (dd, *J* = 8.1, 6.9 Hz, 2H, aryl). <sup>13</sup>C {<sup>1</sup>H} NMR (75.5 MHz, C<sub>6</sub>D<sub>5</sub>Cl, 25 °C, TMS) 1.6 (SiMe<sub>3</sub>), 11.3, 14.2 (C<sub>5</sub>Me<sub>4</sub>), 22.9, 31.8 (NMe<sub>2</sub>), 44.2 (CH<sub>2</sub>), 118.6, 120.3, 126.5, 126.8, 129.1, 130.5, 131.2, 131.5, 133.7 (aromatics and Cp ring carbons), 125.3 (m, C<sub>6</sub>F<sub>5</sub>-1), 136.9 (d, <sup>1</sup>J<sub>CF</sub> = 230.4 Hz, C<sub>6</sub>F<sub>5</sub>-3), 138.7 (d, <sup>1</sup>J<sub>CF</sub> = 247.9 Hz, C<sub>6</sub>F<sub>5</sub>-4), 148.9 (d, <sup>1</sup>J<sub>CF</sub> = 239.3 Hz, C<sub>6</sub>F<sub>5</sub>-2). <sup>11</sup>B NMR (192.6 MHz, C<sub>6</sub>D<sub>5</sub>Cl, 25 °C, BF<sub>3</sub>·Et<sub>2</sub>O) δ = -16.6 (s, 1B, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>). <sup>19</sup>F NMR (564.7 MHz, C<sub>6</sub>D<sub>5</sub>Cl, 25 °C, CCl<sub>3</sub>F) δ = -166.10 (br, 8F, meta-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), -161.33 (br, 4F, para-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), -132.31 (br, 8F, ortho-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>). <sup>29</sup>Si NMR (119.2 MHz, C<sub>6</sub>D<sub>5</sub>Cl, 25 °C, TMS) δ = -7.0 (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>Cl, -45 °C, TMS): δ = 0.23 (s, 9H, C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>), 1.69 (br d, 6H, NMe<sub>2</sub>), 1.93 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 1.93 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 1.93 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 2.35 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 2.48 (br d, 2H, CH<sub>2</sub>), 6.57-6.68 (br, 2H, aryl), 6.71 (br, 2H, aryl); <sup>19</sup>F NMR (564.7 MHz, C<sub>6</sub>D<sub>5</sub>Cl, -45 °C, CCl<sub>3</sub>F) δ = -165.65 (br, 8F, meta-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), -160.99 (br, 4F, para-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), -131.24 (br, 8F, ortho-B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>). Anal. Calcd. for C<sub>45</sub>H<sub>33</sub>BF<sub>20</sub>NSiSc: C 51.40, H 3.16, N 1.33; found: C 51.52, H 3.30, N 1.44.

**A typical procedure for the random copolymerization of 1-hexene (H) with dicyclopentadiene (DCPD) by use of an *in-situ* generated cationic half-sandwich scandium aminobenzyl species (Table 2, entry 3):** In the glove box, 1.32 g of dicyclopentadiene (10 mmol) and 0.84 g of 1-hexene (10 mmol) were added to a toluene solution (2 mL) of (η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)<sub>2</sub> (20 mg, 40 μmol) at 25 °C in a 20-mL flask. A toluene solution (3 mL) of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (37 mg, 40 μmol) was then added under vigorous stirring. After 12 h, the flask was taken outside of the glove box and methanol was added to terminate the polymerization. The mixture was poured into methanol (200 mL) to precipitate the polymer product. The white polymer powder was collected by filtration, and dried under vacuum at 60 °C to a constant weight (1.80 g, 3.8 kg of copolymer/mol-Sc-h). The product obtained is soluble in THF and chloroform at room temperature.

**1-Hexene Contents in the H-DCPD copolymer.** The molar fraction of 1-hexene (*F<sub>H</sub>*) and dicyclopentadiene (*F<sub>D</sub>*) in the copolymer was calculated from the peak area of the signals via the following equation:

$$\frac{F_H}{F_D} = \frac{I_{CH_3}}{(I_{25-60ppm} - 4I_{CH_3}) / 8}$$

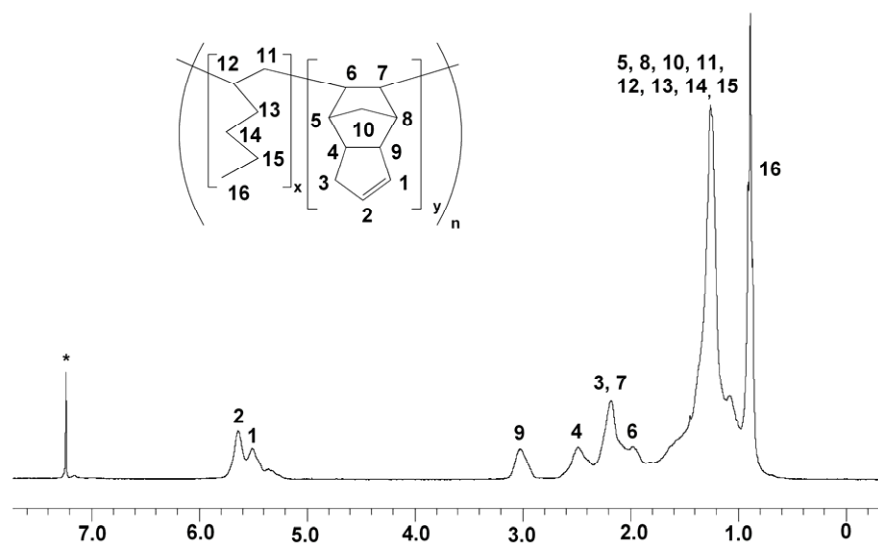
where *I<sub>CH<sub>3</sub></sub>*

 is the observed peak area of the methyl signals at ca. 15 ppm and *I<sub>25-60ppm</sub>* is the sum of the areas of all peaks at 25-60 ppm in the <sup>13</sup>C NMR spectra.

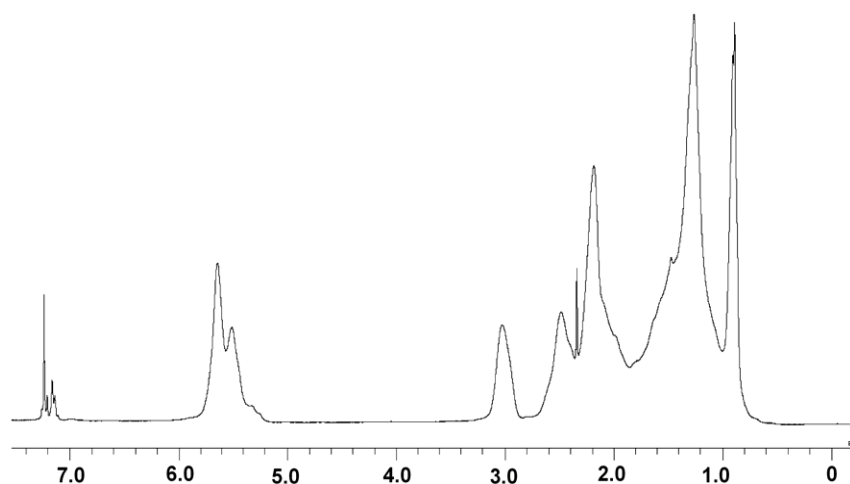
**X-ray Crystallographic Studies:** A crystal was sealed in a thin-walled glass capillary under a microscope in the glove box. Data collections were performed at -100 °C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated Mo K<sub>α</sub> radiation (λ = 0.71069 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.<sup>3</sup> The raw frame data were processed using SAINT<sup>4</sup> and SADABS<sup>5</sup> to yield the reflection data file. The structures were solved by using SHELXTL program.<sup>6</sup> Refinements were performed on *F*<sup>2</sup> 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 non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance.

- (1) Manzer, L. E. *J. Am. Chem. Soc.*, **1978**, *100*, 8068.
- (2) S-D.; Jung, M. W.; Lee, H.; Park, Y-W. *Polyhedron*, **2005**, *24*, 1269.

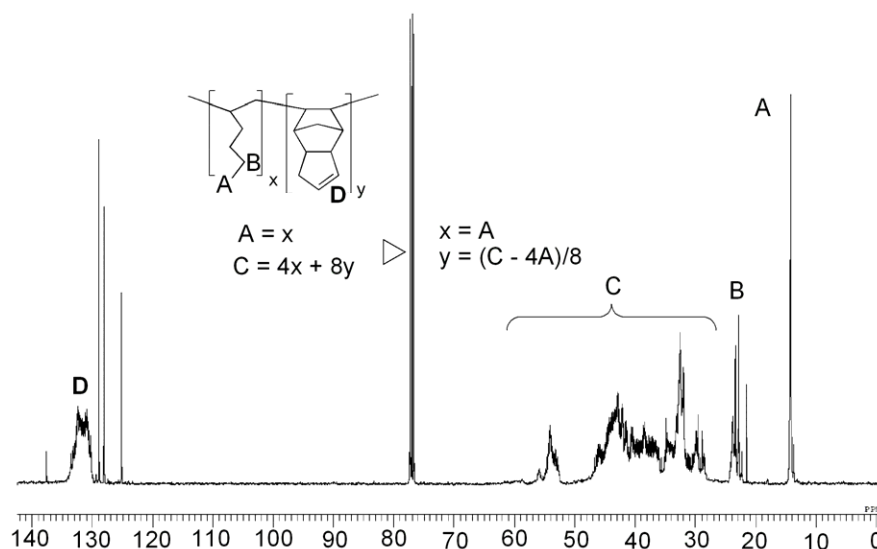
- (3) SMART Software Users Guide, version 4.21; Bruker AXS, Inc.: Madison, WI, 1997.
- (4) SAINT+, Version 6.02; Bruker AXS, Inc.: Madison, WI 1999.
- (5) Sheldrick, G. M. SADABS; Bruker AXS, Inc.: Madison, WI, 1998.
- (6) Sheldrick, G. M. SHELXTL, Version 5.1; BRUKER AXS, INC.: Madison, WI, 1998.



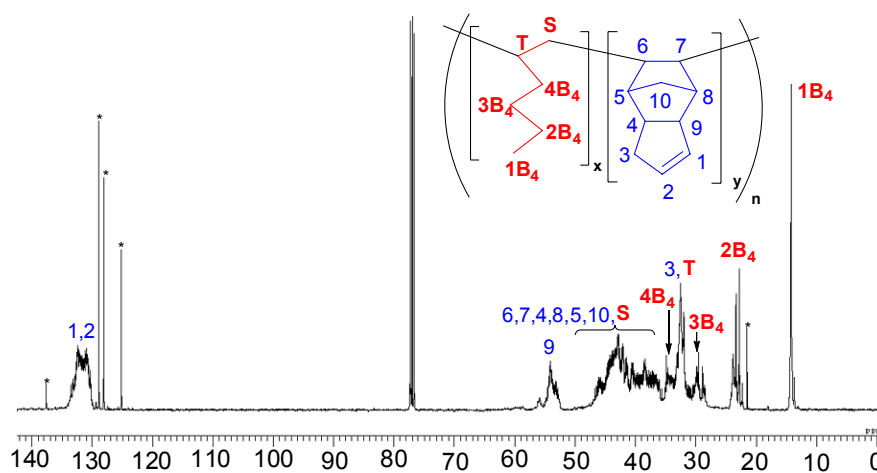
**Figure 1.** <sup>1</sup>H NMR spectrum of the H-DCPD copolymer obtained in Table 1, entry 7.



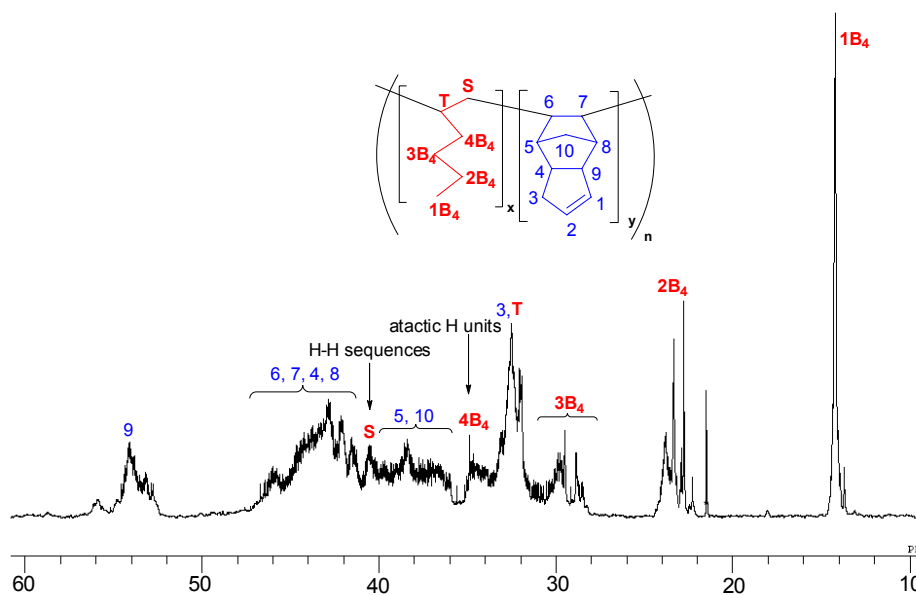
**Figure 2.** <sup>1</sup>H NMR spectrum of the H-DCPD copolymer obtained in Table 1, entry 3.



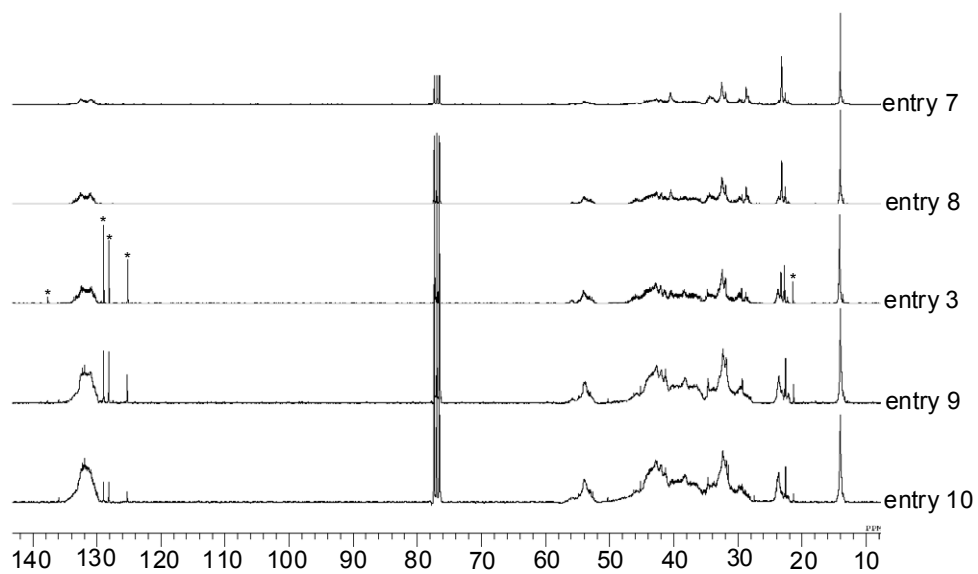
**Figure 3.**  $^{13}\text{C}$  NMR spectrum of the H-DCPD copolymer obtained in Table 1, entry 3.



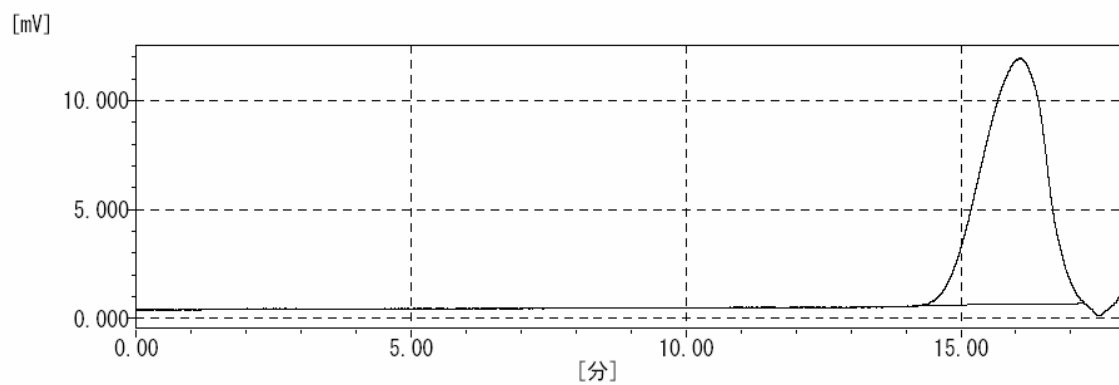
**Figure 4.**  $^{13}\text{C}$  NMR spectrum of the H-DCPD copolymer obtained in Table 1, entry 3.



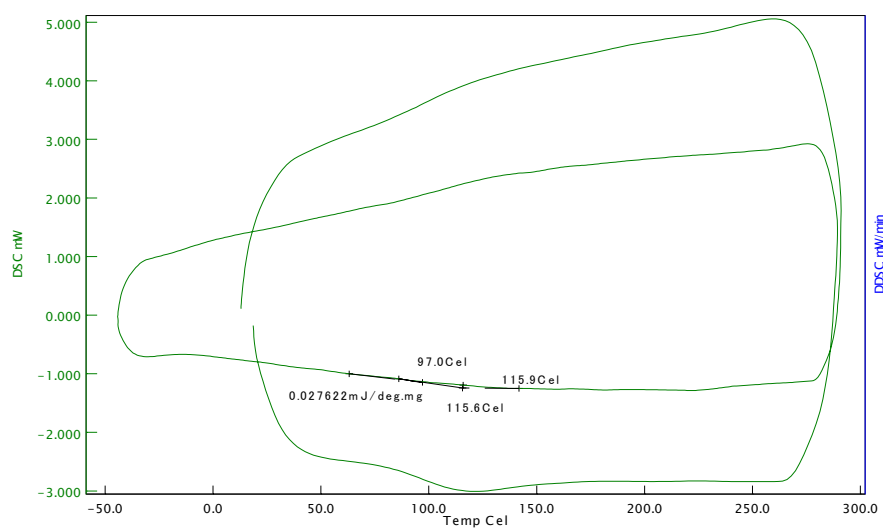
**Figure 5.** Part of  $^{13}\text{C}$  NMR spectrum of the H-DCPD copolymer obtained in Table 1, entry 3.



**Figure 6.**  $^{13}\text{C}$  NMR spectra of H-DCPD copolymers obtained in Table 1, entries 3, 7–10.



**Figure 7.** GPC curve of the H-DCPD copolymer in Table 1, entry 3.



**Figure 8.** DSC curve of the H-DCPD copolymer in Table 1, entry 3.