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Supporting Information

1,4-Specific Copolymerization of 1,3-Cyclohexadiene with Isoprene and Their Terpolymerization with Styrene by Cationic Half-Sandwich Fluorenyl Rare Earth Metal Alkyl Catalysts

Gaixia Du,[‡a] Xinwen Yan[‡a] Pengfei Zhang,[a] Hanghang Wang,[a] Yuping Dong,[b] and Xiaofang Li[a]*

[a] Key Laboratory of Cluster Science of Ministry of Education, Department of Chemistry and Chemical Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing, 100081, China.

[b] School of Material Science and Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing, 100081, China.

[‡] These authors contributed equally.

[*] E-mail: xfli@bit.edu.cn

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Experimental Section

Materials. All manipulations of air and moisture-sensitive compounds were performed under a dry and oxygen-free nitrogen atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glovebox. Nitrogen (Beijing AP Beifen Gases Industrial Co., Ltd.) were purified by being passed through a Dryclean column (4A molecular sieves, Dalian Replete Science And Technology Co., Ltd.) and a Gasclean column (Dalian Replete Science And Technology Co., Ltd.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 0.1 ppm. Anhydrous THF, hexane and toluene were were purified by a solvent purification system (SPS-800, Mbraun), and dried over fresh Na chips in the glovebox. 1,3-Cyclohexadiene (CHD), isoprene (IP) and styrene (S) were purchased from TCI, dried over CaH_2, vacuum-transferred, and degassed by two freeze-pump-thaw cycles. $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ was purchased from Tosoh Finechem Corporation and used without purification. $LnCl_3$ (Ln = Sc, Lu, Y) were purchased from Strem. *n*-BuLi (2.4 M solution in hexane), $LiCH_2SiMe_3$ (1.0 M solution in pentane) and $Al^{i}Bu_3$ (1.1 M solution in hexane) and $C_{13}H_{10}$ were purchased from Aldrich and used as received. Other fluorenyl ligands such as 2,7-$^{t}Bu_2C_{13}H_8$, 9-$SiMe_3C_{13}H_9$ and 2,7-$^{t}Bu_2$-9-$SiMe_3C_{13}H_7$ and their lithium salts were synthesized according to the literature.[1] $Ln(CH_2SiMe_3)_2(THF)_3[B(C_6H_5)_4]$ (Ln = Sc, Lu, Y) were synthesized according to the literature.[2] The deuterated solvents benzene-d_6 (99.6 atom% D), chloroform-d_1 (99.8 atom% D) and 1,1,2,2,-tetrachloroethane-d_2 (99.6 atom% D) were obtained from Cambridge Isotope.

General Methods. Samples of rare earth metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. The NMR (^1H, ^{13}C) spectra of catalyst precursors were recorded on an AVANCE 400 spectrometer at room temperature with C_6D_6 as a solvent. ^1H, ^{13}C NMR spectra of the copolymer and terpolymer samples were recorded on an AVANCE 400 spectrometer in $CDCl_3$ at room temperature Elemental analyses were performed on an Elementary Vario MICRO CUBE (Germany). The molecular weights and the molecular weight distributions of the copolymer and terpolymer samples were determined at 25 ℃ by gel GPC on a HLC-8320 apparatus. THF was employed as the eluent at a flow rate of 0.35 mL/min. All the calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). The TGA measurements were performed on a TA 60 (TA Co.) at a rate of 10 ℃ /min from 30 ℃ to 500 ℃. The DSC measurements were performed on a TA 60 (TA Co.) at a rate of 20 ℃ /min from 30 ℃ to 400 ℃, cooling at 20 ℃ /min to -100 ℃, and then recording the second DSC scan. The X-ray powder diffraction was performed with 2θ ranging from 5 ° to 35 ° by using of a Bruker-AXS X-ray diffractometer.

Synthesis of (Flu)Sc(CH_2SiMe_3)$_2$(THF) (1). To a colorless THF solution (10 mL) of $Sc(CH_2SiMe_3)_2(THF)_3[B(C_6H_5)_4]$ (1.132 g, 1.50 mmol) was added a THF solution(10 mL) of FluLi, which was prepared by the reaction of fluorenyl (Flu) (0.294 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 ℃ to give **1** as light yellow solids (0.479 g, 1.05 mmol, 70% yield). ^1H NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): −0.74 (d, 4H, $CH_2Si(CH_3)_3$), 0.24 (s, 18H, $CH_2Si(CH_3)_3$), 0.98 (br, 4H, THF-*β*-C*H*$_2$), 3.08 (br, 4H, THF-*α*-C*H*$_2$), 6.88−7.80 (m, 9H, fluorenyl). ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ/ppm): 4.0, 24.9, 37.0, 71.5, 87.3, 119.6, 120.0, 122.3, 123.0, 125.5, 132.5. Anal. Calcd for $C_{25}H_{39}OScSi_2$: C, 65.75; H, 8.61. Found: C, 65.29; H, 8.26.

Synthesis of (2,7-^{t}Bu$_2$Flu)Sc(CH$_2$SiMe$_3$)$_2$(THF) (2). To a colorless THF solution (10 mL) of Sc(CH$_2$SiMe$_3$)$_2$(THF)$_3$[B(C$_6$H$_5$)$_4$] (1.132 g, 1.50 mmol) was added a THF solution(10 mL) of 2,7-^{t}Bu$_2$FluLi, which was prepared by the reaction of 2,7-^{t}Bu$_2$Flu (0.417 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 ℃ to give **2** as light yellow solids (0.614 g, 1.08 mmol, 72% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, δ/ppm): −0.79 (d, 4H, C*H*$_2$Si(CH$_3$)$_3$), 0.26 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), 1.11 (br, 4H, THF-*β*-C*H*$_2$), 1.39 (s, 18H, C(C*H*$_3$)$_3$), 3.24 (br, 4H, THF-*α*-C*H*$_2$), 6.95−7.85 (m, 7H, fluorenyl). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C, δ/ppm): 4.0, 25.0, 31.6, 35.2, 45.7, 71.3, 88.0, 117.9, 118.4, 118.9, 121.7, 133.2, 147.6. Anal. Calcd for C$_{33}$H$_{55}$OScSi$_2$: C, 69.67; H, 9.74. Found: C, 69.96; H, 9.96.

Synthesis of (2,7-^{t}Bu$_2$Flu)Lu(CH$_2$SiMe$_3$)$_2$(THF) (3). To a colorless THF solution (10 mL) of Lu(CH$_2$SiMe$_3$)$_2$(THF)$_3$[B(C$_6$H$_5$)$_4$] (1.327 g, 1.50 mmol) was added a THF solution(10 mL) of 2,7-^{t}Bu$_2$FluLi, which was prepared by the reaction of 2,7-^{t}Bu$_2$Flu (0.417 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 ℃ to give **3** as light yellow solids (0.713 g, 1.02 mmol, 68% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, δ/ppm): −1.33 (s, 4H, C*H*$_2$Si(CH$_3$)$_3$), 0.26 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), 1.06 (br, 4H, THF-*β*-C*H*$_2$), 1.40 (s, 18H, C(C*H*$_3$)$_3$), 3.19 (br, 4H, THF-*α*-C*H*$_2$), 6.71−7.82 (m, 7H, fluorenyl). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C, δ/ppm): 4.4, 24.9, 31.7, 35.2, 41.9, 70.5, 84.6, 117.2, 118.1, 121.6, 134.1, 147.9. Anal. Calcd for C$_{33}$H$_{55}$OScSi$_2$: C, 56.71; H, 7.93. Found: C, 56.63; H, 7.85.

Synthesis of (2,7-^{t}Bu$_2$Flu)Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (4). To a colorless THF solution (10 mL) of Y(CH$_2$SiMe$_3$)$_2$(THF)$_3$[B(C$_6$H$_5$)$_4$] (1.198 g, 1.50 mmol) was added a THF solution(10 mL) of 2,7-^{t}Bu$_2$FluLi, which was prepared by the reaction of 2,7-^{t}Bu$_2$Flu (0.417 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 ℃ to give **4** as light yellow solids (0.668 g, 0.98 mmol, 65% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, δ/ppm): −1.11 (s, 4H, C*H*$_2$Si(CH$_3$)$_3$), 0.25 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), 1.23 (br, 8H, THF-*β*-C*H*$_2$), 1.39 (s, 18H, C(C*H*$_3$)$_3$), 3.41 (br, 8H, THF-*α*-C*H*$_2$), 6.71−7.86 (m, 7H, fluorenyl). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C, δ/ppm): 4.3, 25.3, 31.6, 35.2, 37.4, 37.9, 69.3, 85.2, 116.9, 117.5, 118.1, 121.6, 134.0, 147.9. Anal. Calcd for C$_{37}$H$_{63}$O$_2$YSi$_2$: C, 64.88; H, 9.27. Found: C, 64.77; H, 9.13.

Synthesis of (9-SiMe$_3$Flu)Sc(CH$_2$SiMe$_3$)$_2$(THF) (5). To a colorless THF solution (10 mL) of Sc(CH$_2$SiMe$_3$)$_2$(THF)$_3$[B(C$_6$H$_5$)$_4$] (1.132 g, 1.50 mmol) was added a THF solution(10 mL) of 9-SiMe$_3$FluLi, which was prepared by the reaction of 9-SiMe$_3$Flu (0.358 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 ℃ to give **5** as light yellow crystals (0.595 g, 1.13 mmol, 75% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, δ/ppm): −0.42 (d, 2H, C*H*$_2$Si(CH$_3$)$_3$, *J* = 11.6 Hz), −0.26 (d, 2H, C*H*$_2$Si(CH$_3$)$_3$, *J* = 11.2 Hz), 0.14 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), 0.65 (s, 9H, Si(C*H*$_3$)$_3$), 1.03 (m, 4H, THF-*β*-C*H*$_2$), 3.19 (m, 4H, THF-*α*-C*H*$_2$), 7.04–8.02 (m, 8H, fluorenyl). ^{13}C NMR (100 MHz, C$_6$D$_6$, 25 °C, δ/ppm): 2.1, 3.9, 24.6, 47.4, 71.4, 93.2, 120.4, 122.2, 124.7, 125.1, 125.6, 138.7. Anal. Calcd for C$_{28}$H$_{47}$OScSi$_3$: C, 63.59; H, 8.96. Found: C, 63.77; H, 9.27.

Synthesis of (9-SiMe$_3$Flu)Lu(CH$_2$SiMe$_3$)$_2$(THF) (6). To a colorless THF solution (10 mL) of Lu(CH$_2$SiMe$_3$)$_2$(THF)$_3$[B(C$_6$H$_5$)$_4$] (1.327 g, 1.50 mmol) was added a THF solution(10 mL) of 9-SiMe$_3$FluLi, which was prepared by the reaction of 9-SiMe$_3$Flu (0.358 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 °C to give **6** as light yellow crystals (0.692 g, 1.05 mmol, 70% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): −1.05 (s, 4H, C*H*$_2$Si(CH$_3$)$_3$), 0.15 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), 0.66 (s, 9H, Si(C*H*$_3$)$_3$), 0.99 (br, 4H, THF-*β*-C*H*$_2$), 3.11 (br, 4H, THF-*α*-C*H*$_2$), 7.07−8.03 (m, 8H, fluorenyl). ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ/ppm): 2.1, 4.3, 24.6, 43.3, 70.6, 90.2, 119.7, 122.0, 123.9, 124.0, 125.8, 139.2. Anal. Calcd for $C_{28}H_{47}OLuSi_3$: C, 51.04; H, 7.19. Found: C, 50.88; H, 7.12.

Synthesis of (9-SiMe$_3$Flu)Y(CH$_2$SiMe$_3$)$_2$(THF) (7). To a colorless THF solution (10 mL) of Y(CH$_2$SiMe$_3$)$_2$(THF)$_3$[B(C$_6$H$_5$)$_4$] (1.198 g, 1.50 mmol) was added a THF solution(10 mL) of 9-SiMe$_3$FluLi, which was prepared by the reaction of 9-SiMe$_3$Flu (0.358 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 °C to give **7** as light yellow crystals (0.584 g, 1.02 mmol, 68% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): −0.84 (s, 4H, C*H*$_2$Si(CH$_3$)$_3$), 0.16 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), 0.55 (s, 9H, Si(C*H*$_3$)$_3$), 0.99 (m, 4H, THF-*β*-C*H*$_2$), 3.12 (m, 4H, THF-*α*-C*H*$_2$), 7.04−8.04 (m, 8H, fluorenyl). ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ/ppm): 2.0, 4.2, 24.6, 39.3, 39.7, 70.5, 91.1, 119.7, 122.0, 123.7, 123.8, 125.9, 139.0. Anal. Calcd for $C_{28}H_{47}OYSi_3$: C, 58.71; H, 8.27. Found: C, 58.62; H, 8.18.

Synthesis of (2,7-^{t}Bu$_2$-9-SiMe$_3$Flu)Sc(CH$_2$SiMe$_3$)$_2$(THF) (8). To a colorless THF solution (10 mL) of Sc(CH$_2$SiMe$_3$)$_2$(THF)$_3$[B(C$_6$H$_5$)$_4$] (1.132 g, 1.50 mmol) was added a THF solution(10 mL) of 2,7-^{t}Bu$_2$-9-SiMe$_3$FluLi, which was prepared by the reaction of 2,7-^{t}Bu$_2$-9-SiMe$_3$Flu (0.526 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 °C to give **8** as light yellow crystals (0.702 g, 1.10 mmol, 73% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): −0.50 (d, 2H, C*H*$_2$Si(CH$_3$)$_3$, *J* = 11.2 Hz), −0.28 (d, 2H, C*H*$_2$Si(CH$_3$)$_3$, *J* = 11.2 Hz), 0.13 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), 0.76 (s, 9H, Si(C*H*$_3$)$_3$), 1.27 (m, 4H, THF-*β*-C*H*$_2$), 1.43 (s, 18H, C(C*H*$_3$)$_3$), 3.32 (m, 4H, THF-*α*-C*H*$_2$), 7.21−8.12 (m, 6H, fluorenyl). ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ/ppm): 2.1, 3.9, 24.7, 31.6, 35.2, 47.1, 71.3, 93.9, 119.5, 120.3, 121.8, 122.4, 139.4, 147.6. Anal. Calcd for $C_{36}H_{63}OScSi_3$: C, 67.44; H, 9.90. Found: C, 67.02; H, 9.35.

Synthesis of (2,7-^{t}Bu$_2$-9-SiMe$_3$Flu)Lu(CH$_2$SiMe$_3$)$_2$(THF) (9). To a colorless THF solution (10 mL) of Lu(CH$_2$SiMe$_3$)$_2$(THF)$_3$[B(C$_6$H$_5$)$_4$] (1.327 g, 1.50 mmol) was added a THF solution(10 mL) of 2,7-^{t}Bu$_2$-9-SiMe$_3$FluLi, which was prepared by the reaction of 2,7-^{t}Bu$_2$-9-SiMe$_3$Flu (0.526 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 °C to give **9** as light yellow solids (0.787 g, 1.02 mmol, 68% yield). ^{1}H NMR (400MHz, C_6D_6, 25 °C, δ/ppm): −1.09 (s, 4H, C*H*$_2$Si(CH$_3$)$_3$), 0.14 (s, 18H, CH$_2$Si(C*H*$_3$)$_3$), 0.75 (s, 9H, Si(C*H*$_3$)$_3$), 1.09 (m, 4H, THF-*β*-C*H*$_2$), 1.45 (s, 18H, C(C*H*$_3$)$_3$), 3.20 (m, 4H, THF-*α*-C*H*$_2$), 7.23−8.16 (m, 6H, fluorenyl). ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ/ppm): 2.2, 4.4, 24.7, 31.7, 35.2, 42.9, 70.4, 90.2, 118.8, 119.5, 121.5, 121.7, 140.1, 147.9. Anal. Calcd for $C_{36}H_{63}OLuSi_3$: C, 56.07; H, 8.23. Found: C, 55.99; H, 8.15.

Synthesis of (2,7-^{t}Bu$_2$-9-SiMe$_3$Flu)Y(CH$_2$SiMe$_3$)$_2$(THF) (10). To a colorless THF solution (10 mL) of Y(CH$_2$SiMe$_3$)$_2$(THF)$_3$[B(C$_6$H$_5$)$_4$] (1.198 g, 1.50 mmol) was added a THF solution(10 mL) of 2,7-^{t}Bu$_2$-9-SiMe$_3$FluLi, which was prepared by the reaction of 2,7-^{t}Bu$_2$-9-SiMe$_3$Flu (0.526 g, 1.50 mmol) with *n*-BuLi (0.625 mL, 1.50 mmol), and the mixture was stirred at room temperature for 30 min. After removal of all volatiles in vacuo, the residue was recrystallized from hexane at –30 °C to give **10** as light yellow solids (0.646 g, 0.95 mmol, 63% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 °C, δ/ppm): −0.88 (s, 4H, $CH_2Si(CH_3)_3$), 0.15 (s, 18H, $CH_2Si(CH_3)_3$), 0.76 (s, 9H, $Si(CH_3)_3$), 1.07 (m, 4H, THF-*β*-CH_2), 1.44 (s, 18H, $C(CH_3)_3$), 3.25 (m, 4H, THF-*α*-CH_2), 7.22−8.15 (m, 6H, fluorenyl). ^{13}C NMR (100 MHz, C_6D_6, 25 °C, δ/ppm): 2.1, 4.3, 24.7, 31.7, 35.3, 38.8, 39.2, 70.4, 91.2, 118.9, 119.2, 121.4, 121.7, 139.9, 147.9. Anal. Calcd for $C_{36}H_{63}OYSi_3$: C, 63.12; H, 9.27. Found: C, 63.03; H, 9.18.

A typical procedure for the regioselective copolymerization of 1,3-cyclohexadiene with isoprene (Table 1, entry 10). In the glove box, Al^iBu_3 (0.55 mL, 600μmol) and a toluene solution (3 mL) of $[Ph_3C][B(C_6F_5)_4]$ (37 mg, 40 μmol) was added to a toluene solution (2 mL) of $(9\text{-}SiMe_3Flu)Sc(CH_2SiMe_3)_2(THF)$ (21 mg, 40 μmol) in a 100-mL flask. The mixture was stirred at room temperature for a few minutes, and a toluene solution (5 mL) of 1,3-cyclohexadiene (0.84 g, 10.5 mmol) and isoprene (0.72 g, 10.5 mmol) was added under vigorous stirring. After 3 h, the flask was then taken outside of the glove box. The mixture was poured into methanol (200 mL, containing 1% stabilizer BHT) to precipitate the polymer product. The white powder was collected by filtration, and dried under vacuum at 60 °C to a constant weight (1.29 g, 10.8 kg of copolymer mol_{Ln}^{-1} h^{-1}). The product obtained is soluble thoroughly in $CHCl_3$ and THF at 25 °C. The 1,3-cyclohexadiene content of the copolymer was calculated according to the formula:

$$\text{Mol CHD\%} = \{0.5I_{H1}/(0.5I_{H1} + I_{H2} + 0.5I_{H3})\} \times 100$$

In which I_{H1} is the integral area of the hydrogen atoms bound to carbon atoms of the double bonds of the CHD units around 5.6 ppm, I_{H2} is the integration of the resonance at 5.13 ppm (one vinyl proton of the 1,4-isoprene unit) and I_{H3} is the integration of the resonance at 4.72 ppm (two vinyl protons of the 3,4-isoprene unit) in the ^{1}H NMR spectrum.

In the ^{1}H NMR spectra, CHD regioselectivity is determined by the integration ratio of the resonances around 5.5–5.8, 1.9–2.4, and 1.2–1.8 ppm (removing the corresponding integration assigned to IP units) of all these copolymers. The CHD units in the copolymer adopt complete 1,4-selectivity if the integration ratio is 2 : 2 : 4. In the ^{13}C NMR spectra, the peaks at 127.5 and 25.5 ppm display the presence of 1,2-CHD units.

The isomer contents of the isoprene units in the copolymer were calculated from the ^{1}H and ^{13}C NMR spectra according to the following formula (eqs. 1–5):[2]

$$\text{Mol 1,4-IP\%} = \{I_{H1}/(I_{H1} + 0.5I_{H2})\} \times 100 \qquad \text{(eq. 1)}$$

$$\text{Mol 3,4-IP\%} = \{0.5I_{H2}/(I_{H1} + 0.5I_{H2})\} \times 100 \qquad \text{(eq. 2)}$$

$$\text{Mol } \textit{cis}\text{-1,4-IP\%} = \{I_{C1}/(I_{C1} + I_{C2} + I_{C3})\} \times 100 \qquad \text{(eq. 3)}$$

$$\text{Mol } \textit{trans}\text{-1,4-IP\%} = \{I_{C3}/(I_{C1} + I_{C2} + I_{C3})\} \times 100 \qquad \text{(eq. 4)}$$

$$\text{Mol 3,4-IP\%} = \{I_{C2}/(I_{C1} + I_{C2} + I_{C3})\} \times 100 \qquad \text{(eq. 5)}$$

In which I_{H1} is the integration of the resonance at 5.13 ppm (one vinyl proton of the 1,4-isoprene unit), and I_{H2} is the integration of the resonance at 4.72 ppm (two vinyl protons of the 3,4-isoprene unit) in the ^{1}H NMR spectrum. I_{C1} is the integration of the signals at 23.5 ppm assigned as the methyl carbon of the *cis*-1,4-isoprene unit, and I_{C2} is the integration of the signals at 18.8 ppm assigned as the methyl carbon of the 3,4-isoprene unit, while I_{C3} is the integration of the signals at 16.2 ppm assigned as the methyl carbon of the *trans*-1,4-isoprene unit in the ^{13}C NMR spectrum.

A typical procedure for the terpolymerization of 1,3-Cyclohexadiene with styrene and isoprene (Table 3, entry 3): In the glove box, $Al^{i}Bu_3$ (0.55 mL, 600μmol) and a toluene solution (3 mL) of $[Ph_3C][B(C_6F_5)_4]$ (37 mg, 40 μmol) was added to a toluene solution (2 mL) of $(2,7\text{-}9\text{-}SiMe_3Flu)Sc(CH_2SiMe_3)_2(THF)$ (27 mg, 40 μmol) in a 100-mL flask. The mixture was stirred at room temperature for a few minutes, and a toluene solution (10 mL) of 1,3-cyclohexadiene (0.84 g, 10.5 mmol), styrene (1.09 g, 10.5 mmol) and isoprene (0.72 g, 10.5 mmol) was added under vigorous stirring. After 3 h, the flask was then taken outside of the glove box. The mixture was poured into methanol (200 mL, containing 1% stabilizer BHT) to precipitate the polymer product. The white powder was collected by filtration, and dried under vacuum at 60 °C to a constant weight (1.42 g, 11.8 kg of copolymer mol_{Ln}^{-1} h^{-1}). The product obtained is soluble thoroughly in $CHCl_3$ and THF at 25 °C. The 1,3-cyclohexadiene content and the isoprene content of the terpolymer was calculated according to the formula:

$$\text{Mol CHD\%} = \{0.5I_{H1}/(0.5I_{H1} + I_{H2} + 0.5I_{H3} + 0.2I_{H4})\} \times 100$$

$$\text{Mol IP\%} = \{(I_{H2} + 0.5I_{H3})/(0.5I_{H1} + I_{H2} + 0.5I_{H3} + 0.2I_{H4})\} \times 100$$

In which I_{H4} is the integral area of the hydrogen atoms bound to carbon atoms of the aromatic ring of the styrene units around 6.5-7.5 ppm in the ^{1}H NMR spectra.

In the ^{1}H NMR spectra, CHD regioselectivity is determined by the integration ratio of the resonances around 5.5–5.8, 1.9–2.4, and 1.2–1.8 ppm (removing the corresponding integration assigned to IP units) of all these copolymers. The CHD units in the copolymer adopt complete 1,4-selectivity if the integration ratio is 2 : 2 : 4. In the ^{13}C NMR spectra, the peaks at 127.5 and 25.5 ppm display the presence of 1,2-CHD units.

The isomer contents of the isoprene units in the copolymer were calculated from the ^{1}H and ^{13}C NMR spectra according to the following formula (eqs. 1–5):[2]

$$\text{Mol 1,4-IP\%} = \{I_{H1}/(I_{H1} + 0.5I_{H2})\} \times 100 \qquad \text{(eq. 1)}$$

$$\text{Mol 3,4-IP\%} = \{0.5I_{H2}/(I_{H1} + 0.5I_{H2})\} \times 100 \qquad \text{(eq. 2)}$$

$$\text{Mol } \textit{cis}\text{-1,4-IP\%} = \{I_{C1}/(I_{C1} + I_{C2} + I_{C3})\} \times 100 \qquad \text{(eq. 3)}$$

$$\text{Mol } \textit{trans}\text{-1,4-IP\%} = \{I_{C3}/(I_{C1} + I_{C2} + I_{C3})\} \times 100 \qquad \text{(eq. 4)}$$

$$\text{Mol 3,4-IP\%} = \{I_{C2}/(I_{C1} + I_{C2} + I_{C3})\} \times 100 \qquad \text{(eq. 5)}$$

In which I_{H1} is the integration of the resonance at 5.13 ppm (one vinyl proton of the 1,4-isoprene unit), and I_{H2} is the integration of the resonance at 4.72 ppm (two vinyl protons of the 3,4-isoprene unit) in the ^{1}H NMR spectrum. I_{C1} is the integration of the signals at 23.5 ppm assigned as the methyl carbon of the *cis*-1,4-isoprene unit, and I_{C2} is the integration of the signals at 18.8 ppm assigned as the methyl carbon of the 3,4-isoprene unit, while I_{C3} is the integration of the signals at 16.2 ppm assigned as the methyl carbon of the *trans*-1,4-isoprene unit in the ^{13}C NMR spectrum.

1. Li, X.; Wang, X.; Tong, X.; Zhang, H.; Chen, Y.; Liu, Y.; Liu, H.; Wang, X.; Nishiura, M.; He, H.; Lin, Z.; Zhang, S.; Hou, Z. *Organometallics* **2013**, *32*, 1445–1458.
2. Elvidge, B. R.; Arndt, S.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2005**, *44*, 6777−6788.

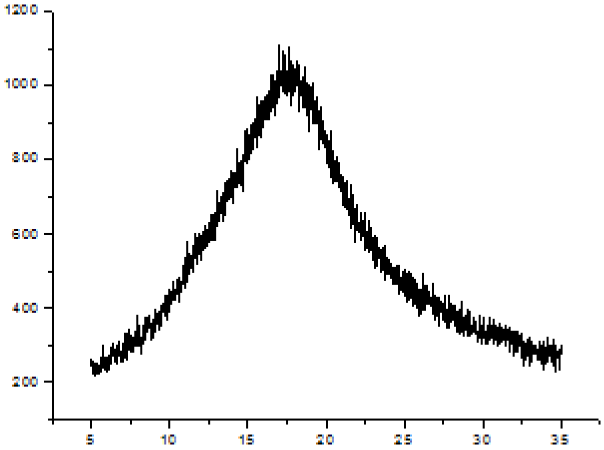


Figure S1. The X-ray powder diffraction pattern of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 10.

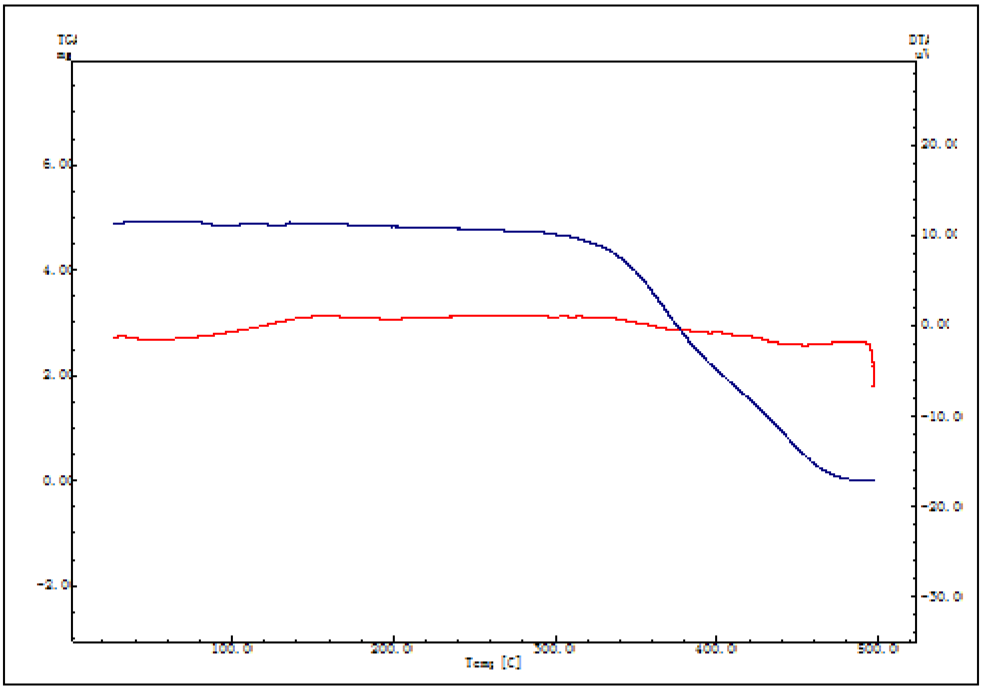


Figure S2. TGA curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 10.

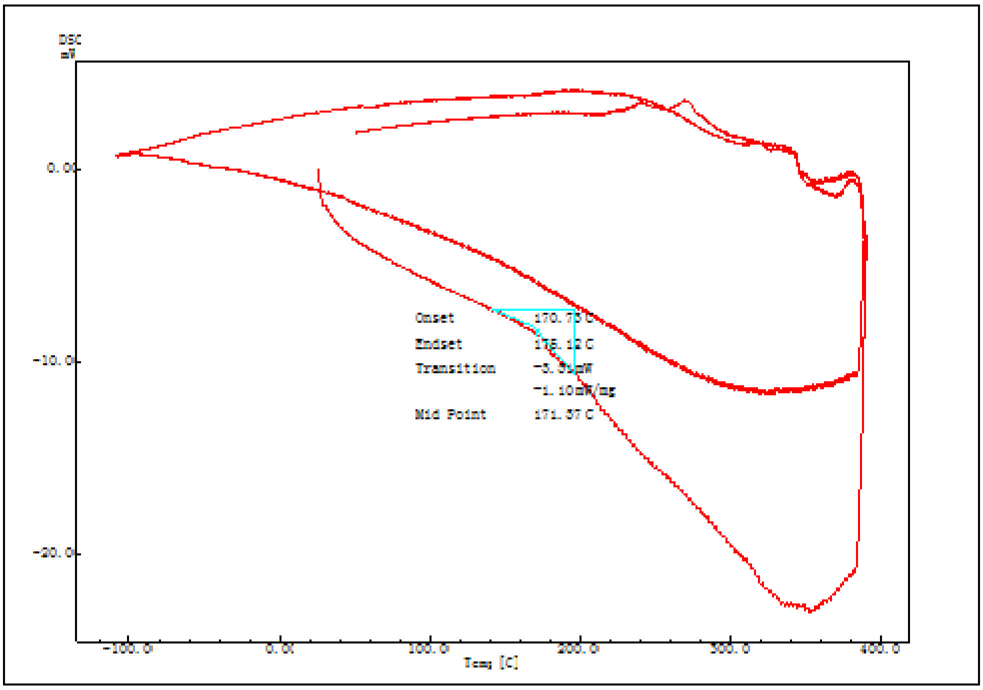
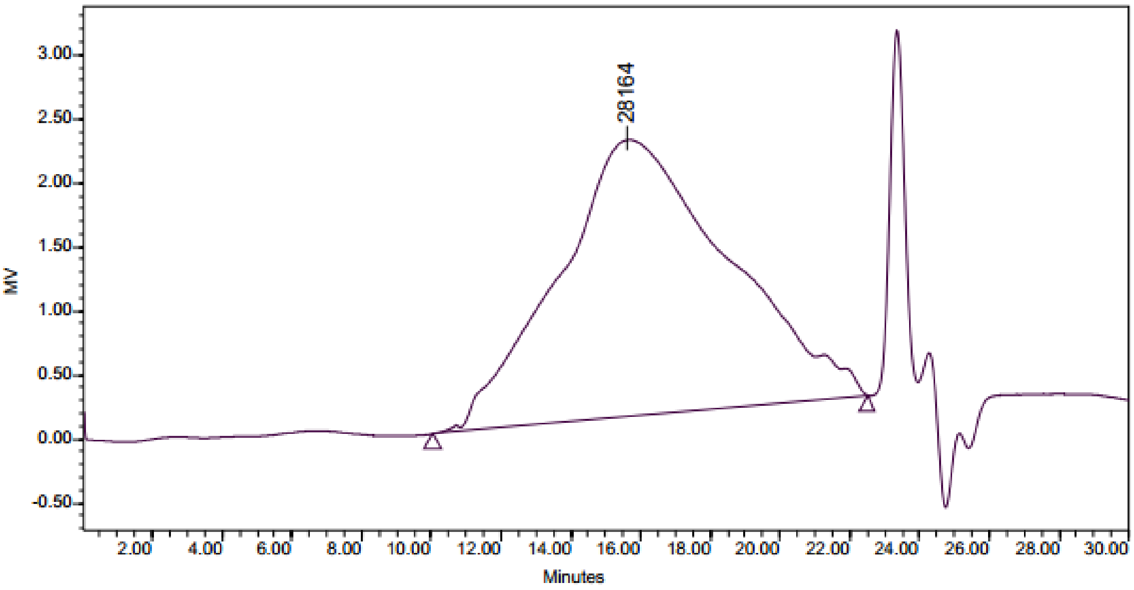


Figure S3. DSC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 7.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		10011	51224	28164	186114	324970	5.116728	3.633343	6.344098

Figure S4. GPC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 7.

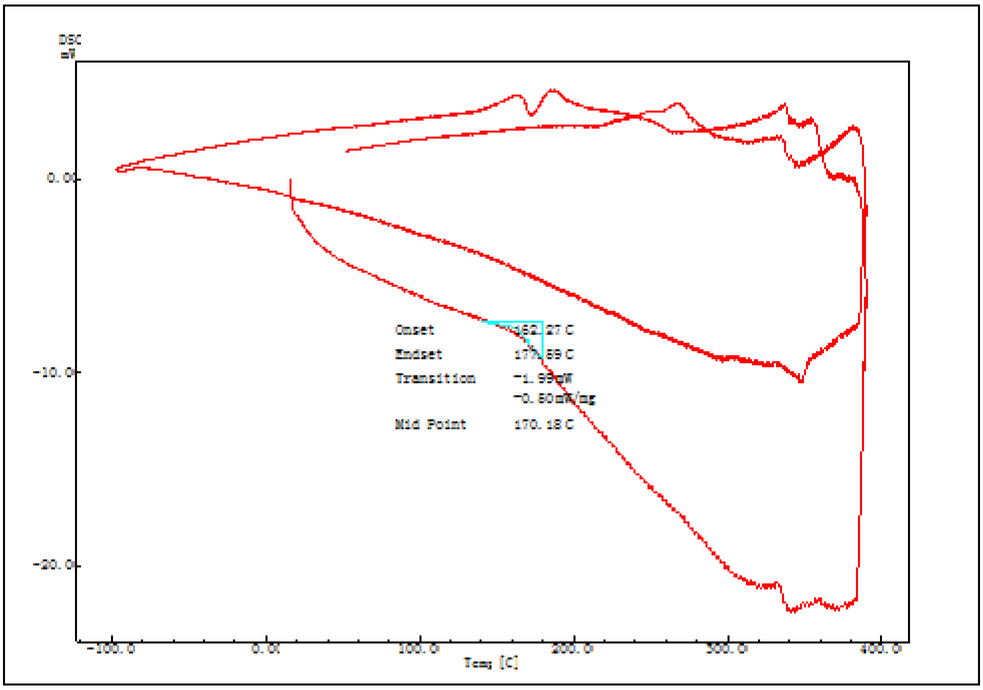
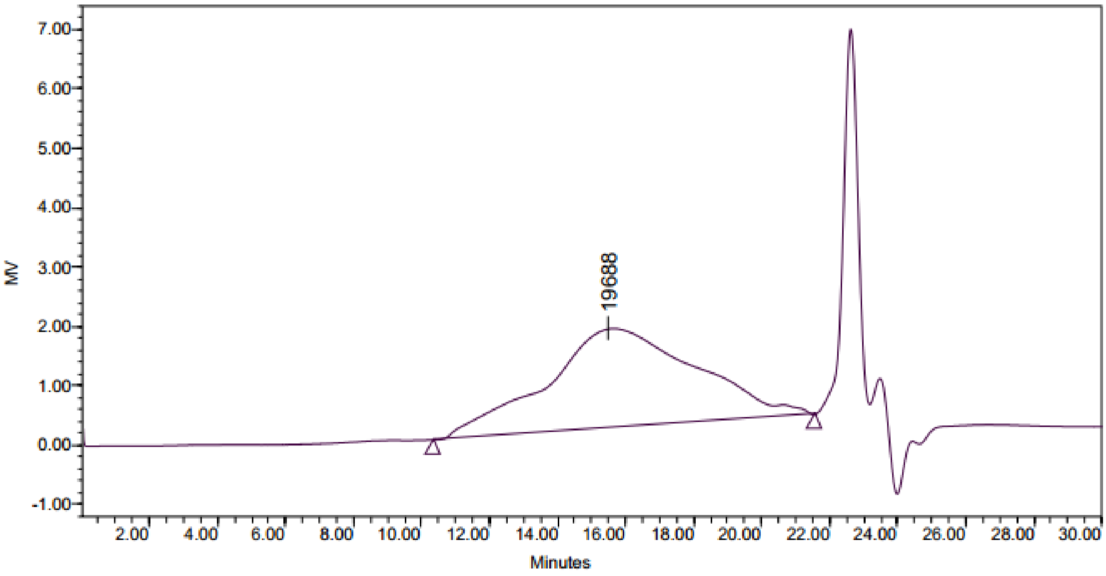


Figure S5. DSC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 8.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		9043	52501	19688	330386	684174	5.805744	6.292929	13.031599

Figure S6. GPC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 8.

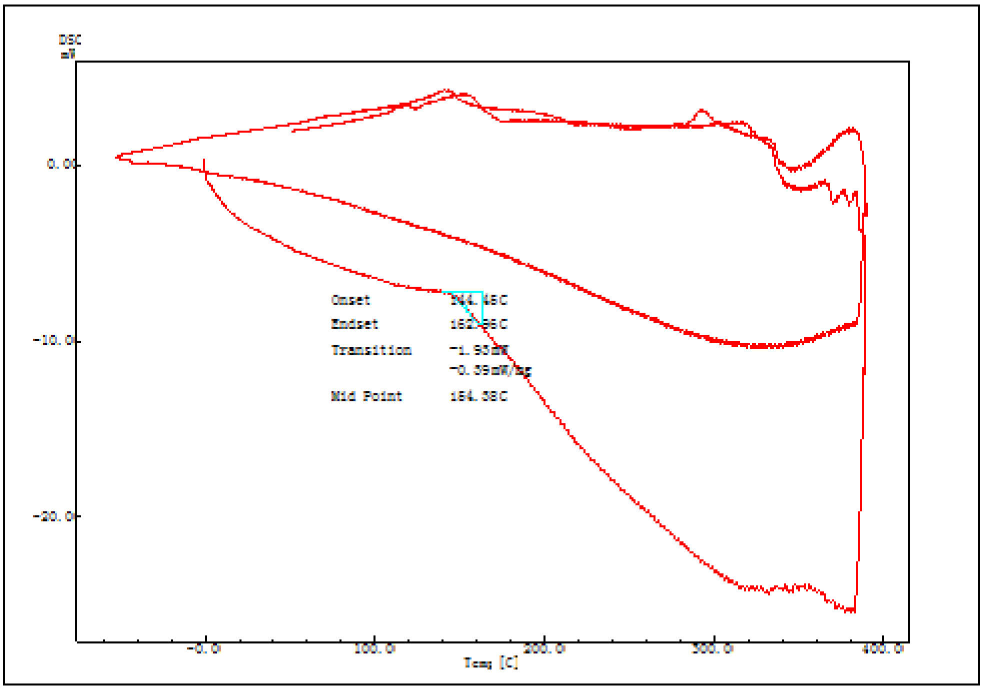
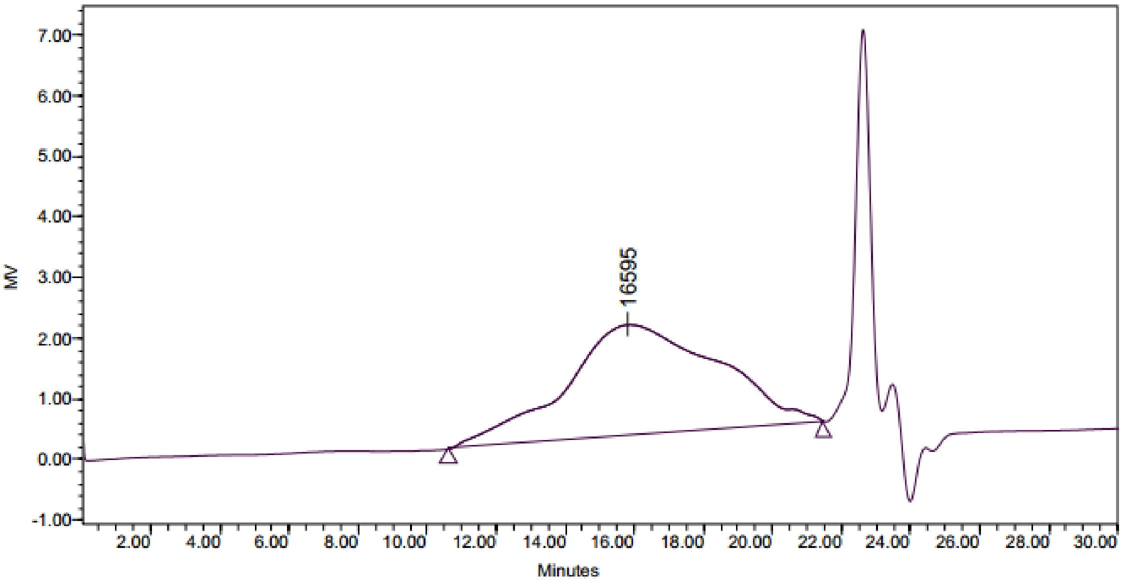


Figure S7. DSC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 9.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		7758	40534	16595	282464	649842	5.224840	6.968614	16.032145

Figure S8. GPC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 9.

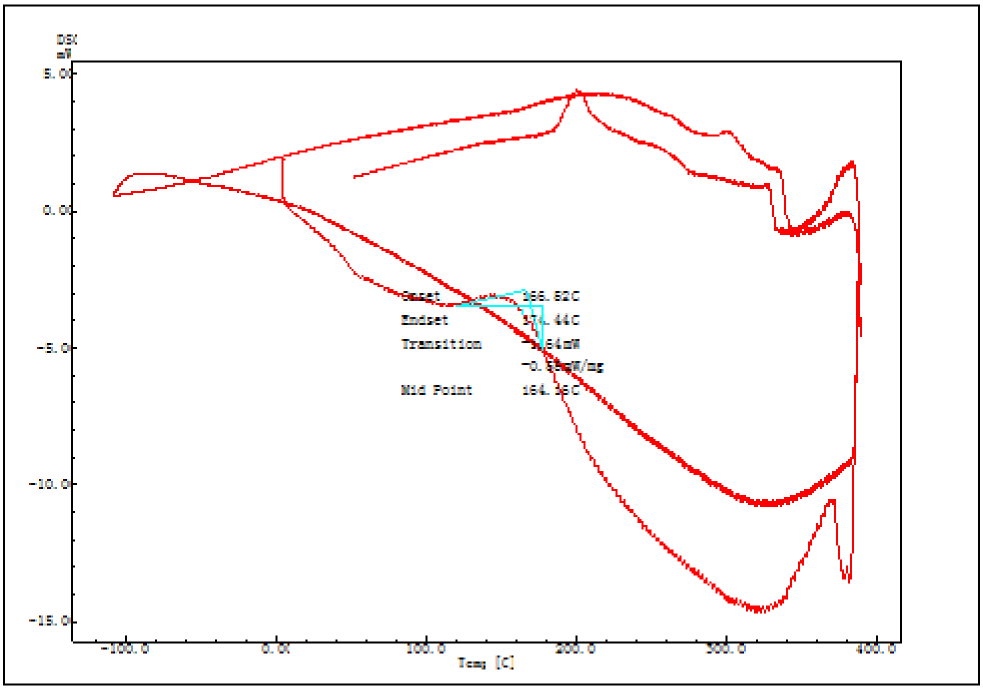
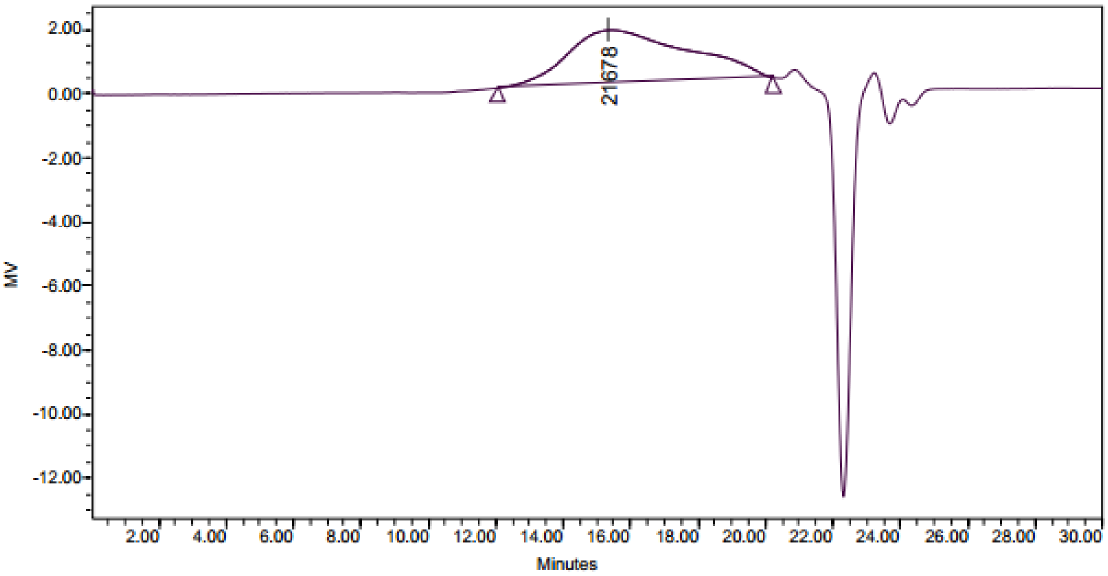


Figure S9. DSC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 10.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		8424	21833	21678	45516	78990	2.591767	2.084770	3.617953

Figure S10. GPC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 10.

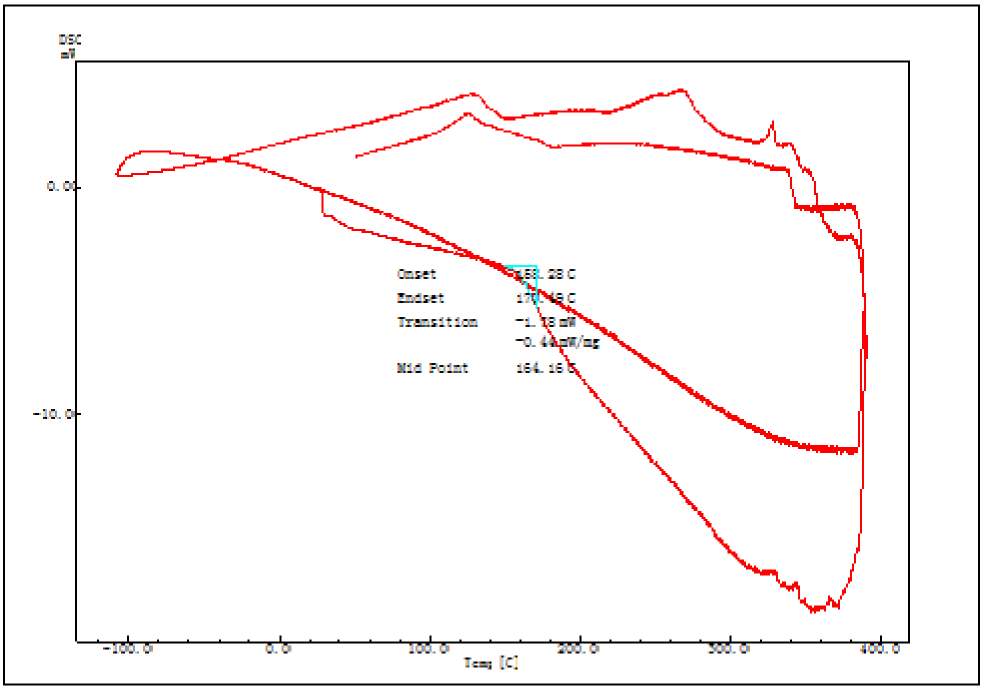
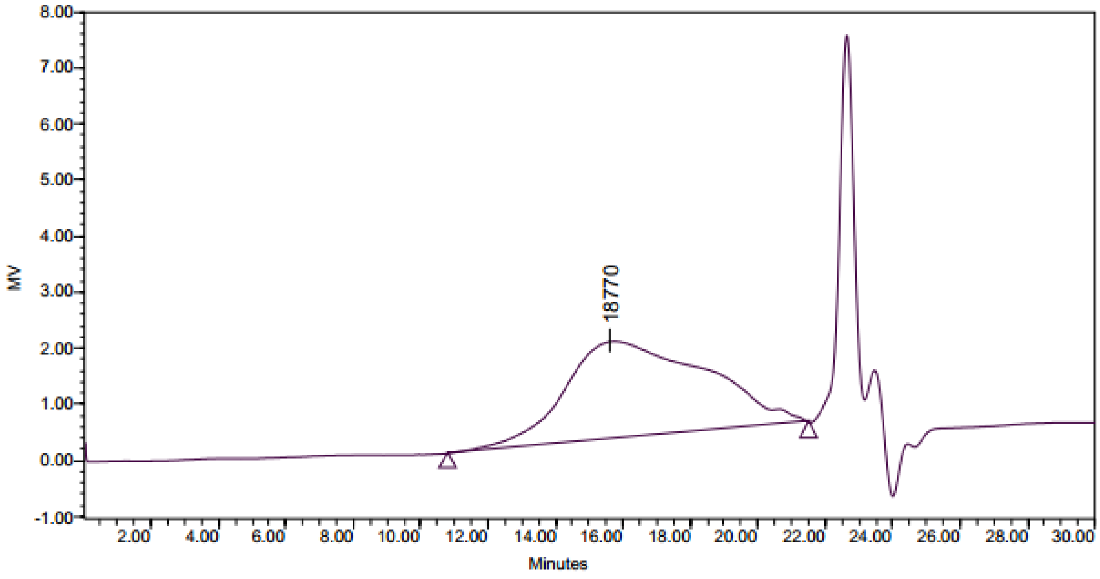


Figure S11. DSC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 11.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		7047	22755	18770	101795	358486	3.229153	4.473587	15.754386

Figure S12. GPC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 11.

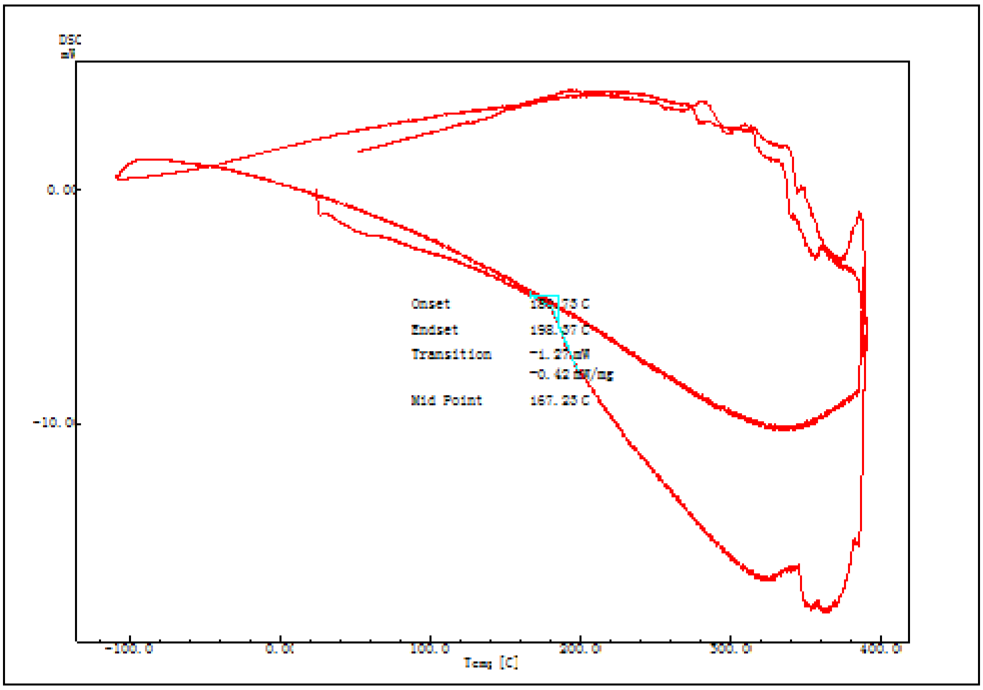
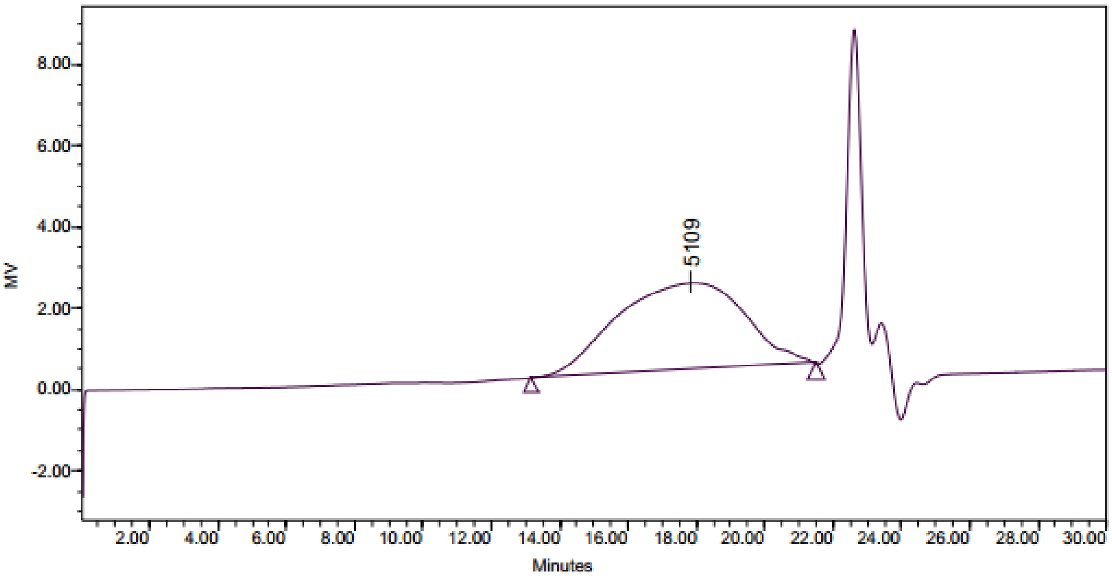


Figure S13. DSC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 12.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		4902	10069	5109	18766	28946	2.054018	1.863638	2.874649

Figure S14. GPC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 12.

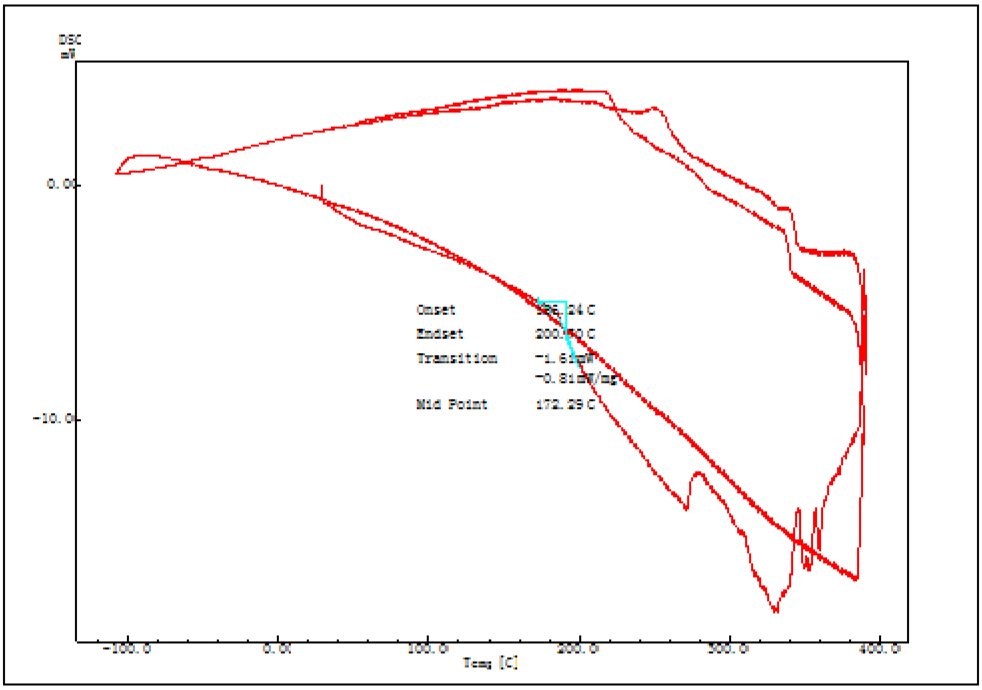
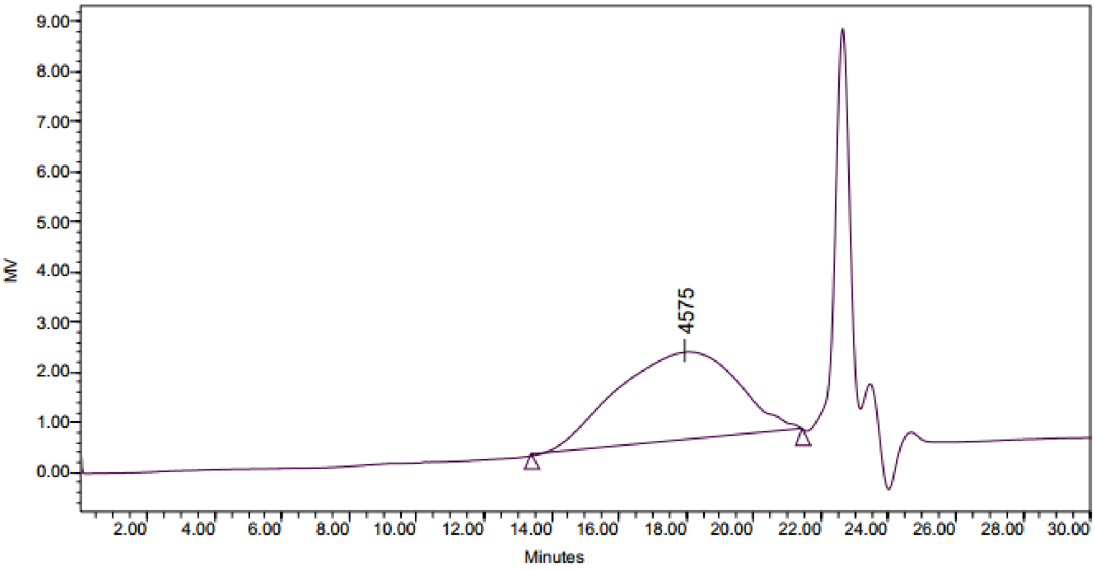


Figure S15. DSC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 13.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		4630	9253	4575	16909	25361	1.998573	1.827455	2.740983

Figure S16. GPC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 13.

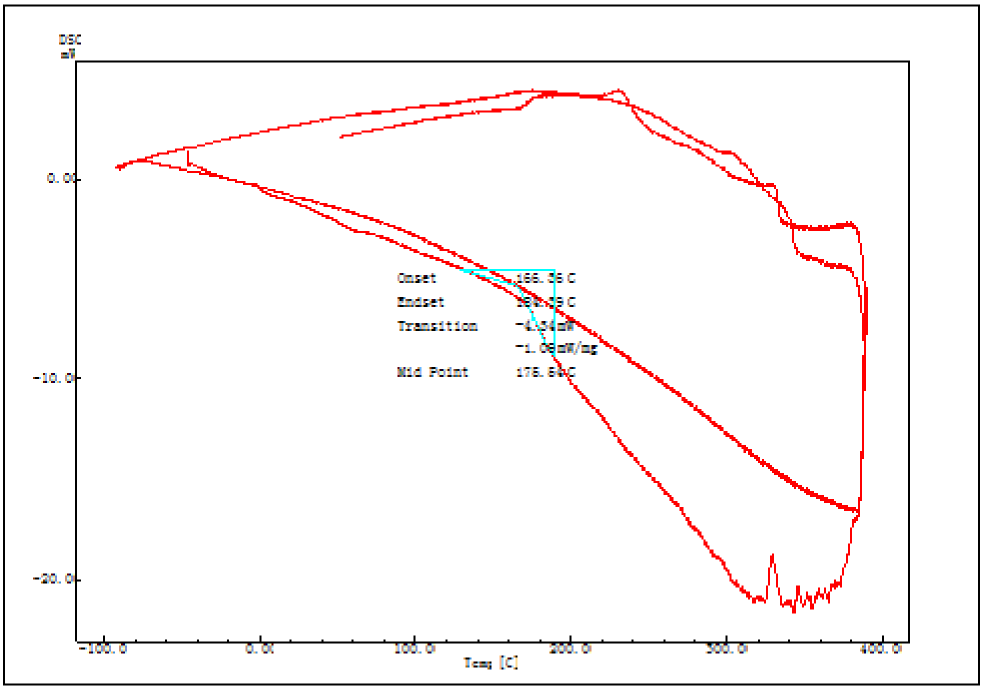
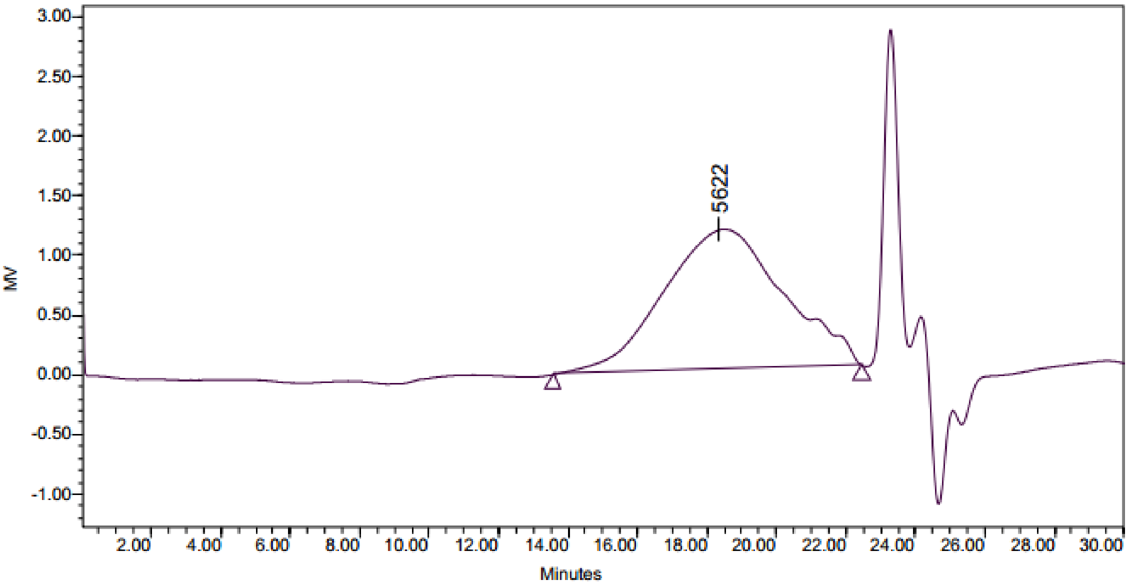


Figure S17. DSC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 14.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		4604	8914	5622	18301	33968	1.936221	2.053079	3.810678

Figure S18. GPC curve of the poly(CHD-*co*-IP) obtained by cationic species generated from complex **5** in Table 1, entry 14.

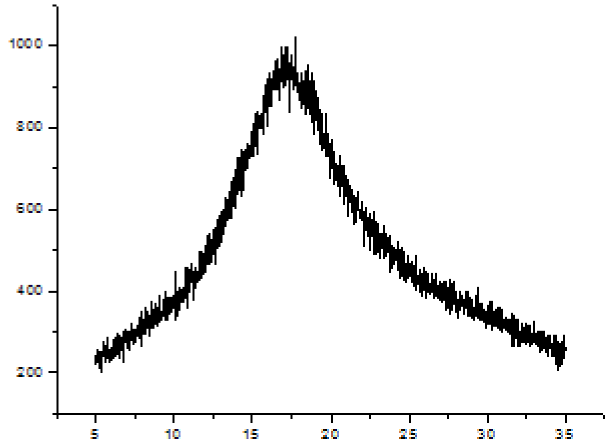


Figure S19. The X-ray powder diffraction pattern of the poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **8** in Table 2, entry 3.

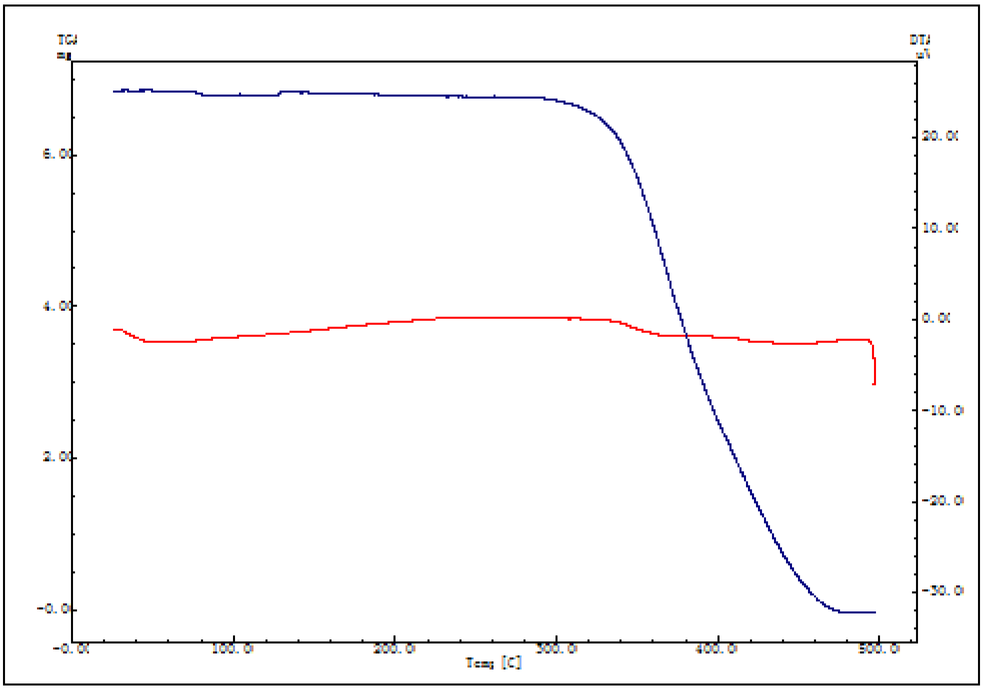


Figure S20. TGA curve of the poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **8** in Table 2, entry 3.

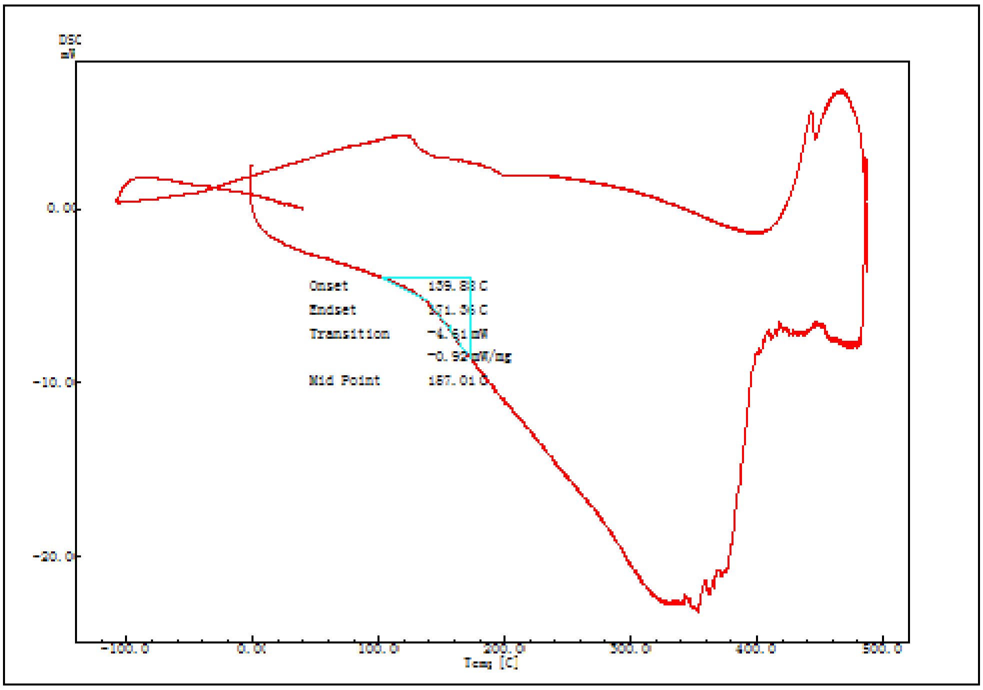
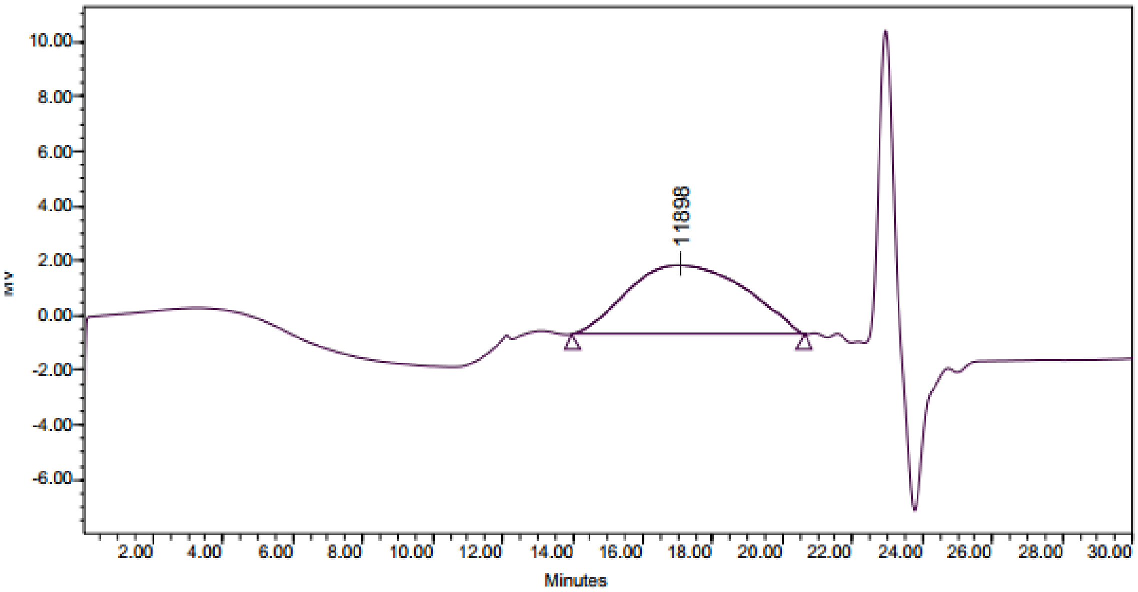


Figure S21. DSC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **8** in Table 2, entry 6.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		7370	14009	11898	23101	32094	1.900798	1.648945	2.290895

Figure S22. GPC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **8** in Table 2, entry 6.

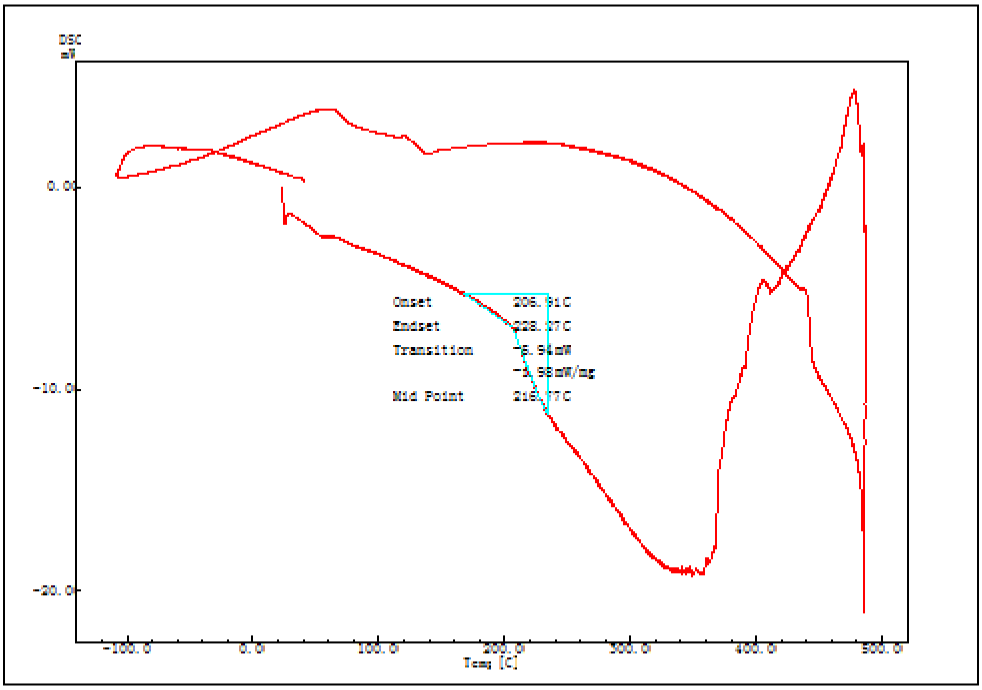
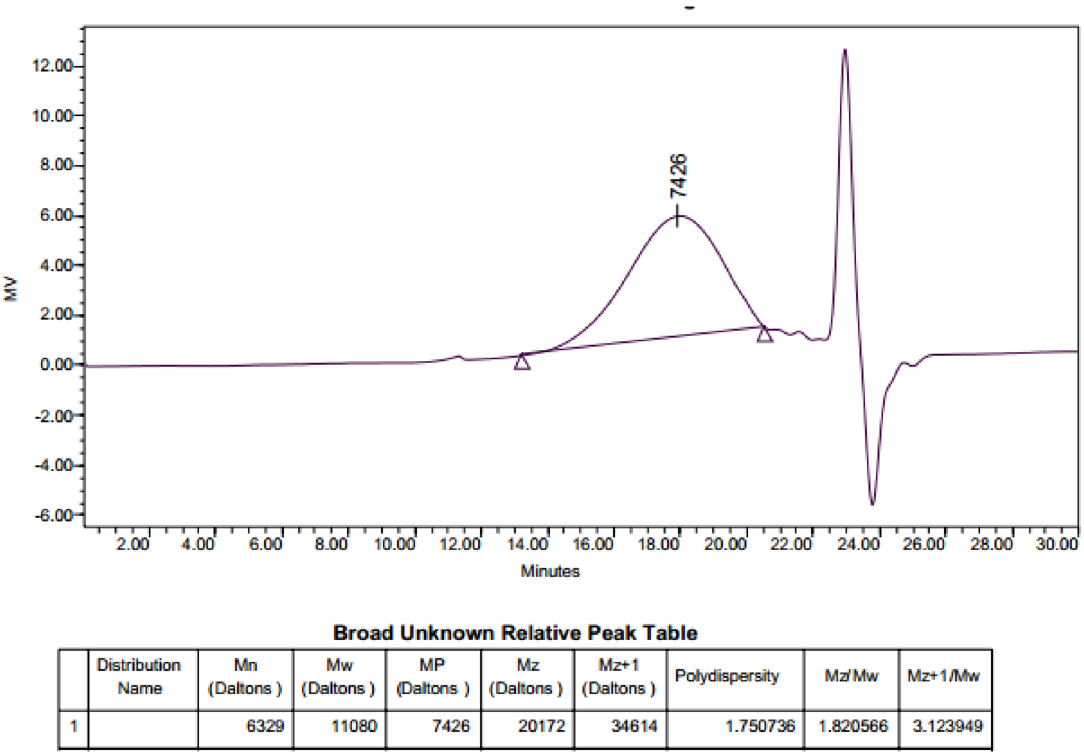


Figure S23. DSC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **8** in Table 2, entry 9.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		6329	11080	7426	20172	34614	1.750736	1.820566	3.123949

Figure S24. GPC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **8** in Table 2, entry 9.

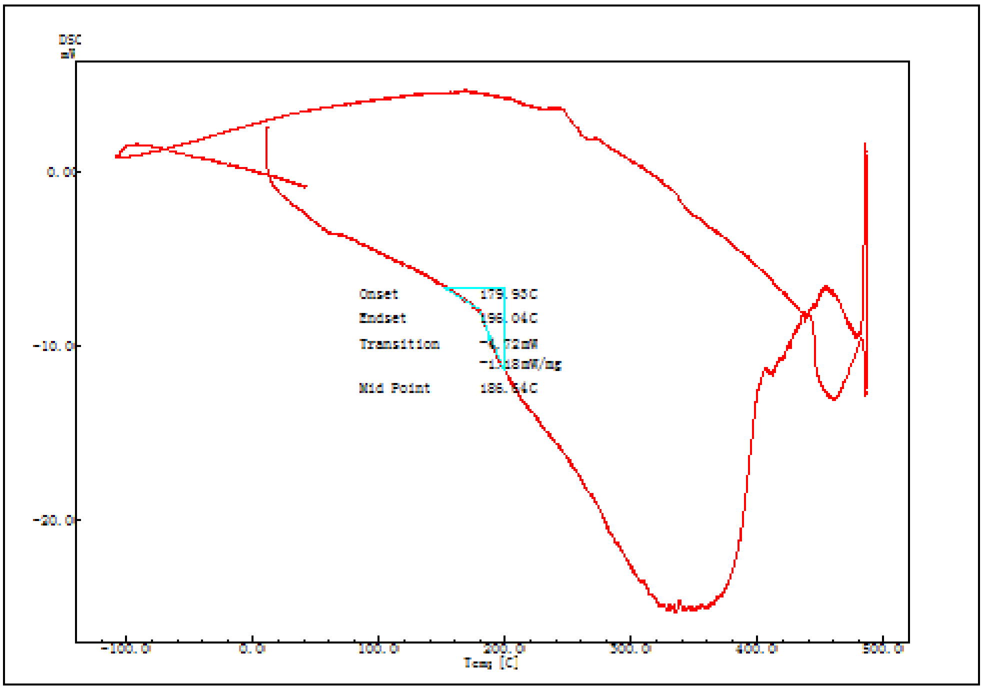
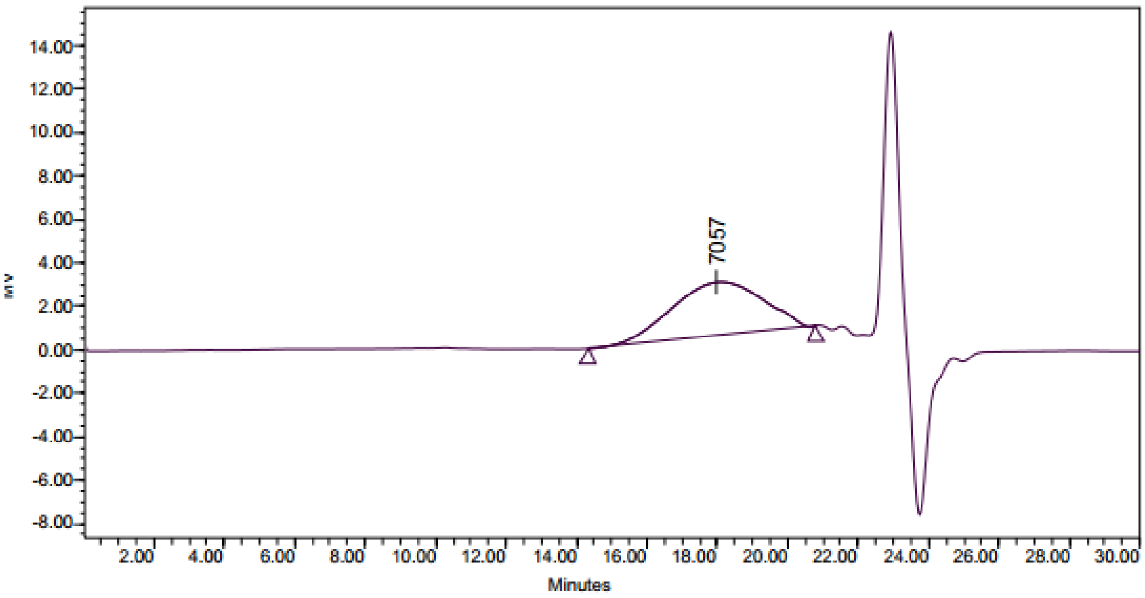


Figure S25. DSC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **8** in Table 2, entry 14.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		5731	8829	7057	12927	17397	1.540750	1.464046	1.970313

Figure S26. GPC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **8** in Table 2, entry 14.

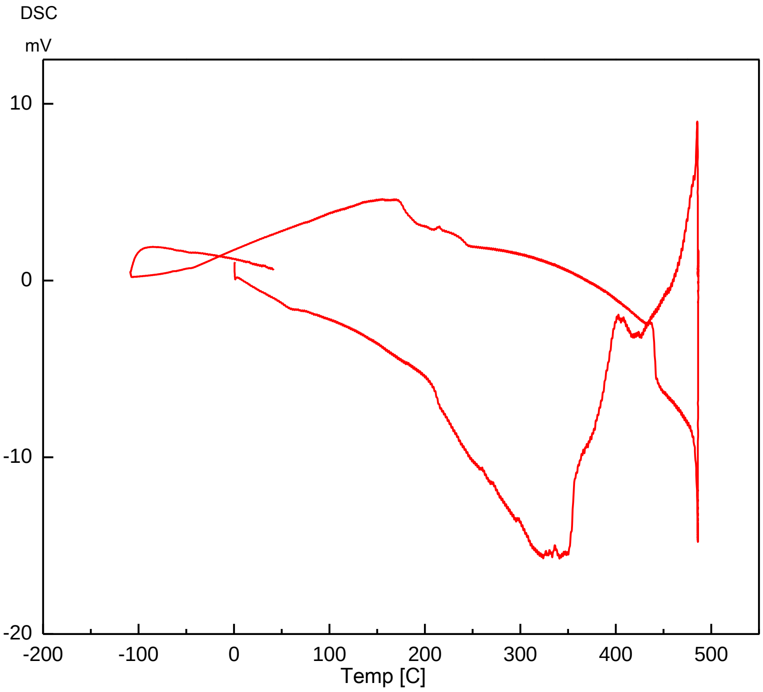
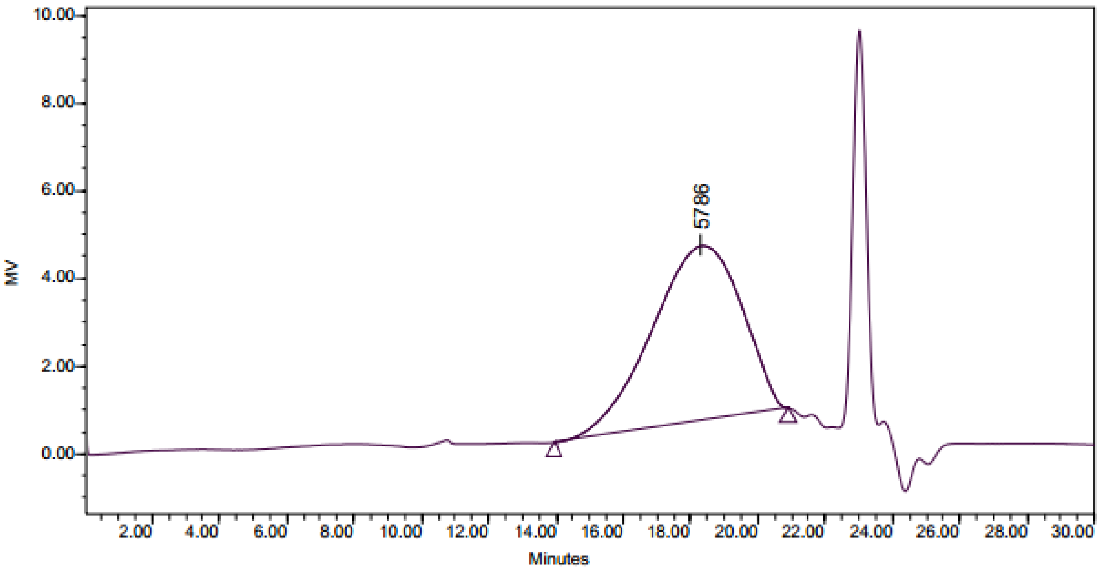


Figure S27. DSC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **9** in Table 2, entry 15.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		5208	8587	5786	14217	21637	1.648672	1.655655	2.519731

Figure S28. GPC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **9** in Table 2, entry 15.

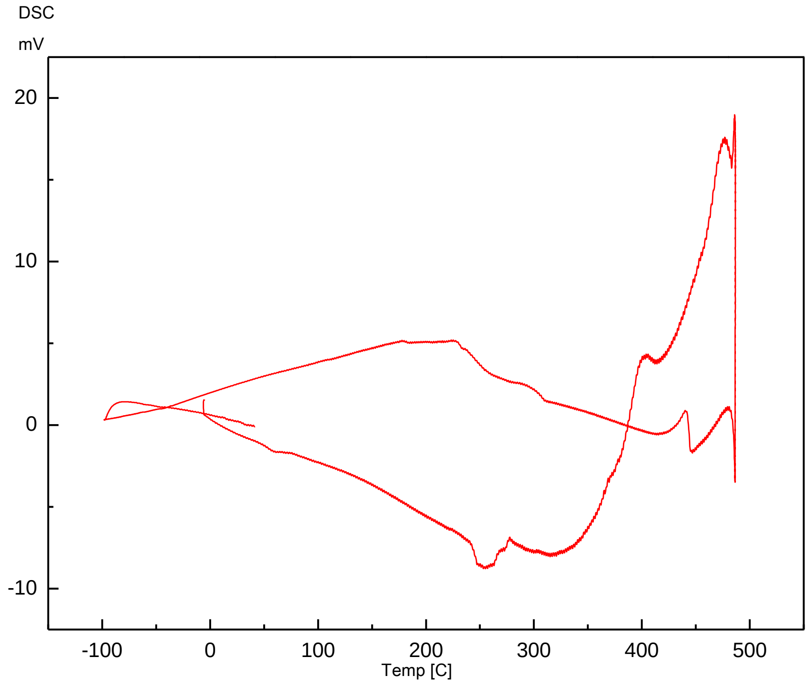
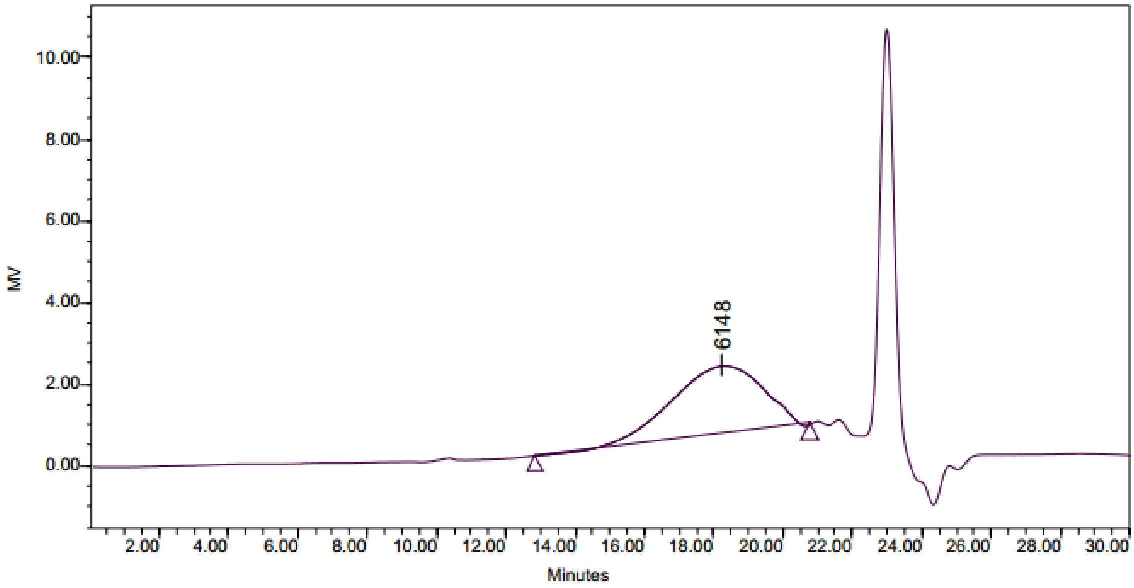


Figure S29. DSC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **10** in Table 2, entry 16.



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		5523	8951	6148	14461	21543	1.620821	1.615489	2.406634

Figure S30. GPC spectrum of poly(CHD-*co*-S-*co*-IP) obtained by cationic species generated from complex **10** in Table 2, entry 16.

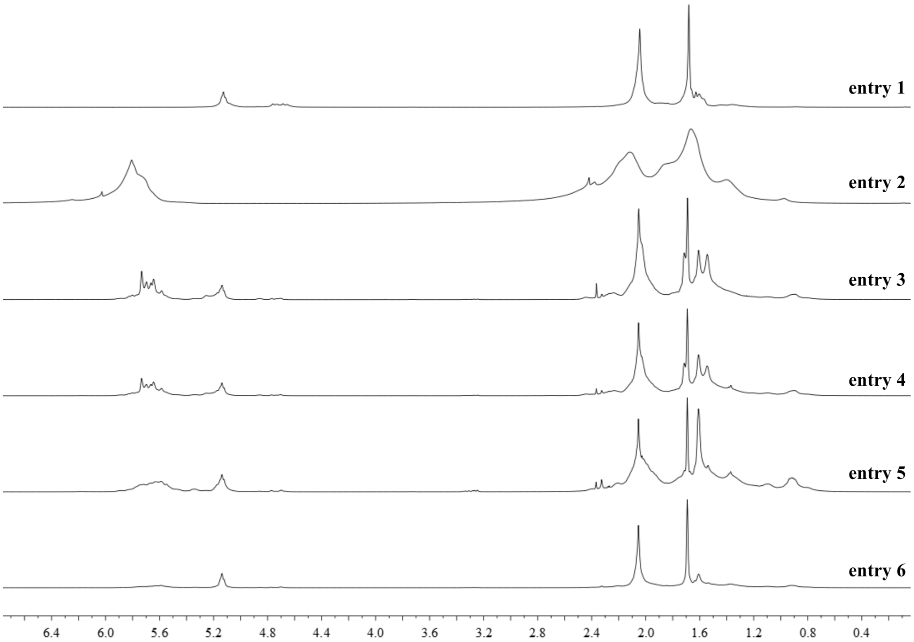


Figure S31. ^{1}H NMR spectra of PIP, PCHD and poly(CHD-*co*-IP)s obtained by cationic species generated from complex **1-5** (Table 1, entries 1–6).

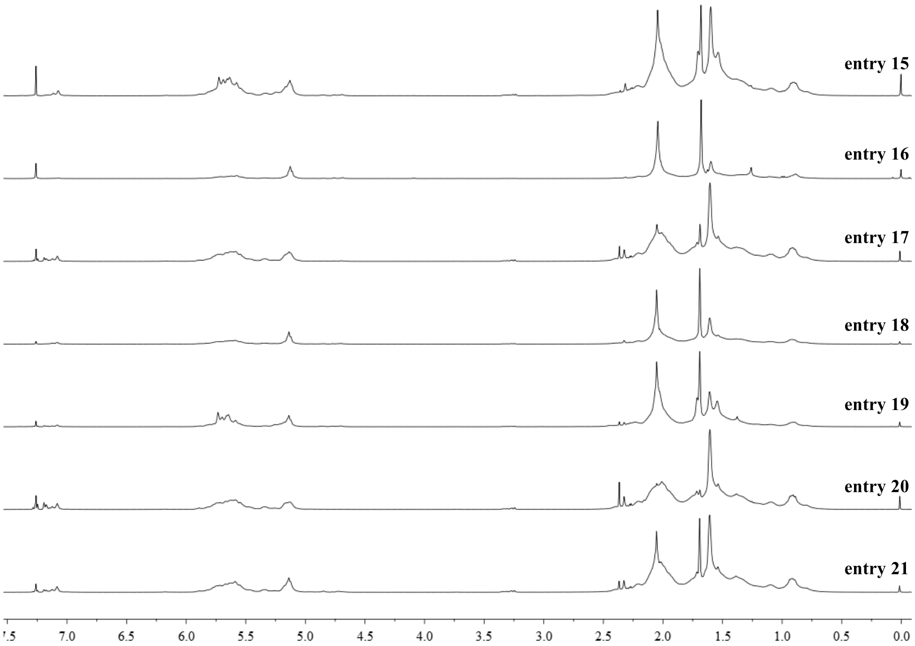


Figure S32. ^{1}H NMR spectra of poly(CHD-*co*-IP)s obtained by cationic species generated from complex **5-10** (Table 1, entries 15–21).

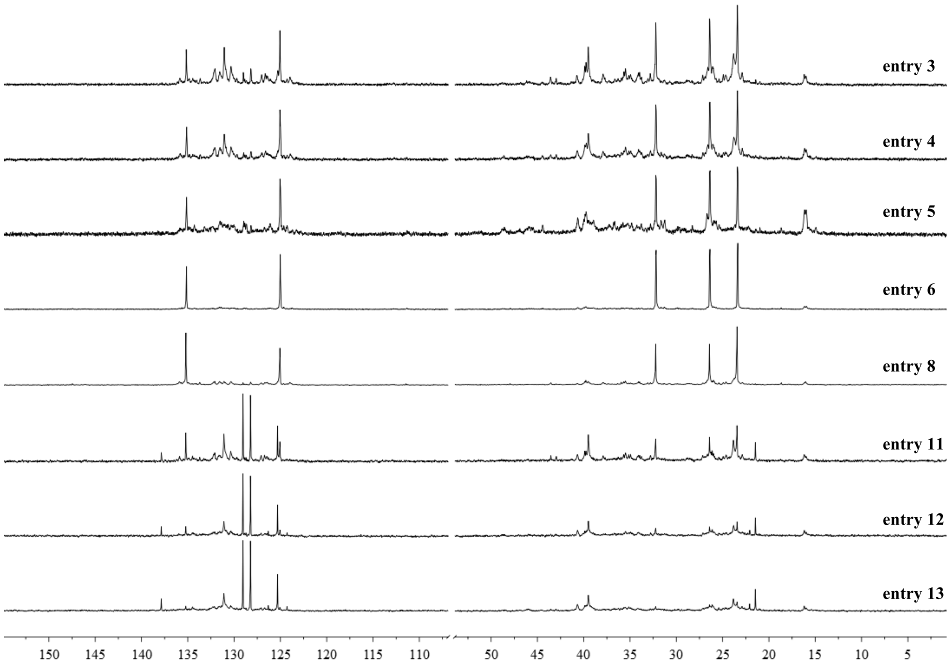


Figure S33. ^{13}C NMR spectra of poly(CHD-*co*-IP)s obtained by cationic species generated from complex **1-5** (Table 1, entries 3–6, 8, 11-13).

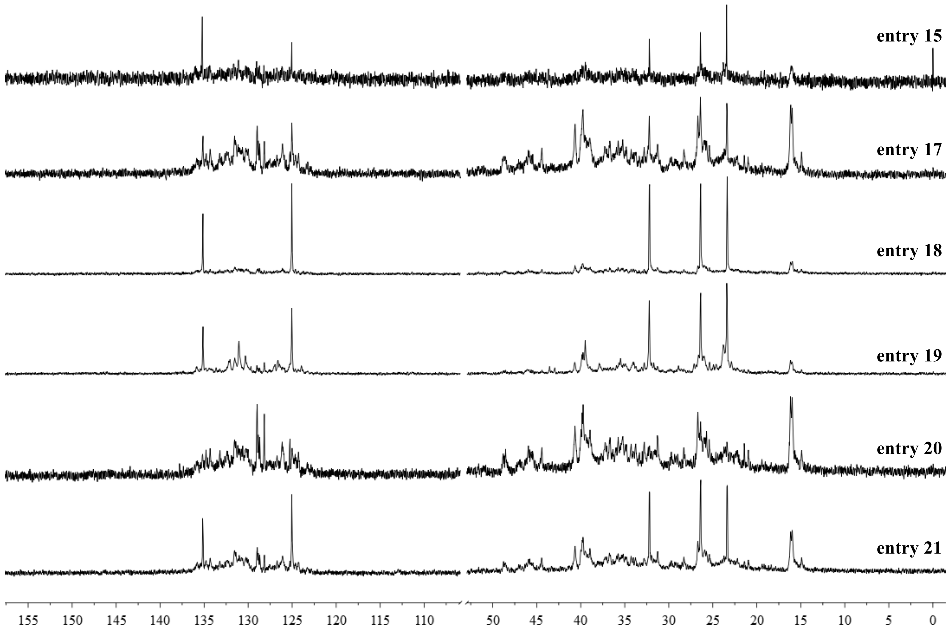


Figure S34. ^{13}C NMR spectra of poly(CHD-*co*-IP)s obtained by cationic species generated from complex **5-10** (Table 1, entries 15, 17-21).

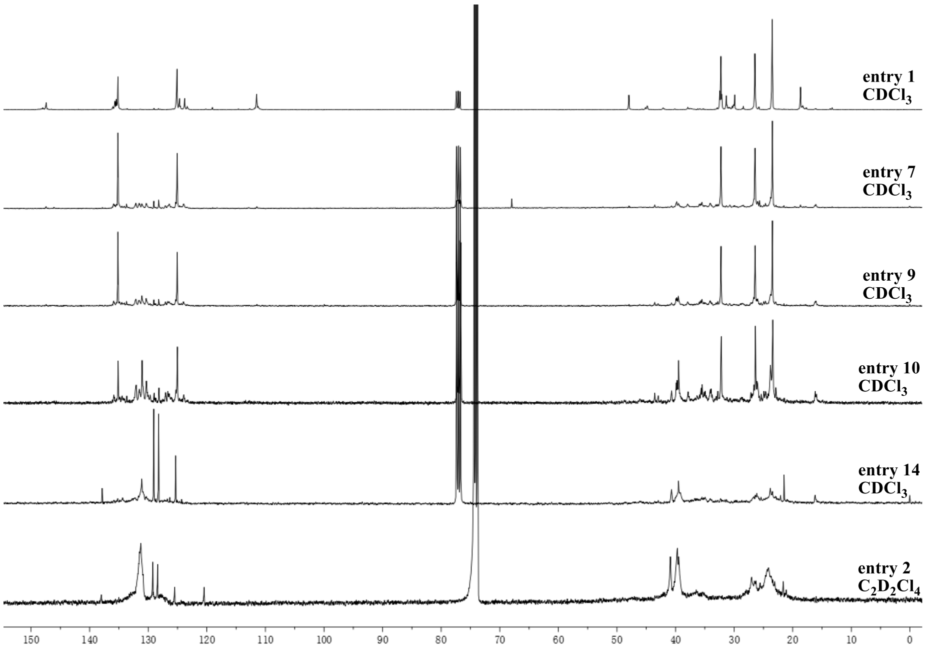


Figure S35. ^{13}C NMR spectra of poly(CHD-*co*-IP)s obtained by cationic species generated from complex **5** (Table 1, entries 1, 2, 7, 9, 10, 14).

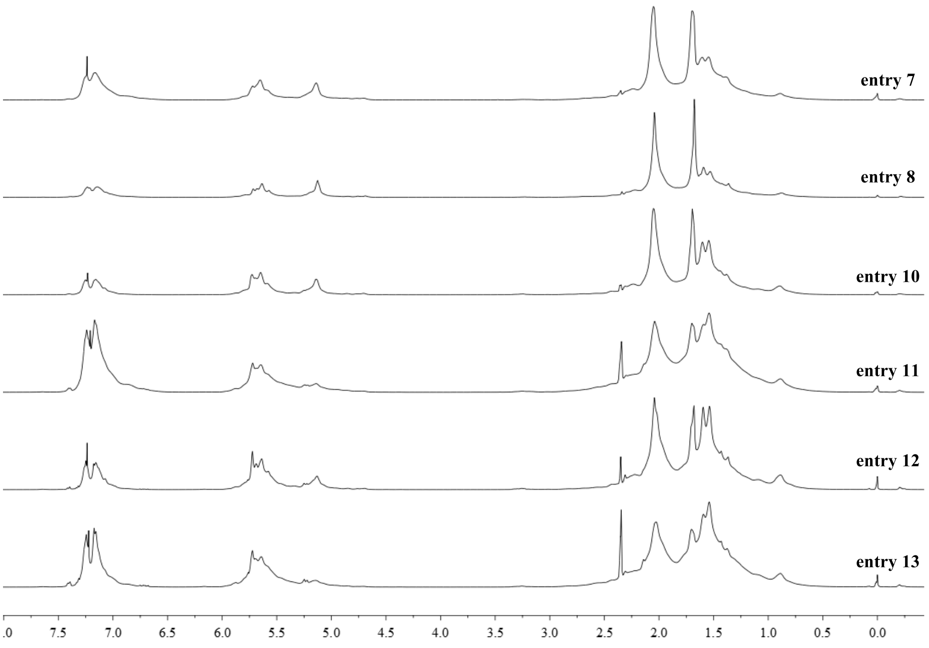


Figure S36. ^{1}H NMR spectra of terpolymers obtained by cationic species generated from complex **8** (Table 2, entries 7, 8, 10, 11–13).

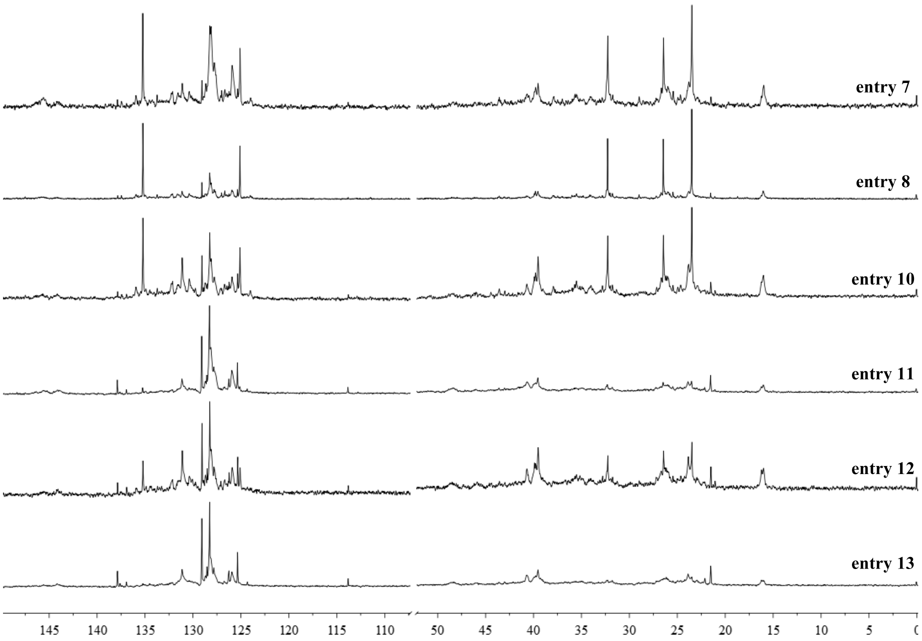


Figure S37. ^{13}C NMR spectra of terpolymers obtained by cationic species generated from complex **8** (Table 2, entries 7, 8, 10, 11–13).

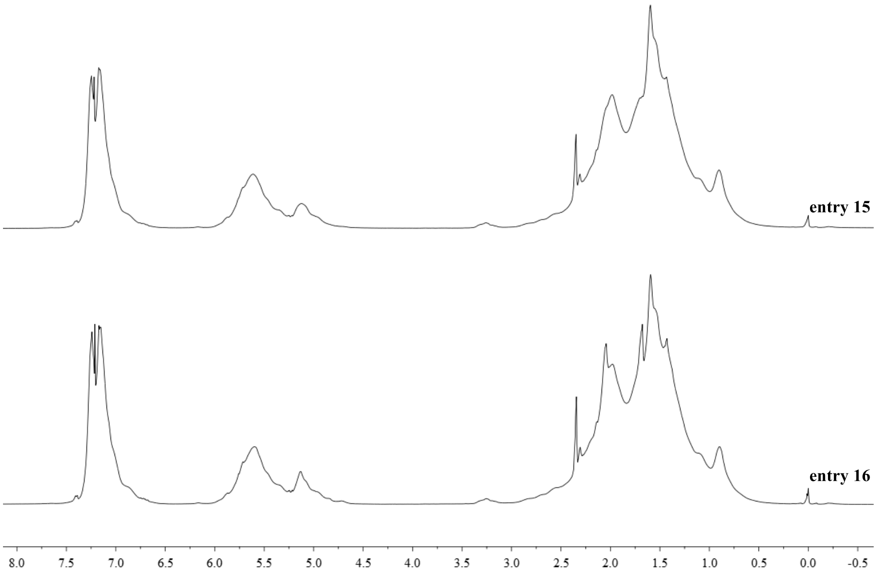


Figure S38. ^{1}H NMR spectra of terpolymers obtained by cationic species generated from complex **9**-**10** (Table 2, entries 15–16).

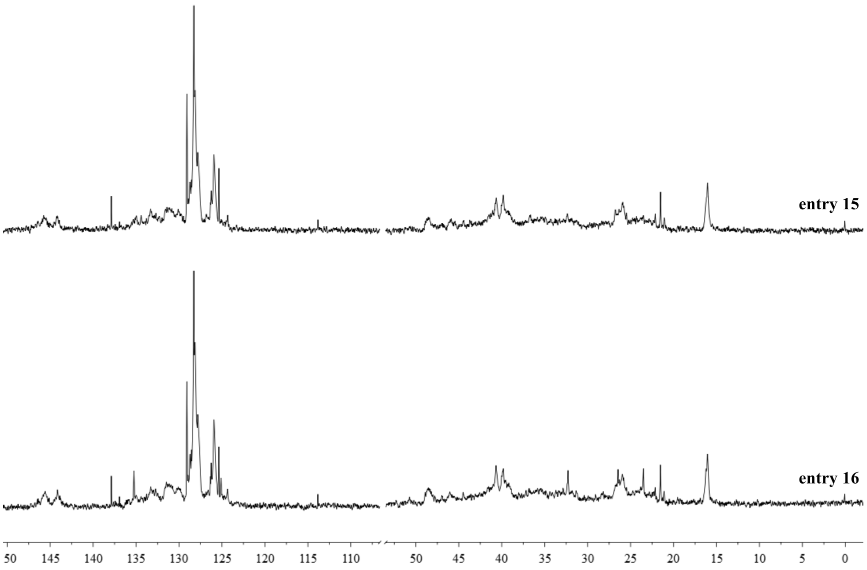


Figure S39. ^{13}C NMR spectra of terpolymers obtained by cationic species generated from complex **9**-**10** (Table 2, entries 15–16).

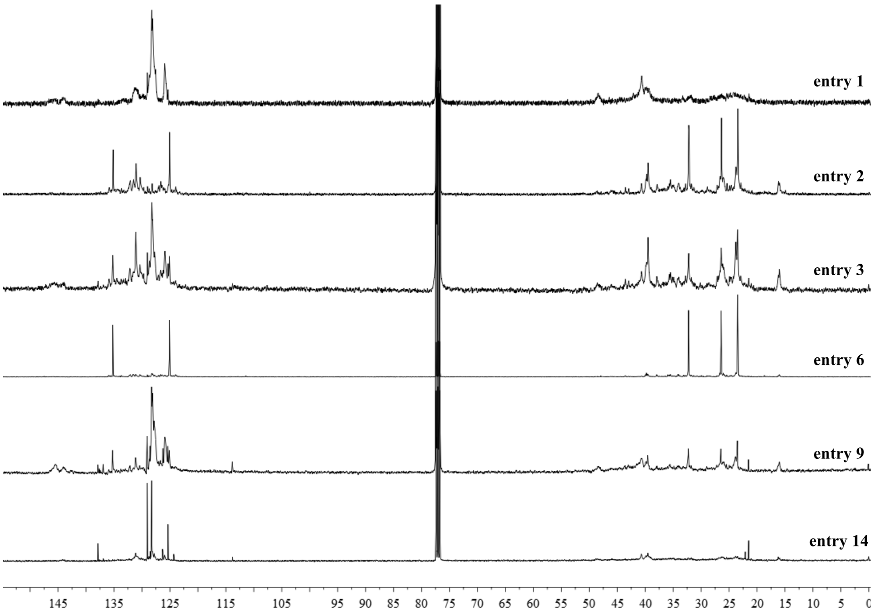


Figure S40. ^{13}C NMR spectra of terpolymers obtained by cationic species generated from complex **8** (Table 2, entries 1–3, 6, 9 and 14).

Scheme 1. Calculation of the Reactivity ratio.

Formula: Fineman-Ross plot

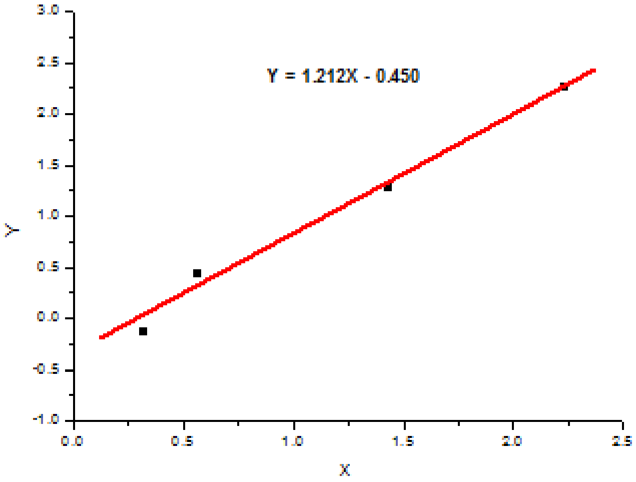
$$\frac{F}{f} * (f - 1) = r_1 * \frac{F^2}{f} - r_2$$

F: CHD/isoprene feed in the reaction

f: CHD/isoprene content in the copolymer

5/[Ph_3C][$B(C_6F_5)_4$]/Al^iBu_3 system:

Run	F	f	X	Y
1	3	4.030	2.233	2.256
2	2	2.795	1.431	1.284
3	1	1.765	0.567	0.433
4	0.5	0.785	0.318	-0.137



$$Y = 1.212X - 0.450$$

$r_{CHD} = k_{CC}/k_{CIP} = 1.212$ $r_{IP} = k_{IPIP}/k_{IPC} = 0.450$