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

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42. **Scheme 1.** Calculation of the Reactivity ratio.
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_{2}O Combi-Analyzer (Mbraun) to ensure both were always below 0.1 ppm. Anhydrous THF, hexane and toluene 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_{3}C][B(C_{6}F_{5})_{4}], [PhMe_{2}NH][B(C_{6}F_{5})_{4}], and B(C_{6}F_{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_{2}SiMe_{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-^2Bu_{2}C_{6}H_{4}, 9-SiMe_{2}C_{13}H_{4} and 2,7-^2Bu_{2}-9-SiMe_{2}C_{13}H_{7} and their lithium salts were synthesized according to the literature. Ln(C_{5}SiMe_{2})_{2}(THF)_{2}[B(C_{6}H_{4})_{4}] (Ln = Sc, Lu, Y) were synthesized according to the literature. The deuterated solvents benzene-d_{6} (99.6 atom% D), chloroform-d_{l} (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 (\textsuperscript{1}H, \textsuperscript{13}C) spectra of catalyst precursors were recorded on an AVANCE 400 spectrometer at room temperature with C_{6}D_{6} as a solvent. \textsuperscript{1}H, \textsuperscript{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 °C 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 °C/min from 30 °C to 500 °C. The DSC measurements were performed on a TA 60 (TA Co.) at a rate of 20 °C/min from 30 °C to 400 °C, cooling at 20 °C/min to -100 °C, 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_{3}SiMe_{3})_{2}(THF) (1). To a colorless THF solution (10 mL) of Sc(CH_{3}SiMe_{3})_{2}(THF)_{2}[B(C_{6}H_{4})_{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 °C to give 1 as light yellow solids (0.479 g, 1.05 mmol, 70% yield). \textsuperscript{1}H NMR (400 MHz, C_{6}D_{6}, 25 °C, δ/ppm): −0.74 (d, 4H, CH_{2}Si(CH_{3})_{3}), 0.24 (s, 18H, CH_{2}Si(CH_{3})_{3}), 0.98 (br, 4H, THF−β-CH_{2}), 3.08 (br, 4H, THF−α-CH_{2}), 6.88–7.80 (m, 9H, fluorenyl). \textsuperscript{13}C NMR (100 MHz, C_{6}D_{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_{30}OScSi_{2}: C, 65.75; H, 8.61. Found: C, 65.29; H, 8.26.
Synthesis of (2,7'-Bu2Flu)Sc(CH3SiMe3)2(THF)2 (2). To a colorless THF solution (10 mL) of Sc(CH3SiMe3)2[THF]2[B(C6H5)4] (1.132 g, 1.50 mmol) was added a THF solution (10 mL) of 2,7'-Bu2FluLi, which was prepared by the reaction of 2,7'-Bu2Flu (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 °C to give 2 as light yellow solids (0.614 g, 1.08 mmol, 72% yield). 1H NMR (400 MHz, C6D6, 25 °C, δ/ppm): −0.79 (d, 4H, CH2Si(CH3)3), 0.26 (s, 18H, CH2Si(CH3)3), 1.11 (br, 4H, THF-β-CH2), 1.39 (s, 18H, C(CH3)3), 3.24 (br, 4H, THF-α-CH2), 6.95–7.85 (m, 7H, fluorenyl). 13C NMR (100 MHz, C6D6, 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 C33H35OScSi3: C, 69.67; H, 9.74. Found: C, 69.96; H, 9.96.

Synthesis of (2,7'-Bu2Flu)Lu(2,7'-Me2Flu)2(THF)2 (3). To a colorless THF solution (10 mL) of Lu(CH3SiMe3)2[THF]2[B(C6H5)4] (1.327 g, 1.50 mmol) was added a THF solution (10 mL) of 2,7'-Bu2FluLi, which was prepared by the reaction of 2,7'-Bu2Flu (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 °C to give 3 as light yellow solids (0.713 g, 1.02 mmol, 68% yield). 1H NMR (400 MHz, C6D6, 25 °C, δ/ppm): −0.79 (d, 4H, CH2Si(CH3)3), 0.26 (s, 18H, CH2Si(CH3)3), 1.11 (br, 4H, THF-β-CH2), 1.39 (s, 18H, C(CH3)3), 3.24 (br, 4H, THF-α-CH2), 6.95–7.85 (m, 7H, fluorenyl). 13C NMR (100 MHz, C6D6, 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 C33H35OScSi3: C, 69.67; H, 9.74. Found: C, 69.96; H, 9.96.

Synthesis of (2,7'-Bu2Flu)Y(2,7'-Me2Flu)2(THF)2 (4). To a colorless THF solution (10 mL) of Y(CH3SiMe3)2[THF]2[B(C6H5)4] (1.198 g, 1.50 mmol) was added a THF solution (10 mL) of 2,7'-Bu2FluLi, which was prepared by the reaction of 2,7'-Bu2Flu (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 °C to give 4 as light yellow solids (0.668 g, 0.98 mmol, 65% yield). 1H NMR (400 MHz, C6D6, 25 °C, δ/ppm): −0.11 (s, 4H, CH2Si(CH3)3), 0.25 (s, 18H, CH2Si(CH3)3), 1.23 (br, 8H, THF-β-CH2), 1.39 (s, 18H, C(CH3)3), 3.41 (br, 8H, THF-α-CH2), 6.71–7.86 (m, 7H, fluorenyl). 13C NMR (100 MHz, C6D6, 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 C37H40OYSi2: C, 64.88; H, 9.27. Found: C, 64.77; H, 9.13.

Synthesis of (9-SiMe2Flu)Sc(2,7'-Me2Flu)2(THF)2 (5). To a colorless THF solution (10 mL) of Sc(CH3SiMe3)2[THF]2[B(C6H5)4] (1.132 g, 1.50 mmol) was added a THF solution (10 mL) of 9-SiMe2FluLi, which was prepared by the reaction of 9-SiMe2Flu (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 5 as light yellow crystals (0.595 g, 1.13 mmol, 75% yield). 1H NMR (400 MHz, C6D6, 25 °C, δ/ppm): −0.42 (d, 2H, CH2Si(CH3)3, J = 11.6 Hz), −0.26 (d, 2H, CH2Si(CH3)3, J = 11.2 Hz), 0.14 (s, 18H, CH2Si(CH3)3), 0.65 (s, 9H, Si(CH3)3), 1.03 (m, 4H, THF-β-CH2), 3.19 (m, 4H, THF-α-CH2), 7.04–8.02 (m, 8H, fluorenyl). 13C NMR (100 MHz, C6D6, 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 C38H42O3ScSi3: C, 63.59; H, 8.96. Found: C, 63.77; H, 9.27.

Synthesis of (9-SiMe2Flu)Lu(2,7'-Me2Flu)2(THF)2 (6). To a colorless THF solution (10 mL) of Lu(CH3SiMe3)2[THF]2[B(C6H5)4] (1.327 g, 1.50 mmol) was added a THF solution (10 mL) of 9-SiMe2FluLi, which was prepared by the reaction of 9-SiMe2Flu (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). 1H NMR (400 MHz, C6D6, 25 °C, δ/ppm): −1.05 (s, 4H, CH2Si(CH3)3), 0.15 (s, 18H, CH2Si(CH3)3), 0.66 (s, 9H, Si(CH3)3), 0.99 (br, 4H, THF-β-CH2), 3.11 (br, 4H, THF-α-CH2), 7.07–8.03 (m, 8H, fluorenyl). 13C NMR (100 MHz, C6D6, 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 C28H40OLuSi3: C, 51.04; H, 7.19. Found: C, 50.88; H, 7.12.

Synthesis of (9-SiMe3)FluY(CH2SiMe3)2(THF)2 (7). To a colorless THF solution (10 mL) of Y(CH2SiMe3)2(THF)3[B(C6H5)4] (1.198 g, 1.50 mmol) was added a THF solution (10 mL) of 9-SiMe3FluLi, which was prepared by the reaction of 9-SiMe3Flu (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). 1H NMR (400 MHz, C6D6, 25 °C, δ/ppm): −0.84 (s, 4H, CH2Si(CH3)3), 0.16 (s, 18H, CH2Si(CH3)3), 0.55 (s, 9H, Si(CH3)3), 0.99 (m, 4H, THF-β-CH2), 3.12 (m, 4H, THF-α-CH2), 7.04–8.04 (m, 8H, fluorenyl). 13C NMR (100 MHz, C6D6, 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 C28H40OLuSi3: C, 58.71; H, 8.27. Found: C, 58.62; H, 8.18.

Synthesis of (2,7′-Bu2-9-SiMe3Flu)Sc(CH2SiMe3)2(THF)2 (8). To a colorless THF solution (10 mL) of Sc(CH2SiMe3)2(THF)3[B(C6H5)4] (1.132 g, 1.50 mmol) was added a THF solution (10 mL) of 2,7′-Bu2-9-SiMe3FluLi, which was prepared by the reaction of 2,7′-Bu2-9-SiMe3Flu (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). 1H NMR (400 MHz, C6D6, 25 °C, δ/ppm): −0.50 (d, 2H, CH2Si(CH3)3), J = 11.2 Hz), −0.28 (d, 2H, CH2Si(CH3)3), J = 11.2 Hz), 0.13 (s, 18H, CH2Si(CH3)3), 0.76 (s, 9H, Si(CH3)3), 1.27 (m, 4H, THF-β-CH2), 1.43 (s, 18H, C(CH3)3), 3.32 (m, 4H, THF-α-CH2), 7.21–8.12 (m, 6H, fluorenyl). 13C NMR (100 MHz, C6D6, 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 C36H46OScSi3: C, 67.44; H, 9.90. Found: C, 67.02; H, 9.35.

Synthesis of (2,7′-Bu2-9-SiMe3Flu)Lu(CH2SiMe3)2(THF)2 (9). To a colorless THF solution (10 mL) of Lu(CH2SiMe3)2(THF)3[B(C6H5)4] (1.327 g, 1.50 mmol) was added a THF solution (10 mL) of 2,7′-Bu2-9-SiMe3FluLi, which was prepared by the reaction of 2,7′-Bu2-9-SiMe3Flu (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). 1H NMR (400MHz, C6D6, 25 °C, δ/ppm): −1.09 (s, 4H, CH2Si(CH3)3), 0.14 (s, 18H, CH2Si(CH3)3), 0.75 (s, 9H, Si(CH3)3), 1.09 (m, 4H, THF-β-CH2), 1.45 (s, 18H, C(CH3)3), 3.20 (m, 4H, THF-α-CH2), 7.23–8.16 (m, 6H, fluorenyl). 13C NMR (100 MHz, C6D6, 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 C38H48OLuSi3: C, 56.07; H, 8.23. Found: C, 55.99; H, 8.15.

Synthesis of (2,7′-Bu2-9-SiMe3Flu)Y(CH2SiMe3)2(THF)2 (10). To a colorless THF solution (10 mL) of Y(CH2SiMe3)2(THF)3[B(C6H5)4] (1.198 g, 1.50 mmol) was added a THF solution (10 mL) of 2,7′-Bu2-9-SiMe3FluLi, which was prepared by the reaction of 2,7′-Bu2-9-SiMe3Flu (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
A typical procedure for the regioselective copolymerization of 1,3-cyclohexadiene with isoprene (Table 1, entry 10). In the glove box, M′Bu3 (0.55 mL, 600 μmol) and a toluene solution (3 mL) of [Ph3C][Br(C6F5)4] (37 mg, 40 μmol) was added to a toluene solution (2 mL) of (9-SiMe2Flu)Sc(CH2SiMe3)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 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). 1H NMR (400 MHz, CD6, 25 °C, δ/ppm): 8 -0.88 (s, 4H, CH2Si(CH3)3), 0.15 (s, 18H, CH3Si(CH3)3), 0.76 (s, 9H, Si(CH3)3), 1.07 (m, 4H, THF-β-CH2), 1.44 (s, 18H, C(CH3)3), 3.25 (m, 4H, THF-α-CH2), 7.22–8.15 (m, 6H, fluorenyl). 13C NMR (100 MHz, CD6, 25 °C, δ/ppm): 21.4, 43.3, 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 C30H30OYSi3: C, 63.12; H, 9.27. Found: C, 63.03; H, 9.18.

In the 1H NMR spectra, CHD regioselectivity is determined by the integration ratio of the resonances at 1.18 ppm (one vinyl proton of the 1,4-isoprene unit) and I13 is the integration of the resonance at 4.72 ppm (two vinyl protons of the 3,4-isoprene unit) in the 1H NMR spectrum.

In the 13C 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 1H and 13C NMR spectra according to the following formula (eqs. 1–5):2

\[
\text{Mol CHD\%} = \frac{0.5I_{H1}/(0.5I_{H1} + I_{H2} + 0.5I_{H3})}{100}
\]

\[
\text{Mol 1,4-IP\%} = \frac{I_{H1}/(I_{H1} + 0.5I_{H2})}{100}
\]

(eq. 1)

\[
\text{Mol 3,4-IP\%} = \frac{0.5I_{H2}/(I_{H1} + 0.5I_{H2})}{100}
\]

(eq. 2)

\[
\text{Mol cis-1,4-IP\%} = \frac{I_{C1}/(I_{C1} + I_{C2} + I_{C3})}{100}
\]

(eq. 3)

\[
\text{Mol trans-1,4-IP\%} = \frac{I_{C3}/(I_{C1} + I_{C2} + I_{C3})}{100}
\]

(eq. 4)

\[
\text{Mol 3,4-IP\%} = \frac{I_{C2}/(I_{C1} + I_{C2} + I_{C3})}{100}
\]

(eq. 5)

In which I11 is the integration of the resonance at 5.13 ppm (one vinyl proton of the 1,4-isoprene unit), and I12 is the integration of the resonance at 4.72 ppm (two vinyl protons of the 3,4-isoprene unit) in the 1H NMR spectrum. I1 is the integration of the signals at 23.5 ppm assigned as the methyl carbon of the cis-1,4-isoprene unit, and I2 is the integration of the signals at 18.8 ppm assigned as the methyl carbon of the 3,4-isoprene unit, while I3 is the integration of the signals at 16.2 ppm assigned as the methyl carbon of the trans-1,4-isoprene unit in the 13C 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\textsuperscript{III}Bu\textsubscript{3} (0.55 mL, 600\,\mu mol) and a toluene solution (3 mL) of [Ph\textsubscript{3}C][Br(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] (37 mg, 40 \, \mu mol) was added to a toluene solution (2 mL) of (2,7-9-SiMe\textsubscript{3}Flu)Sc(CH\textsubscript{3}SiMe\textsubscript{3})\textsubscript{2}(THF) (27 mg, 40 \, \mu mol) 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\textsubscript{Ln}\textsuperscript{−1} h\textsuperscript{−1}). The product obtained is soluble thoroughly in CHCl\textsubscript{3} and THF at 25 °C. The 1,3-cyclohexadiene content and the isoprene content of the terpolymer was calculated according to the formula:

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

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

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 \(^1\text{H} \) NMR spectra.

In the \(^1\text{H} \) 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 \(^13\text{C} \) 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 \(^1\text{H} \) and \(^13\text{C} \) NMR spectra according to the following formula (eqs. 1–5):²

\[
\text{Mol 1,4-IP\%} = \frac{I_{H1}}{I_{H1} + 0.5I_{H2}} \times 100
\]

\[
\text{Mol 3,4-IP\%} = \frac{0.5I_{H2}}{I_{H1} + 0.5I_{H2}} \times 100
\]

\[
\text{Mol cis-1,4-IP\%} = \frac{I_{C1}}{I_{C1} + I_{C2} + I_{C3}} \times 100
\]

\[
\text{Mol trans-1,4-IP\%} = \frac{I_{C1}}{I_{C1} + I_{C2} + I_{C3}} \times 100
\]

\[
\text{Mol 3,4-IP\%} = \frac{I_{C2}}{I_{C1} + I_{C2} + I_{C3}} \times 100
\]

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 \(^1\text{H} \) 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 \(^13\text{C} \) NMR spectrum.

**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.

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.

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.

**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.

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.

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.

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.

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.

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.

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.

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.

**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.

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.

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

\[
\frac{F}{f} \times (f - 1) = r_1 \times \frac{f^2}{f} - r_2
\]

F: CHD/isoprene feed in the reaction
f: CHD/isoprene content in the copolymer
5\text{[Ph}_3\text{C]}\text{[B(C}_6\text{F}_5)_4]}/\text{Al}^1\text{Bu}_3 \text{ system:}

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</table>

$Y = 1.212X - 0.450$

$r_{\text{CHD}} = k_{\text{CC}}/k_{\text{CP}} = 1.212$ \hspace{1cm} $r_{\text{IP}} = k_{\text{IP}}/k_{\text{PC}} = 0.450$