

Supporting Information

Sequence and Regularity Controlled Coordination Copolymerization of Butadiene and Styrene: Strategy and Mechanism

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Experimental Section

General Procedures and Materials. All operations were performed under dry argon by using Schlenk techniques. Toluene was purified through alumina column (Mbraun SPS). 1, 3-butadiene was purchased from Beifang Special Gases Corporation and used without purification, the gas was dissolved in toluene at -30 °C. Styrene was dried over CaH₂ under stirring for 48 h and distilled under reduced pressure before use. The complexes (Py-CH₂-Flu)Ln(CH₂SiMe₃)₂(THF)_n (Ln = Sc, Tm, Y, Nd) were synthesized according to literature procedures.^[1] [Ph₃C][B(C₆F₅)₄] was prepared following the literature procedures.^[2]

Preparation of butadiene toluene solution. An ampoules with 140 g dried toluene, an empty ampoules, butadiene steel bottle and the Schlenk line were connected to a four-way joint tube. The system was pumped and charged in with nitrogen for three times, then the empty ampoules was put into a Dewar flask with liquid nitrogen, butadiene can be condensed in the ampoules from the butadiene steel bottle at the low temperature (-196 °C). When the liquid butadiene was enough, the toluene was poured into the ampoule with butadiene. After the system was warmed to room temperature slowly, the butadiene in toluene solution was obtained. The solution should be weighted to calculate the concentration of the butadiene. If the concentration exceeded 30%, a certain quality of toluene can be added into this solution. And, the solutions should be stored at -30 °C.

Typical procedure for butadiene and styrene copolymerization. A typical polymerization reaction is given below (entry 3, Table 1). In the glove box, styrene (2.08 g, 20 mmol) and butadiene (1.08g, 20 mmol, 30% butadiene in toluene) was added into a toluene solution(10mL) of AlⁱBu₃(50 μ mol) in 25 mL flask. Then, a toluene solution (3 mL) of **1** (6.5mg, 10 μ mol), 1 equiv [Ph₃C][B(C₆F₅)₄] (9.2 mg, 10 μ mol) and AlⁱBu₃(100 μ mol) was added to the flask. After stirring for 24 h (the magnetic stirring was ceased within some hours), methanol was injected to terminate the polymerization. The mixture was poured into a large quantity of methanol to precipitate the polymer product. The obtained white polymer was filtered and then dried under vacuum at 40 °C to a constant weight.

Typical procedure for kinetics investigation for the butadiene and styrene copolymerization. In the glove box, styrene (8.32 g, 80 mmol) and butadiene (4.32 g, 80 mmol, 30% butadiene in toluene) was added into a toluene solution (55.0 g) of

Al^iBu_3 (200 μmol) in 100 mL flask. Then, a toluene solution (5.0 g) of the precursor (40 μmol), 1 equiv $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (36.8 mg, 40 μmol) and Al^iBu_3 (200 μmol) were added to the flask. After stirring for 2 minute, the solution was divided into 15 reaction bottles immediately. The weights of the solution in every reaction bottle could be obtained from the difference value between the total weight of reaction bottle and the weight of empty bottle, so that the monomer in every reaction bottle can be obtained by calculation. The polymerization in the 15 reaction bottles should be quenched by methanol at different reaction time. Then, the mixture was poured into a large quantity of methanol to precipitate the polymer product. The obtained polymer was filtered and then dried under vacuum at 40 °C to a constant weight. The compositions of resulting copolymers were determined by ^1H NMR analysis.

Typical procedure for experimental evaluation of monomer reactivity ratios for the butadiene and styrene copolymerization. More than five copolymerizations at different monomer feed ratios were used to determinate the monomer reactivity ratios. A typical copolymerization reaction is given below (St:BD = 2000:2000). In the glove box, styrene (2.08 g, 20 mmol) and butadiene (1.08g, 20 mmol, 30% butadiene in toluene) was added into a toluene solution(10mL) of Al^iBu_3 (50 μmol) in 25 mL flask. Then, a toluene solution (3 mL) of the precursor (10 μmol), 1 equiv $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (9.2 mg, 10 μmol) and Al^iBu_3 (100 μmol) was added to the flask. After stirring for some minutes, methanol was injected to terminate the polymerization (the conversion of the copolymerization should be low than 5%). The mixture was poured into a large quantity of methanol to precipitate the polymer product. The obtained polymer was filtered and then dried under vacuum at 40 °C to a constant weight. The compositions of resulting copolymers were determined by ^1H NMR analysis.

Characterization of polymers. ^1H , ^{13}C NMR spectra of polymer samples were recorded on a Bruker AV400 (FT, 400 MHz for ^1H ; 100MHz for ^{13}C) spectrometer in tetrachloroethane- d_2 or 1, 2-dichlorobenzene - d_4 at 120 °C. The molecular weight and molecular weight distribution of the polymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220 type high-temperature chromatography equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C. T_g and T_m of polystyrene samples was measured through differential scanning calorimetry (DSC) analyses, which were carried out on a Q 100 DSC from TA Instruments under nitrogen atmosphere at heating and cooling rates of 10 °Cmin $^{-1}$ (temperature range: -120-300 °C). AFM was used to study the surface

topography of the spin-coated film. Images were obtained using a SPI3800N AFM (Seiko Instruments Inc., Japan) with a Si tip with a spring constant of 40 N m⁻¹. The cantilevers were operated slightly below their resonance frequency of around 200–400 kHz. The image acquisition was performed under ambient conditions. The AFM was used in tapping mode to reduce tip-induced surface degradation and sample damages. Imaging was conducted in the height and phase mode. Sample preparation: three drops (150 mL) of a 1.0 wt % solution in 1, 1, 2, 2-tetrachloroethane of the copolymer were spin-coated on a glass surface for 15–20 s under ambient conditions at a speed of 1500 rpm. The sample was then analyzed by AFM after drying overnight. The stress-strain behavior of four butadiene-styrene copolymers under uniaxial tension was performed on a WSM-20 kN instrument. The tensile specimens were cut from the compression-molded films with the thickness of 1.0 mm. The distance of two grips was 18 mm, and the specimen width was 4.0 mm. A strain rate of 50 mm/min was applied to uniaxial tension.

Equations used to determine composition.

$$\%1, 4\text{-selectivity} = \frac{A(5.22\text{-}5.44 \text{ ppm})}{A(5.22\text{-}5.44 \text{ ppm}) + A(4.84\text{-}4.98 \text{ ppm})} \times 100\%$$

$$\%St\text{-content} = \frac{A(6.32\text{-}6.84 \text{ ppm})}{A(6.32\text{-}6.84 \text{ ppm}) + A(5.22\text{-}5.44 \text{ ppm}) + A(4.84\text{-}4.98 \text{ ppm})} \times 100\%$$

X-ray Crystallographic Studies. The crystals were manipulated in a glovebox. Data collections were performed at 0 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The structures were solved by using SHELXTL program. Refinement was performed on F² anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. CCDC-1457830 (**3**) and 1457829 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

DFT calculations. All the calculations were performed with the Gaussian 09 program.^[3] The geometry structures of all species were optimized without constraints by DFT calculations at the B3LYP level. The effective core potential (ECP) Stuttgart/Dresden triple- ζ SDD basis set^[4] were chosen to describe Sc and Nd atoms,

and for H, C, N, and Si atoms, the 6-31G* basis set was used. Frequency calculations were carried out at the same level of theory to identify all of the stationary points as transition states (one imaginary frequency) or as minima (zero imaginary frequencies) and to provide the free energies at 298.15 K and 1 atm.

Reference

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Figure S8. ^1H NMR spectrum of BD-St copolymer (Table 1, entry 8) ($1, 2\text{-C}_6\text{D}_4\text{Cl}_2$, 120°C , 400 M Hz).

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Figure S17. Free energy profiles (in kcal/mol) for chain initiation of butadiene and styrene copolymerization catalyzed by Sc(4) based cationic active species **1Sc**.

Figure S18. X-ray structure of complex Tm(3) with thermal ellipsoids drawn at the 30% probability level.

Figure S19. X-ray structure of complex Sc(4)·THF with thermal ellipsoids drawn at the 30% probability level.

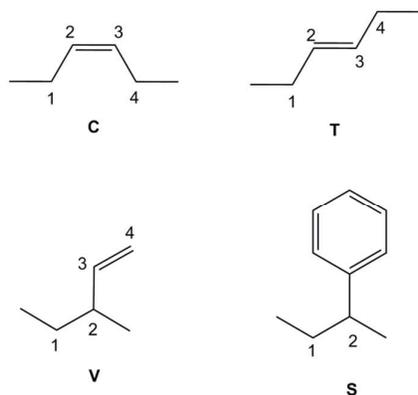


Chart 1

Table S1. Chemical Shifts of Alifatic Region in ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 100 MHz, 120 °C) of Copolymers Prepared by Precursor Nd(1)

chemical shift (ppm)	assignment	chemical shift (ppm)	assignment
25.32	C_4VC	34.70	CV_1C
27.78	CC_1C, CC_4C	41.35	SS_2S
32.83	T_1, T_4	43.73	CV_2C
33.01	CVC_1	44.56	SS_1S

Table S2. Chemical Shifts of Alifatic Region in ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 100 MHz, 120 °C) of Copolymers Prepared by Precursor Y(2)

chemical shift (ppm)	assignment	chemical shift (ppm)	assignment
25.33	C_4VC	40.89, 41.08	SS_2SC
27.78	$CC_1C, CC_4C, SSSC_4$	41.38	SS_2S, SS_2C
30.35	SSC_1	43.73	CV_2C
32.89	T_1, T_4	43.97	SS_1C
33.02	CVC_1	44.57	SS_1S, SS_1SC
34.70	CV_1C		

Table S3. Chemical Shifts of Alifatic Region in ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 100 MHz, 120 °C) of Copolymers Prepared by Precursor Tm(3)

chemical shift (ppm)	assignment	chemical shift (ppm)	assignment
25.32-25.45	C_4VC	41.50	SS_2C
27.77, 27.91	CC_1C, CC_4C, C_1SC	43.09	CCS_1
30.27-30.66	SC_1S, SSC_1, CSC_1	43.25	CS_2C
32.83	T_1, T_4	43.72	CV_2C
33.00	CVC_1	43.98	SS_1C

34.62	CV_1C	44.58	SS_1S
37.49	CCS_2	45.11	CS_1C
41.37	SS_2S		

Table S4. Chemical Shifts of Alifatic Region in ^{13}C NMR ($C_2D_2Cl_4$, 100 MHz, 120 °C) of Copolymers Prepared by Precursor Sc(4)

chemical shift (ppm)	assignment	chemical shift (ppm)	assignment
25.48	C_4VC	40.63	S_2T
27.77	$C_1SS, CC_1C, CC_4C, C_1SC$	41.37	SS_2S
29.80-30.43	SC_1S, SSC_1, CSC_1	41.50	SS_2C
32.83	T_1, T_4	43.25	CS_2S
34.46	CV_1C	43.88	CV_2C
37.49	CCS_2	43.98	SS_1C
38.17	V_1S	44.58	SS_1S
39.39	S_2V	45.11	CS_1C
40.06	V_2S		

Table S5. Monomer Feed Ratio F and Composition of Resulting Copolymer f during BD/St Copolymerization Catalyzed by Precursor Y(2).

Entry	$M_1(St)$ (mmol)	$M_2(BD)$ (mmol)	$F = M_1/M_2$ (in the feed)	$f=m_1/m_2$ (in the copolymer)	F_2/f	$F(f-1)/f$
1	20	1.25	16	3.3265	76.95776	11.19014
2	20	2.5	8	1.1685	54.77107	1.153616
3	20	5	4	0.3927	40.74357	-6.18589
4	20	10	2	0.1386	28.86003	-12.43
5	20	15	1.33	0.0762	23.21391	-16.1241

Table S6. Monomer Feed Ratio F and Composition of Resulting Copolymer f during BD/St Copolymerization Catalyzed by Precursor Tm(3).

Entry	$M_1(St)$ (mmol)	$M_2(BD)$ (mmol)	$F = M_1/M_2$ (in the feed)	$f=m_1/m_2$ (in the copolymer)	F_2/f	$F(f-1)/f$
1	20	10	2.000	0.3233	12.372	-4.186
2	20	15	1.333	0.1652	10.761	-6.738
3	20	20	1.000	0.1062	9.416	-8.416
4	15	20	0.750	0.0754	7.460	-9.197
5	10	20	0.500	0.0450	5.556	-10.611
6	5	20	0.250	0.0192	3.255	-12.771
7	2.5	20	0.125	0.0088	1.776	-14.080

Table S7. Monomer Feed Ratio F and Composition of Resulting Copolymer f during BD/St Copolymerization Catalyzed by Precursor Sc(4).

Entry	$M_1(St)$ (mmol)	$M_2(BD)$ (mmol)	$F = M_1/M_2$ (in the feed)	$f=m_1/m_2$ (in the copolymer)	F_2/f	$F(f-1)/f$
1	20	10	2.000	2.103	1.902	1.049
2	20	15	1.333	1.124	1.581	0.148

3	20	20	1.000	0.699	1.430	-0.430
4	15	20	0.750	0.549	1.025	-0.617
5	5	20	0.250	0.129	0.485	-1.689
6	2.5	20	0.125	0.061	0.256	-1.921

Table S8. Stress-Strain Data for Copolymers.^a

Sample	Tensile strength(MPa)	Elongation at failure (%)	Young's Modulus(MPa)
A	18.8	104.5	135.5
B	20.2	218.6	137.1
C	21.8	206.4	120.1
D	36.7	17.3	212.1

^a Strain rate =50 mm/min, 15 °C.

Table S9. Selected Bond Distances (Å) and Angles (deg) of Complexes Nd(1), Y(2), Tm(3) and Sc(4).

Precursor	Ln-Flu _{cent} distance(Å)	Ln-N distance(Å)	Ln-C ^a distancea(Å)	Bite angles(deg)
Nd(1)	2.595(4)	2.605(4)	2.462(4)	88.20(8)
Y(2)	2.465(5)	2.513(4)	2.388(6)	92.01(9)
Tm(3)	2.545(4)	2.477(4)	2.345(5)	91.71(10)
Sc(4)	2.879(6)	2.280(5)	2.233(6)	96.29(12)

^a an average distance of Ln-C_{alkyl}.

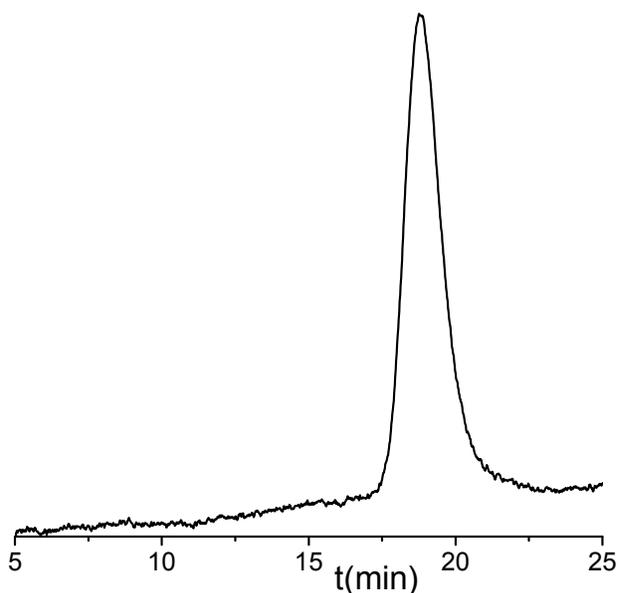


Figure S1. GPC curve of BD-St copolymer (Table 1 entry 1, $M_n = 16.8 \times 10^4$, $M_w/M_n = 1.34$).

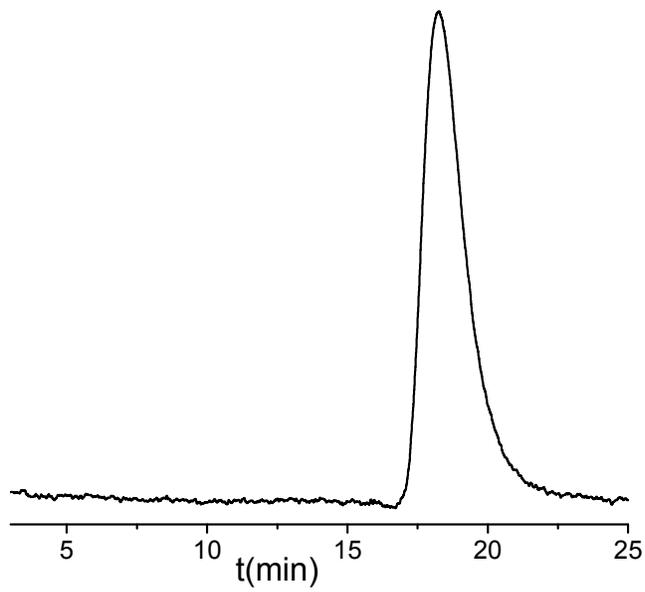


Figure S2. GPC curve of BD-St copolymer (Table 1 entry 2, $M_n = 23.8 \times 10^4$, $M_w/M_n = 1.29$).

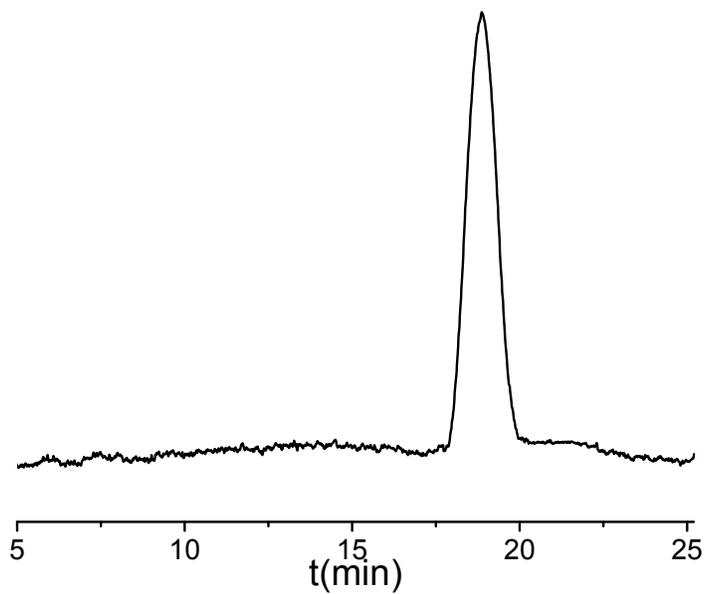


Figure S3. GPC curve of BD-St copolymer (Table 1 entry 5, $M_n = 16.1 \times 10^4$, $M_w/M_n = 1.15$).

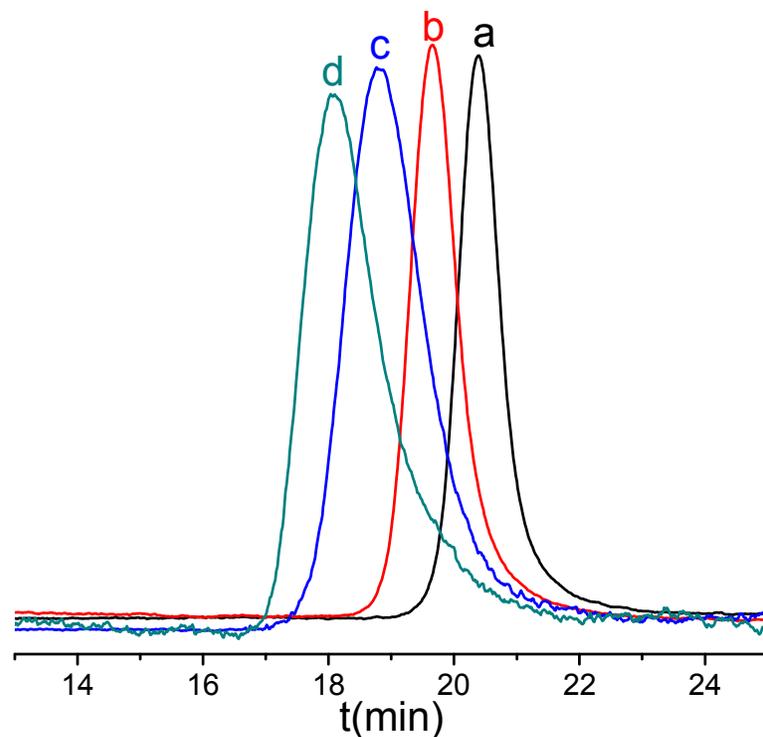


Figure S4. GPC curves of butadiene and styrene copolymer with different conversion catalyzed by precursor Nd(**1**). (a) 25.5% conversion, $M_n = 6.2 \times 10^4$, $M_w/M_n = 1.15$; (b) 44.8% conversion, $M_n = 10.9 \times 10^4$, $M_w/M_n = 1.18$; (c) 68.5 % conversion, $M_n = 14.4 \times 10^4$, $M_w/M_n = 1.23$. (d) 86.6 % conversion, $M_n = 26.3 \times 10^4$, $M_w/M_n = 1.26$. Conditions: (Nd(**1**)) (40 μ mol), [Ln]/[Al^{*i*}Bu₃]/[Ph₃C][B(C₆F₅)₄]/[St]/[BD] = 1/10/1/2000/2000 (mol/mol), total volume = 120 mL, $T_p = 15$ °C.)

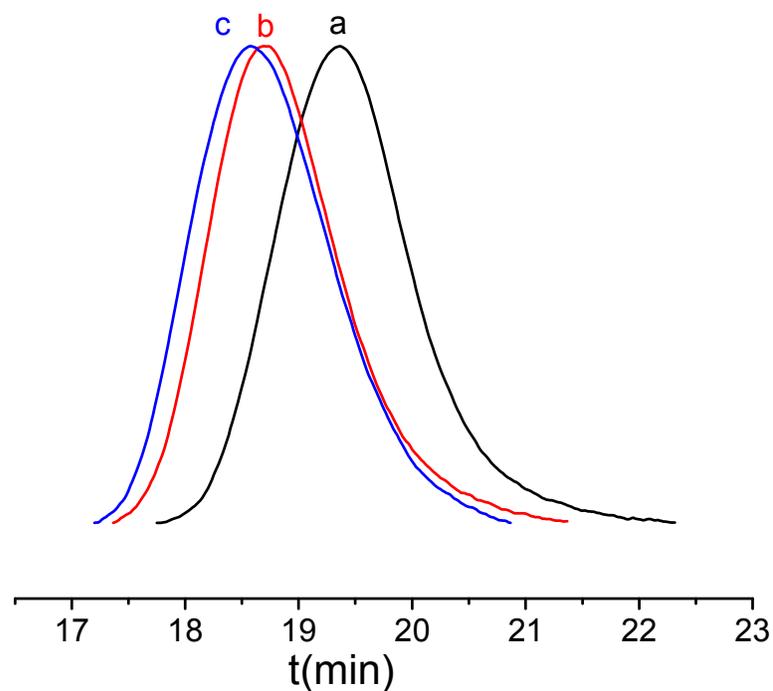


Figure S5. GPC curves of butadiene and styrene copolymer with different conversion catalyzed by precursor **Y(2)**. (a) 40.5% conversion, $M_n = 14.8 \times 10^4$, $M_w/M_n = 1.39$; (b) 88.3% conversion, $M_n = 25.6 \times 10^4$, $M_w/M_n = 1.35$; (c) 97.5 % conversion, $M_n = 29.4 \times 10^4$, $M_w/M_n = 1.33$. Conditions: (**Y(2)** ($40\mu\text{mol}$), $[\text{Ln}]/[\text{Al}^i\text{Bu}_3]/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/[\text{St}]/[\text{BD}] = 1/10/1/2000/2000$ (mol/mol), total volume = 100 mL, $T_p = 15$ °C.)

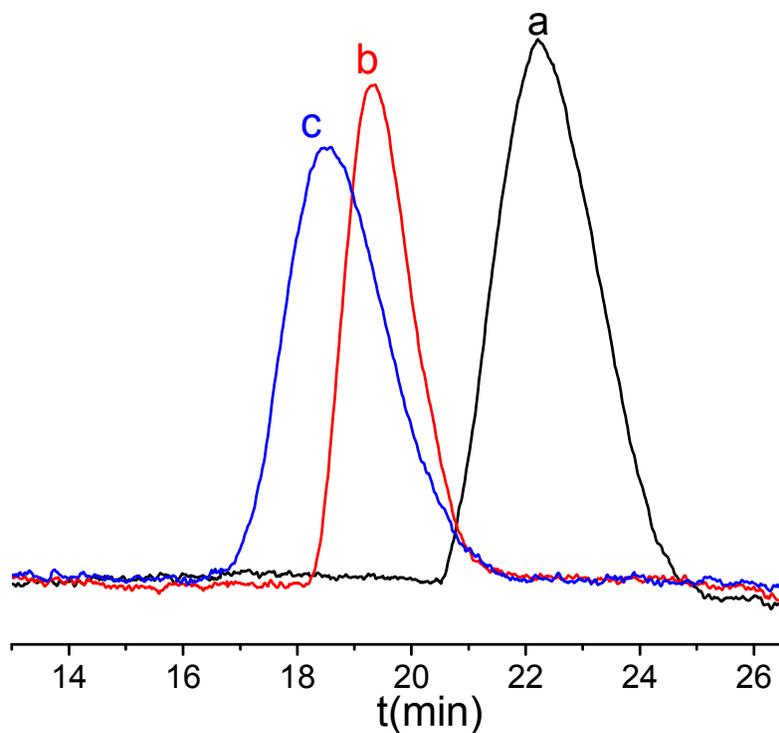


Figure S6. GPC curves of butadiene and styrene copolymer with different conversion catalyzed by precursor Tm(**3**). (a) 9.6 % conversion, $M_n = 2.1 \times 10^4$, $M_w/M_n = 1.60$; (b) 70.3% conversion, $M_n = 15.1 \times 10^4$, $M_w/M_n = 1.48$; (c) 90.5 % conversion, $M_n = 20.3 \times 10^4$, $M_w/M_n = 1.74$. Conditions: (Tm(**3**)) (40 μ mol), [Ln]/[AlⁱBu₃]/[Ph₃C][B(C₆F₅)₄]/[St]/[BD] = 1/10/1/2000/2000 (mol/mol), total volume = 100 mL, $T_p = 15$ °C.)

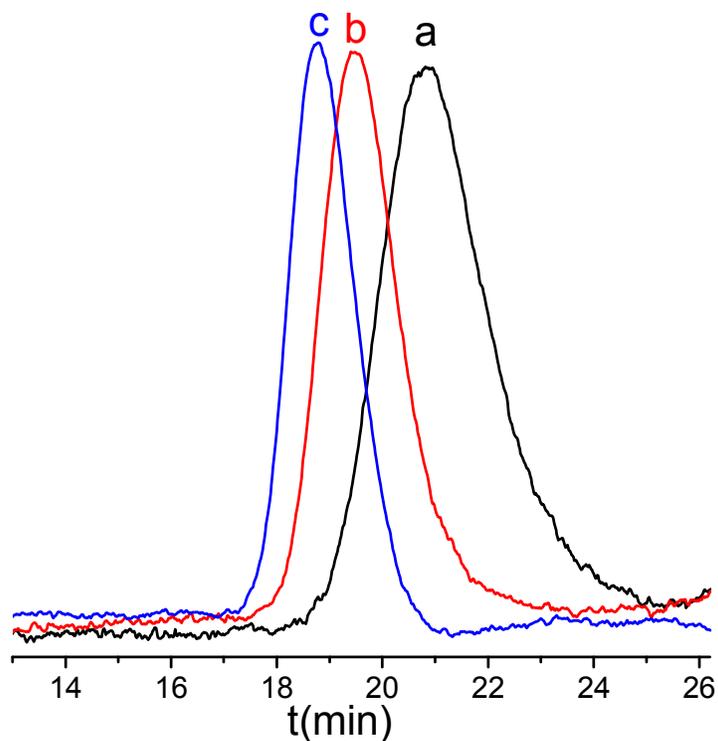


Figure S7. GPC curves of butadiene and styrene copolymer with different conversion catalyzed by precursor Sc(**4**). (a) 18.7% conversion, $M_n = 3.8 \times 10^4$, $M_w/M_n = 1.61$; (b) 40.3% conversion, $M_n = 13.1 \times 10^4$, $M_w/M_n = 1.37$; (c) 100 % conversion, $M_n = 25.4 \times 10^4$, $M_w/M_n = 1.30$. Conditions: (Sc(**4**)) ($40 \mu\text{mol}$), $[\text{Ln}]/[\text{Al}^i\text{Bu}_3]/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/[\text{St}]/[\text{BD}] = 1/10/1/2000/2000$ (mol/mol), total volume = 100 mL, $T_p = 15 \text{ }^\circ\text{C}$.)

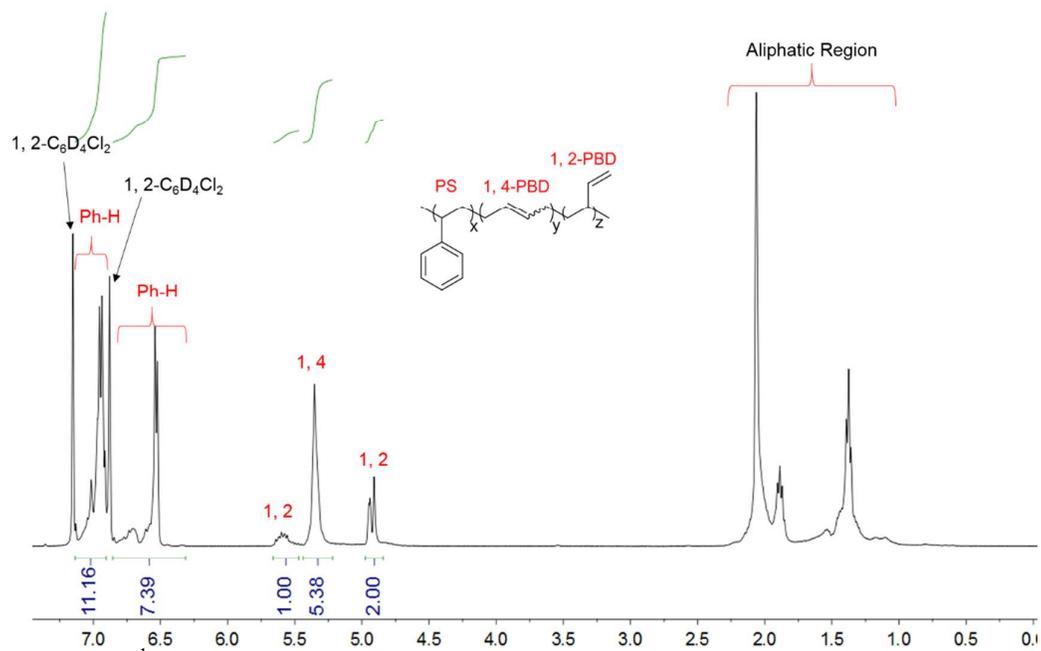


Figure S8. ^1H NMR spectrum of BD-St copolymer (Table 1, entry 8, St content = 50.0%, 1,4 selectivity = 72.8%) ($1, 2\text{-C}_6\text{D}_4\text{Cl}_2$, 120°C , 400 M Hz).

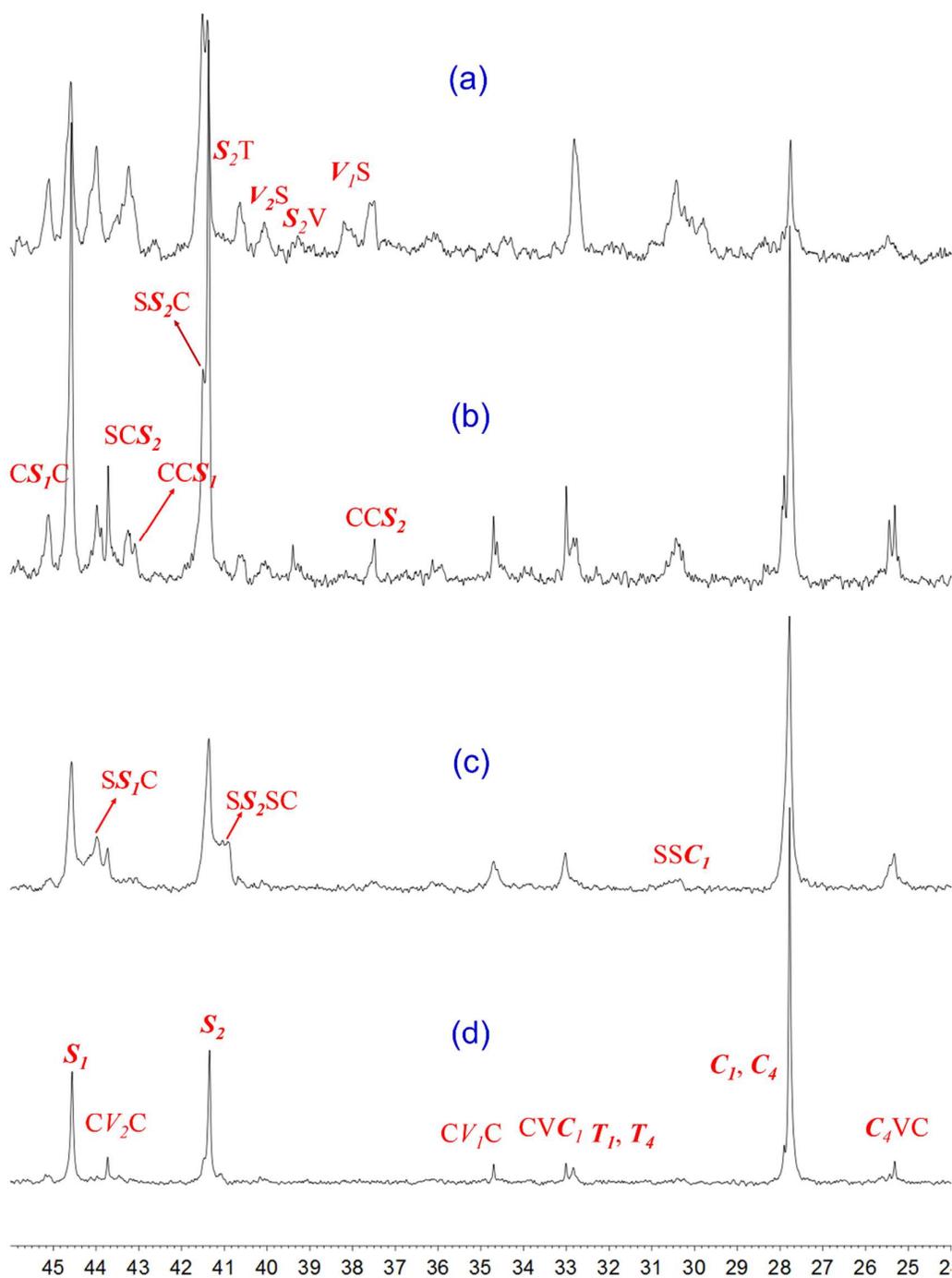


Figure S9. Aliphatic region of the ^{13}C NMR spectra ($\text{C}_2\text{D}_2\text{Cl}_4$, 120°C , 100 M Hz) of butadiene-styrene polymers: a (Table 1, entry 18, random), b (Table 1, entry 13, tapered), c (Table 1, entry 8, gradient) and d (Table 1, entry 3, diblock).

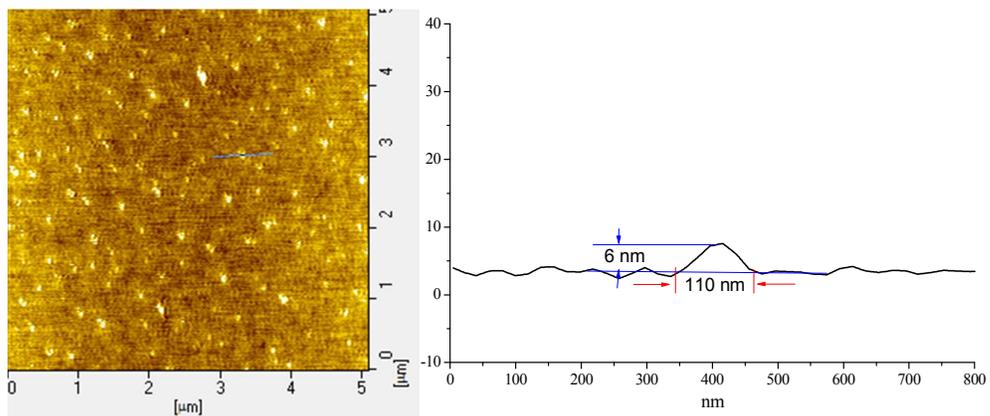
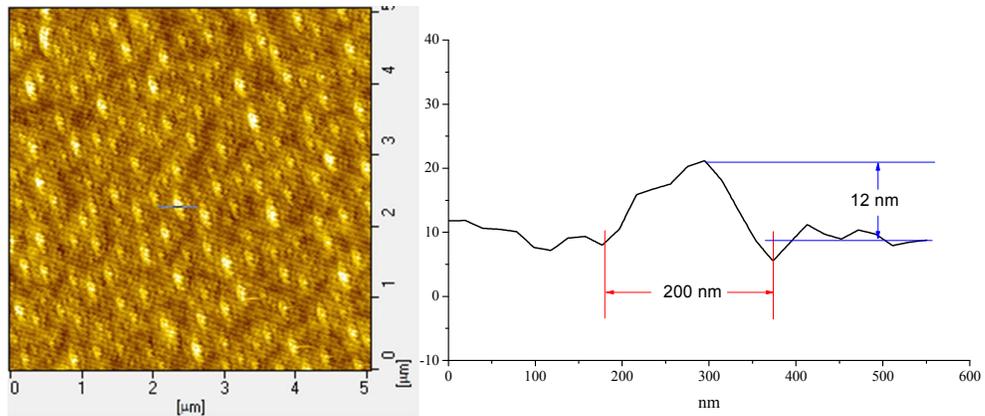
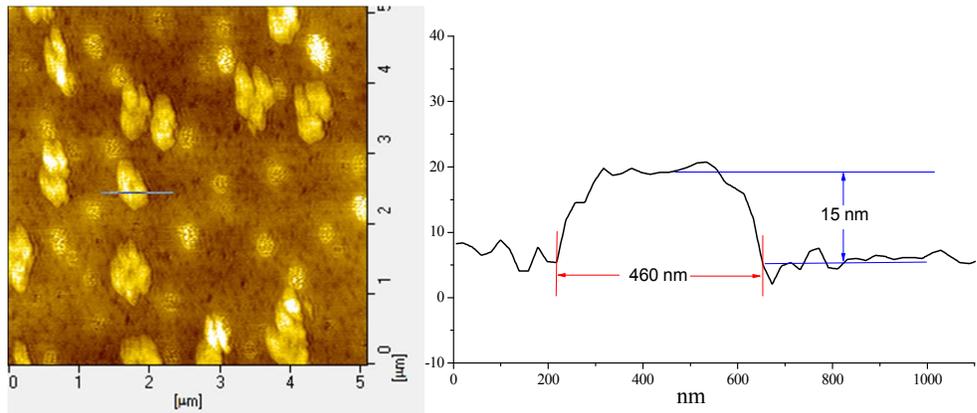
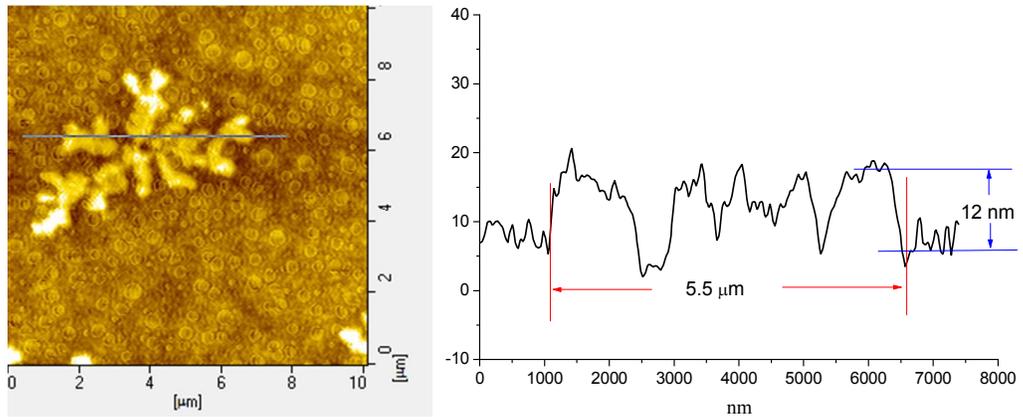


Figure S10. Line profile analysis of a hard nanodomain (entry 3, 8, 13 and 18).

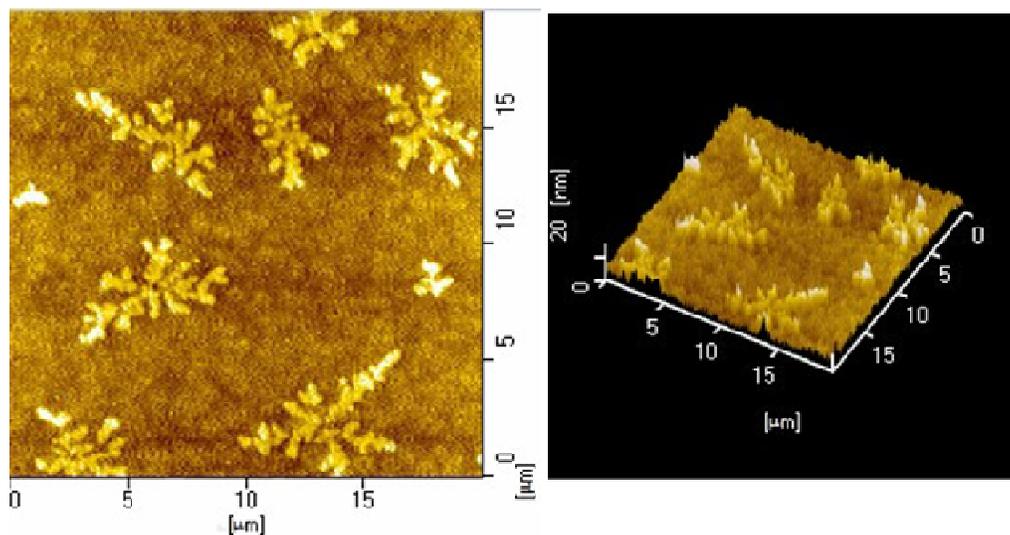


Figure S11. AFM phase contrast images with larger visual field of samples from Table 1, entry 3.

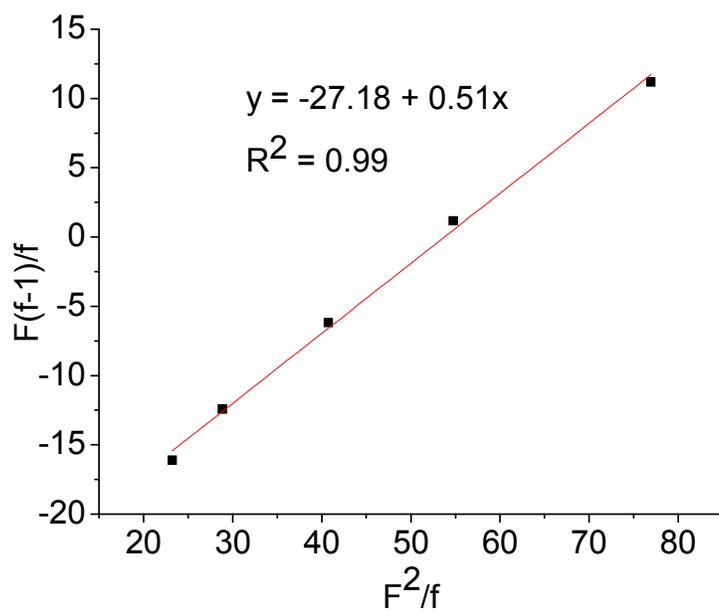


Figure S12. Fineman-Ross plot for copolymerization of BD/St catalyzed by Y(3) precursor ($r_{\text{St}}=0.51$, $r_{\text{BD}}=27.18$, $R^2=0.99$).

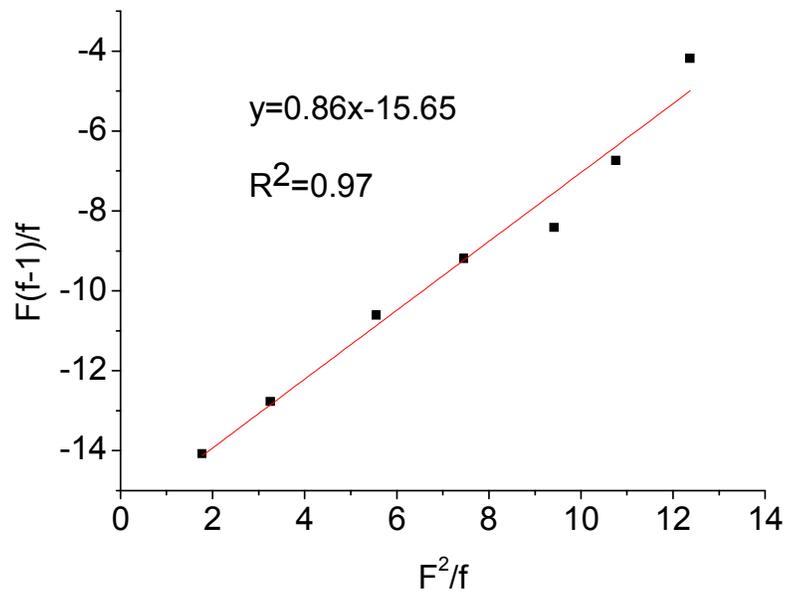


Figure S13. Fineman–Ross plot for copolymerization of BD/St catalyzed by Tm(3) precursor ($r_{St}=0.86$, $r_{BD}=15.65$, $R^2=0.97$).

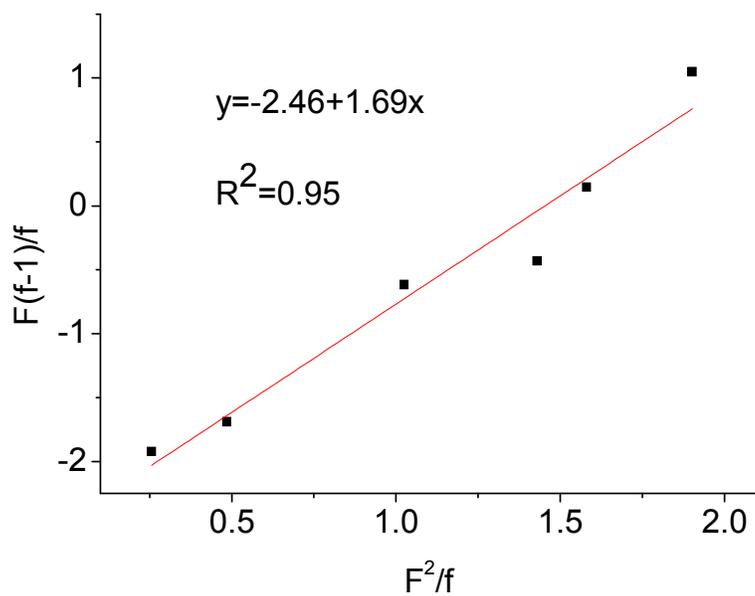


Figure S14. Fineman–Ross plot for copolymerization of BD/St catalyzed by Sc(4) precursor ($r_{St}=1.69$, $r_{BD}=2.46$, $R^2=0.95$).

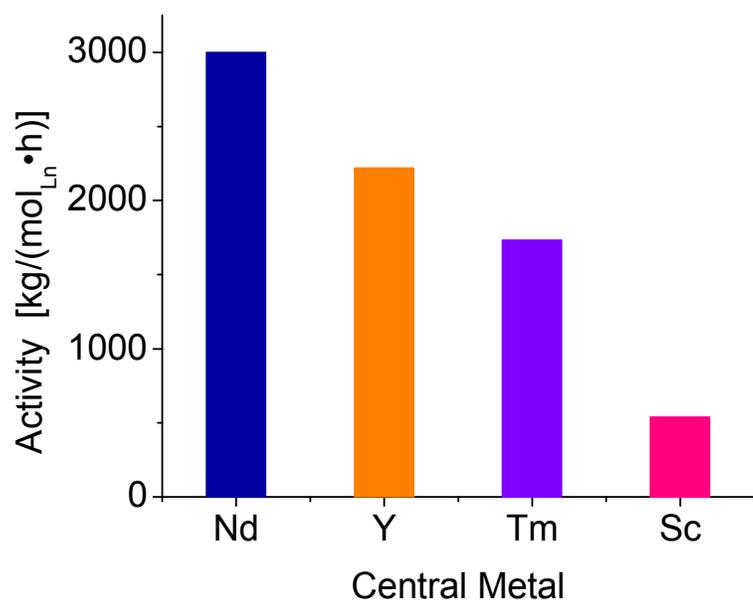


Figure S15. Butadiene polymerization activity of complexes Nd(1), Y(2), Tm(3) and Sc(4) [Ln (10 μ mol), 1:5:1:2000 [Ln]/[AlⁱBu₃]/[Ph₃C][B(C₆F₅)₄]/[BD] (molar ratio), toluene/monomer = 30/1 (v/v), T_p = 15 °C, t = 2 min].

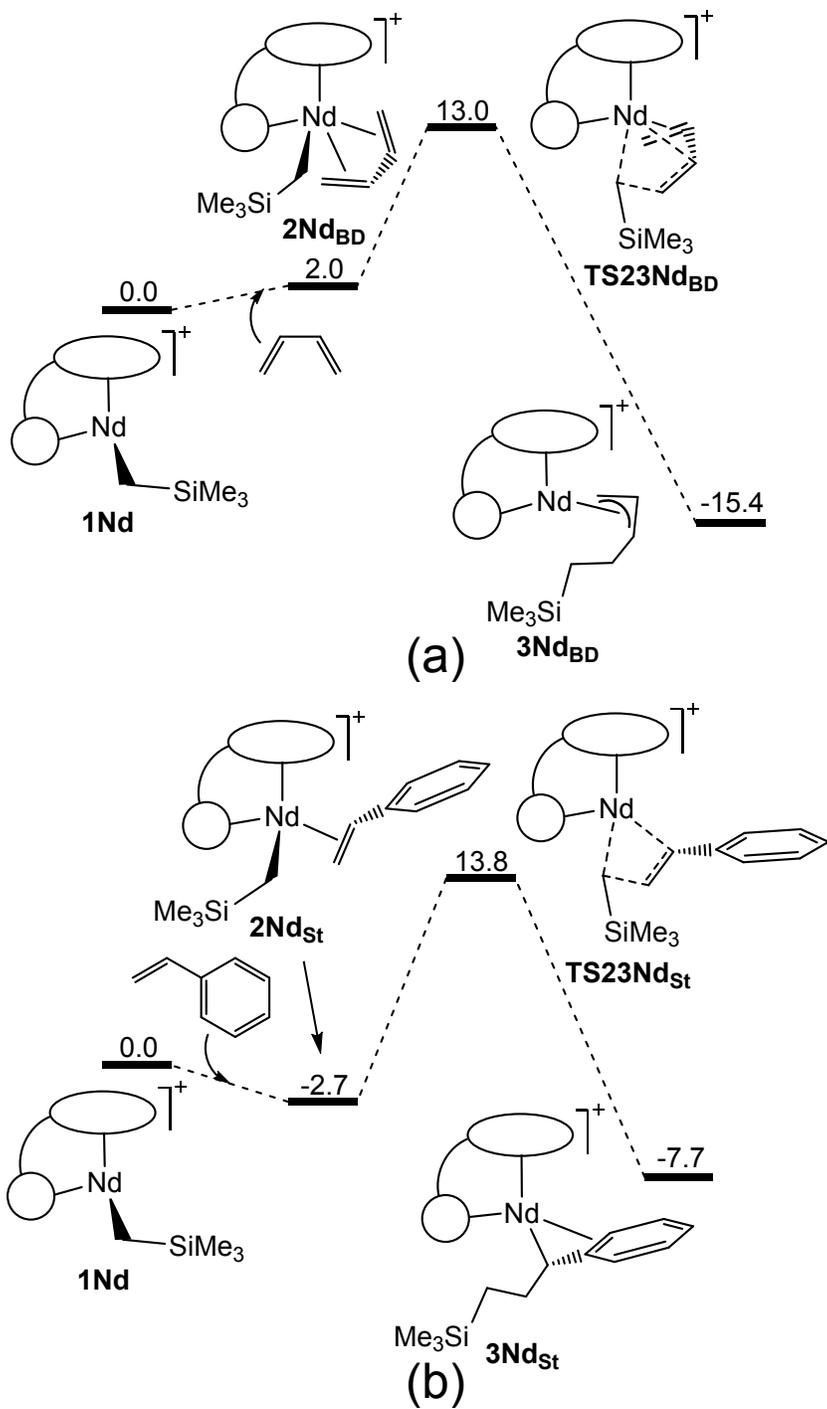


Figure S16. Free energy profiles (in kcal/mol) for chain initiation of butadiene and styrene copolymerization catalyzed by Nd(1) based cationic active species **1Nd**. (a) Insertion of butadiene. The energy reference points is **1Nd** + *trans*-butadiene. (b) Insertion of styrene. The energy reference points is **1Nd** + styrene.

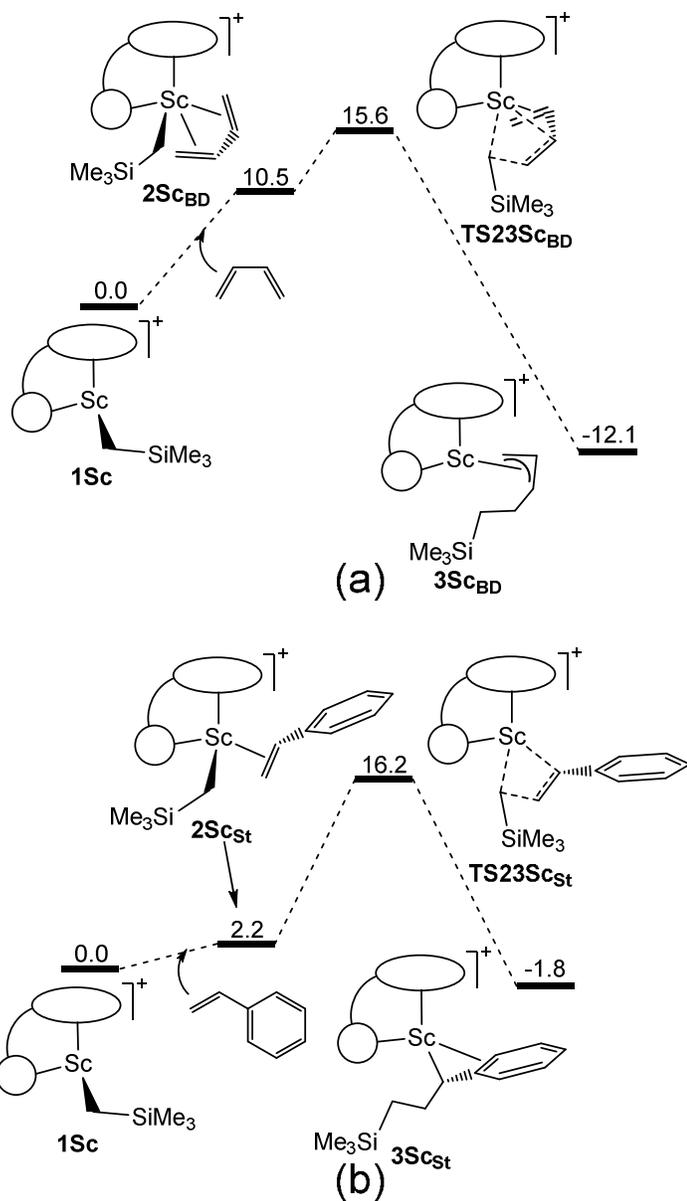


Figure S17. Free energy profiles (in kcal/mol) for chain initiation of butadiene and styrene copolymerization catalyzed by Sc(4) based cationic active species **1Sc**. (a) Insertion of butadiene. The energy reference points is **1Sc** + *trans*-butadiene. (b) Insertion of styrene. The energy reference points is **1Sc** + styrene.

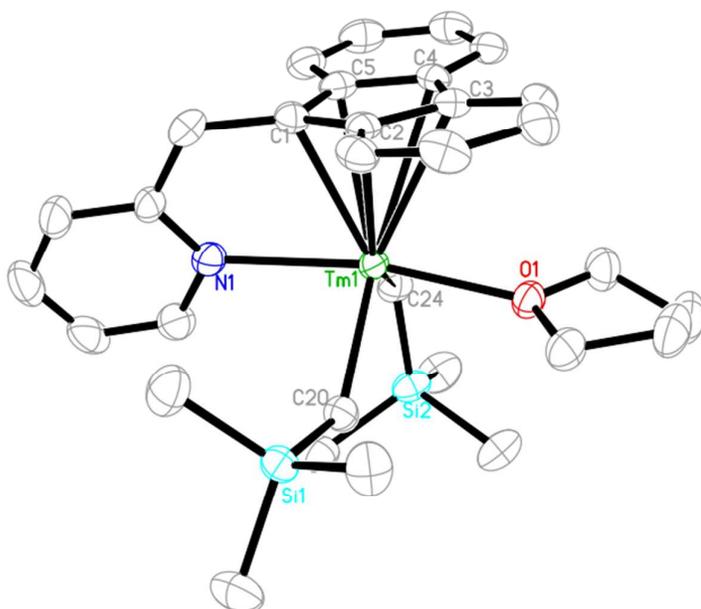


Figure S18. X-ray structure of complex Tm(3) with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

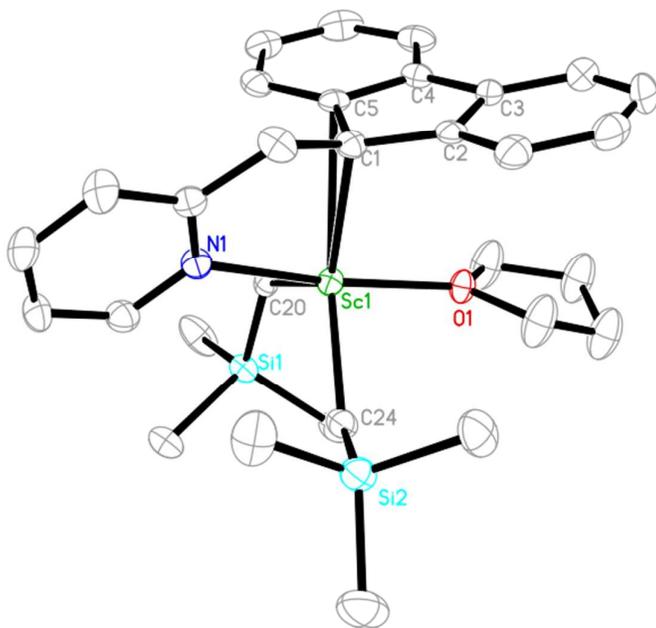


Figure S19. X-ray structure of complex Sc(4) with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity.

