

Supporting Information

Synthesis of High Molecular Weight Isobutylene- α -Methylstyrene Copolymers Containing Alkenyl Groups with a Half Sandwich Scandium Initiator System at Mild Conditions

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Experimental section

Materials

IB (Air Products; purity grade, 99.5 %) was purified by passage through columns of 3-Å molecular sieves and bariumoxide and was condensed into a graduated flask attached to the reactor. α -methylstyrene from Energy Chemical was dried over CaH_2 overnight, distilled, and degassed by three freeze-pump-thaw cycles. Solvents were purified by SPS-800 solvent purification system (Mbraun) and stored over fresh Na chips in the glove box (MBraun Labmaster). $\text{C}_5\text{Me}_4\text{SiMe}_3\text{Sc}(\text{CH}_2\text{SiMe}_3)_2\text{THF}$ and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ complex was synthesized as reported in the literature.

Measurements

^1H and ^{13}C NMR (5 wt%, CDCl_3) spectra were recorded on Bruker Avancell (400M NMR for ^1H and 100M for ^{13}C) spectrometer. Gel Permeation Chromatography (GPC) analyses were performed on Waters HPLC component system (2414 refractive index detector) at a flow rate of 1.0 ml min^{-1} in THF at $30 \text{ }^\circ\text{C}$ with polystyrene calibration. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed using a Waters MALDI micro MX spectrometer. The samples were prepared using the dried droplet method. Separately prepared THF solutions of DCTB matrix (20 mg/mL), PIB sample (10 mg/mL), and AgTFA cationizing agent (10 mg/mL) were mixed in a volumetric ratio of matrix/sample/cationizing agent = 4:1:0.2, and a 0.5 μL aliquot was applied to a MALDI sample target for analysis. Glass transition temperature (T_g) was measured under nitrogen atmosphere on TA Instrument differential scanning calorimeter (DSC Q2000), with the heating rate of $10^\circ\text{C min}^{-1}$ in range of -90 to $200 \text{ }^\circ\text{C}$.

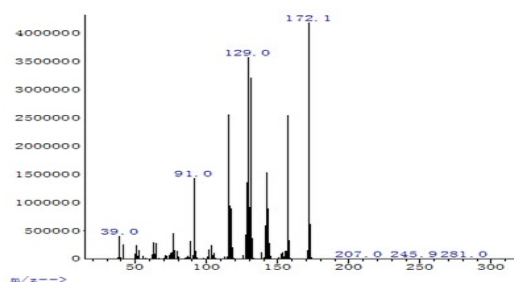
Synthesis of 4-(2-methyl-2-propenyl)- α -methylstyrene (FSt1)

The Grignard reagent in THF (100 mL), prepared from 4-chloro- α -methylstyrene (10 g, 65 mmol) and magnesium (3 g, 125 mmol) were added dropwise into the ice-cooled THF solution (20 mL) containing 3-bromo-2-methylpropene (10.8 g, 80 mmol) and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (0.704 g, 1.3 mmol). The resulting mixture was stirred at 25°C overnight. It was then extracted with ethyl acetate, dried over anhydrous MgSO_4 . Removal of the solvent under reduced pressure followed by flash column

chromatography (hexanes) yielded the colorless liquid. It was further dried over CaH_2 and purified by fractional distillation under reduced pressure. Ultimately, 4.8 g FSt1 (28 mmol, 43 %) was obtained.

^1H NMR (400 MHz, Chloroform- d) δ 7.46 – 7.41 (m, 2H), 7.18 (d, J = 8.1 Hz, 2H), 5.41 – 5.36 (m, 1H), 5.08 (p, J = 1.5 Hz, 1H), 4.84 (t, J = 1.8 Hz, 1H), 4.77 (dd, J = 2.3, 1.2 Hz, 1H), 3.34 (s, 2H), 2.19 – 2.16 (m, 3H), 1.71 (t, J = 1.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 145.02 , 142.98 , 138.97 (d, J = 3.3 Hz), 128.73 , 125.37 , 111.91 , 111.75 , 44.25 , 22.06 , 21.80 .



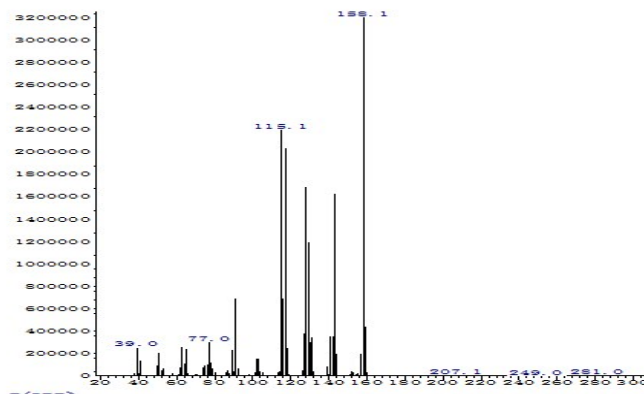
GC-MS spectrum of FSt1

Synthesis of 4-(2-Propenyl)- α -methylstyrene (FSt2)

The Grignard reagent in THF (100 mL), prepared from 4-chloro- α -methylstyrene (10 g, 65 mmol) and magnesium (3 g, 125 mmol) were added dropwise into the ice-cooled THF solution (20 mL) containing allyl bromide (9.7 g, 80 mmol) and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (0.704 g, 1.3 mmol). The resulting mixture was stirred at 25°C overnight. It was then extracted with ethyl acetate, dried over anhydrous MgSO_4 . Removal of the solvent under reduced pressure followed by flash column chromatography (hexanes) yielded the colorless liquid. It was further dried over CaH_2 and purified by fractional distillation under reduced pressure. Ultimately, 5.2 g FSt2 (33 mmol, 51 %) was obtained.

^1H NMR (400 MHz, Chloroform- d) δ 7.46 (dd, J = 8.2, 1.3 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 5.40 (s, 1H), 5.19 – 5.07 (m, 2H), 3.44 (d, J = 6.8 Hz, 2H), 2.20 (s, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 142.98 , 139.25 , 139.04 , 137.32 , 128.40 , 125.52 , 115.78 , 111.82 , 39.84 , 21.81 .



GC-MS spectrum of FSt2

Copolymerizations of isobutylene with α -methylstyrene and functional comonomers by $[\text{C}_5\text{Me}_4\text{SiMe}_3\text{Sc}(\text{CH}_2\text{SiMe}_3)_2\text{THF}]/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$

All the copolymerizations were carried out using a 100mL Schlenk tube in cold bath under nitrogen atmosphere. A typical copolymerization process was illustrated. After the 50mL Schlenk tube was immersed in cold alcohol at -35°C , the mixture of IB and comonomer was condensed into the 50mL Schlenk tube. $\text{C}_5\text{Me}_4\text{SiMe}_3\text{Sc}(\text{CH}_2\text{SiMe}_3)_2\text{THF}$ (9.7mg, 2×10^{-5} mol) and 1 equiv $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (18.5 mg, 2×10^{-5} mol) were dissolved in 3 ml of toluene and added into the sealed injector in glove box. Then the sealed injector was moved out from the glove box and the initiator system was quickly injected into 0.4g IB (2ml toluene) in the 100mL Schlenk tube at -35°C under nitrogen atmosphere. After 5 min, 100ml tube connected with 50ml tube at -35°C under nitrogen and the mixture of IB and comonomer in the 50ml tube was quickly poured into the 100ml tube. After the reactive system was stirred at -35°C for 60 min, the reaction was terminated by injecting 10ml cold methanol. This polymer solution was poured into a large amount of ethanol to precipitate the polymer product. The obtained product dried under vacuum at 45°C to a constant weight.

Epoxidation reactions of functional polyisobutylene based materials with pendant alkenyl groups

All epoxidation reactions were carried out in a 100ml glass flask. A typical reaction process was illustrated. 0.1 g functional copolymer (C=C content = 10 mol%) was added into 30 ml chloroform in the glass flask. Then, 0.02g m-chloroperoxybenzoic acid (in 5 ml chloroform) was added into the glass flask. After the mixture was stirred overnight at 25°C , the reaction was terminated by pouring into 50 ml methanol and the white solid was filtered. Then the product was dried under vacuum at 45°C to a constant weight.

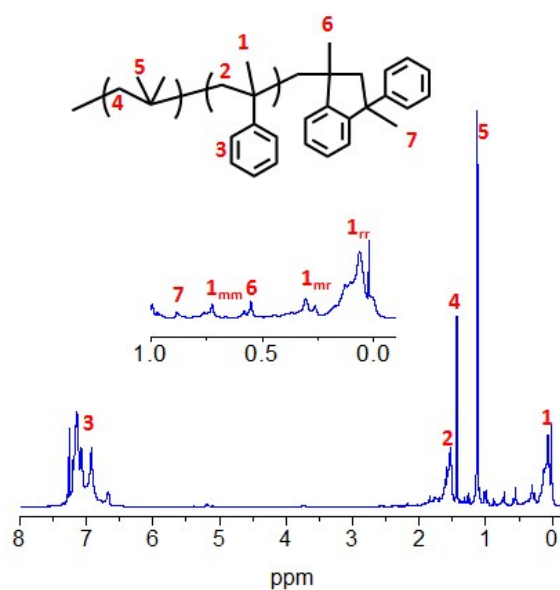


Fig.S1 ^1H NMR spectrum of poly(IB-b- α -MeSt) block copolymers

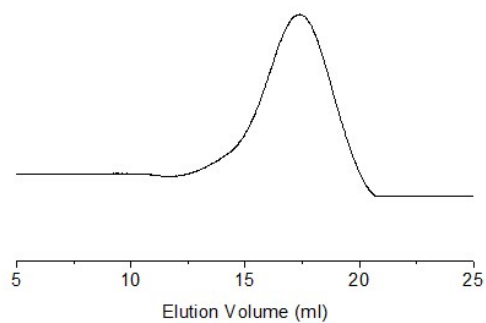


Fig.S2 GPC curve of poly(IB-b- α -MeSt) block copolymers

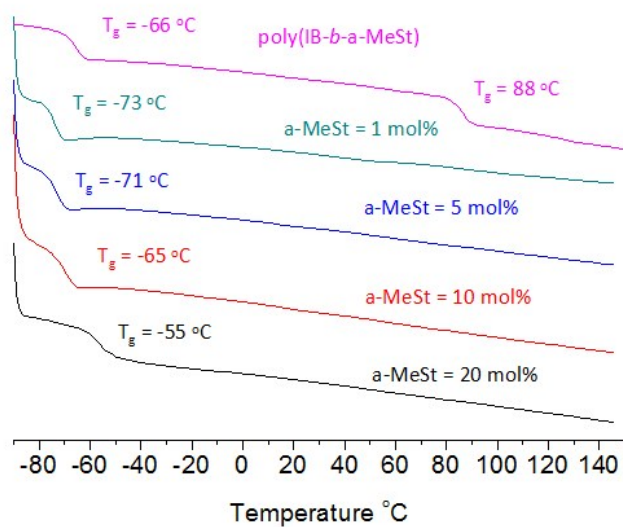


Fig.S3 DSC curve of poly(IB- α -MeSt) copolymers

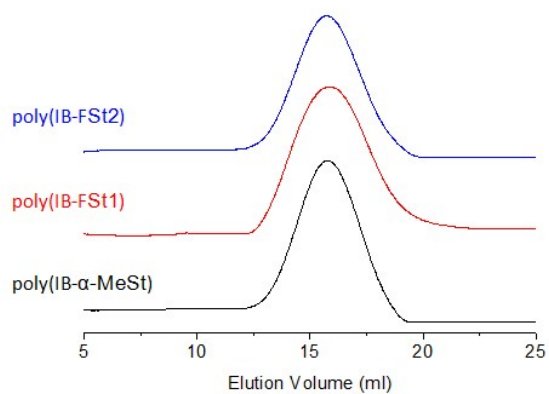


Fig.S4 GPC curves of polyisobutylene based copolymers (comonomer = 20 mol%)

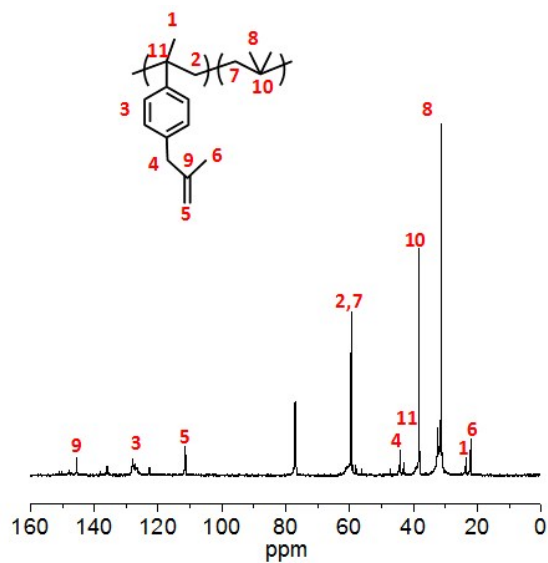


Fig.S5 ^{13}C NMR spectrum of poly(IB-FSt1) copolymers

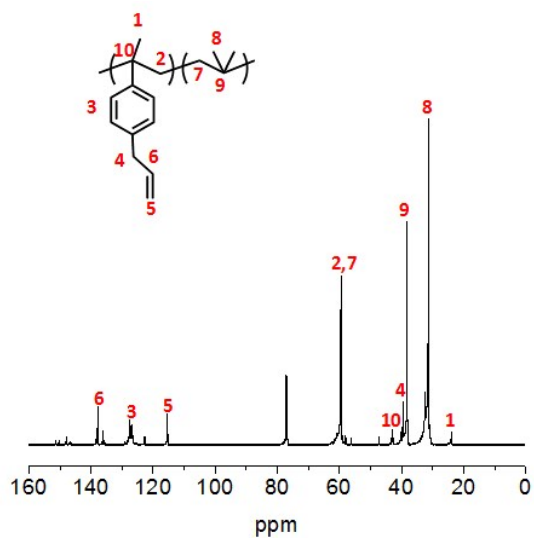


Fig.S6 ^{13}C NMR spectrum of poly(IB-FSt2) copolymers

Table S1 Copolymerizations within different time under $[\text{C}_5\text{Me}_4\text{SiMe}_3\text{Sc}(\text{CH}_2\text{SiMe}_3)_2\text{THF}]/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]^a$

Run	Fst	Fst in feed (mol%)	Time (min)	Yield (%)	M_n^b (10^4)	MWD^b	FSt in polymer ^c (mol%)
1	α -MeSt	10	15	24	8.5	1.7	10
2	α -MeSt	10	30	36	11.8	1.6	10
3	α -MeSt	10	60	52	13.2	1.5	13
4	α -MeSt	10	120	61	13.8	1.6	13
5	1	10	15	18	9.3	1.5	10
6	1	10	30	39	12.7	1.7	11
7	1	10	60	53	13.9	1.6	12

8	1	10	120	61	14.1	1.7	12
9	2	10	15	30	8.7	1.6	12
10	2	10	30	50	12.9	1.7	13
11	2	10	60	63	14.8	1.6	13
12	2	10	120	65	15.1	1.7	13

^a. [Sc]= 20 umol, [Ph₃C][B(C₆F₅)₄]=20 umol, Toluene = 5 ml, -35°C, 0.4 g IB was added 5 min in advance, then 3 g IB and various amount of the comonomer mixture was added. ^b. M_n and MWD were determined using GPC. ^c. determined by ¹H NMR.

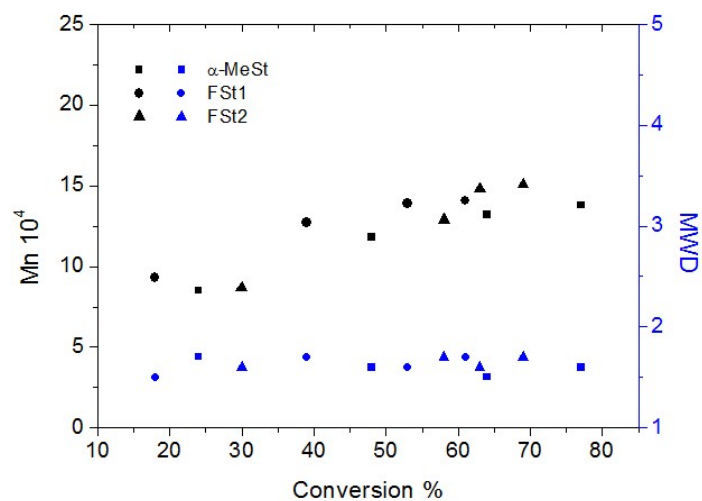


Fig.S7 M_n and MWD versus conversion plot

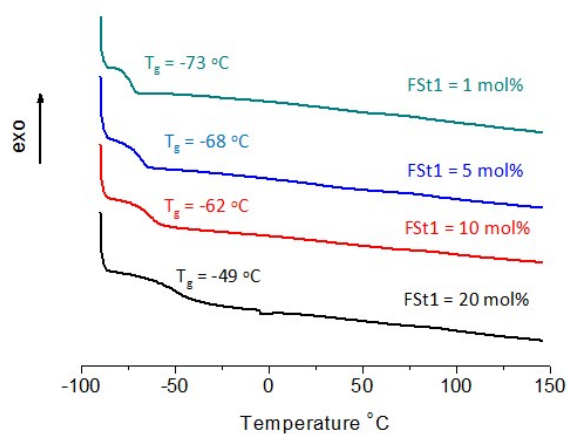


Fig.S8 DSC curve of poly(IB-FSt1) copolymers

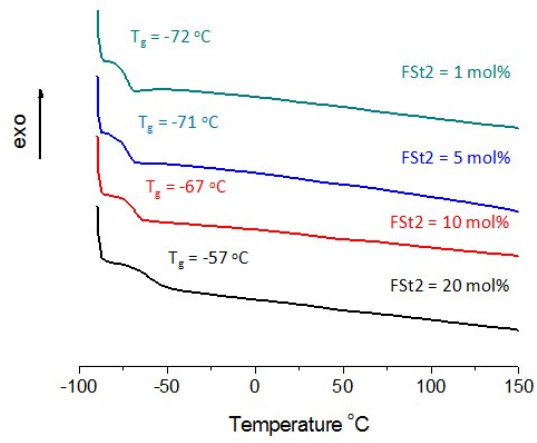


Fig.S9 DSC curve of poly(IB-FSt2) copolymers