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-Åmolecular sieves and bariumoxide and was condensed into a graduated flask attached to the reactor. α-methylstyrenefrom Energy Chemicalwas dried over CaH₂ 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). C₅Me₄SiMe₃Sc(CH₂SiMe₃)₂THF and [Ph₃C][B(C₆F₅)₄] complex was synthesized as reported in the literature.

Measurements

¹H and ¹³C NMR (5 wt%, CDCl₃) spectra were recorded on Bruker Avance II (400M NMR for ¹H and 100M for ¹³C) spectrometer. Gel Permeation Chromatography (GPC) analyses were performed on Waters HPLC component system (2414refractive index detector) at a flow rate of 1.0 ml min⁻¹ in THF at 30 °C with polystyrene calibration. Matrix-assisted laser desorption/ionization time-of-flight massspectrometry (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 uL aliquot was applied to aMALDI 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°C min⁻¹ in range of 90 to 200 °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 MgSO₄. 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.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 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) $\delta$ 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 .

**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.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 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) $\delta$ 142.98 , 139.25 , 139.04 , 137.32 , 128.40 , 125.52 , 115.78 , 111.82 , 39.84 , 21.81 .
Copolymerizations of isobutylene with α-methylstrene and functional comonomers by 
\([\text{C}_5\text{Me}_4\text{SiMe}_3\text{Sc(CH}_2\text{SiMe}_3)_2\text{THF}]/[\text{Ph}_3\text{C}][\text{B(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. \(\text{C}_5\text{Me}_4\text{SiMe}_3\text{Sc(CH}_2\text{SiMe}_3)_2\text{THF} (9.7\text{mg}, 2\times10^{-5}\text{ mol})\) and 1 equiv \([\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]\) (18.5 mg, 2\times10^{-5}\text{ 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 \(^1\text{H NMR spectrum of poly(IB-b-α-MeSt) block copolymers}\)
**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%)
**Table S1** Copolymerizations within different time under $[C_9Me_4SiMe_3Sc(CH_2SiMe_3)_2THF]/[Ph_3C][B(C_6F_5)_4]^\alpha$

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<th>Yield (%)</th>
<th>$M_n$ (10$^4$)</th>
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**Fig.S5** $^{13}$C NMR spectrum of poly(IB-FSt1) copolymers

**Fig.S6** $^{13}$C NMR spectrum of poly(IB-FSt2) copolymers
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\[ \text{[Sc]} = 20 \text{ umol}, \text{[Ph}_3\text{C][B(C}_6\text{F}_5\text{F}_3\text{]}_4] = 20 \text{ umol}, \text{Toluene} = 5 \text{ ml}, -35^\circ\text{C}, 0.4 \text{ g IB was added 5 min in advance, then 3 g IB and various amount of the comonomer mixture was added.} \]

\[ a. \] \( M_n \) and \( M_{WD} \) were determined using GPC. \[ b. \] determined by \(^1\text{H NMR.} \)

**Fig. S7** \( M_n \) and \( M_{WD} \) versus conversion plot

**Fig. S8** DSC curve of poly(IB-FSt1) copolymers
Fig. S9 DSC curve of poly(IB-FSt2) copolymers