## **Supporting Information**

## "Arm-First" Approach for the Synthesis of Star-Shaped Stereoregular Polymers through Living Coordination Polymerization

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## **Experimental Section**

**General Procedures and Materials.** All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques or Mbraun glovebox. The solvents used were analytically pure and purified by use of a SPS-800 solvent purification system (Mbraun) and stored over fresh sodium chips in the glovebox. Butadiene (Bd, Yanshan Petrochem. Co., China, polymerization grade) was treated with n-butyllithium (*n*-BuLi) to remove the moisture and inhibitor and then dissolved in toluene at a concentration of 3.3 mol/L. Isoprene (Ip) and styrene (St) was purchased from Aldrich and purified by distillation over CaH<sub>2</sub> then degassed using three freeze-pump-thaw cycles, and was kept at -40 °C in the glovebox. Divinylbenzene compounds, including *m*-divinylbenzene (*m*-DVB), *p*-divinylbenzene (*p*-DVB) and 1,2-bis(4-vinylphenyl)ethane (BVPE) were synthesized according to the literatures and purified just before use.<sup>1-2</sup> The half-sandwich scandium catalyst (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) was synthesized following the literature procedures.<sup>3</sup>

**Polymerization Procedure.** Polymerization was carried out in the glovebox at room temperature. A typical procedure of preparing star polybutadiene was as follows (Table 1, run 2): In the glovebox, Bd solution (0.6 mL, 2 mmol) was added under vigorous stirring to a reaction mixture of  $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$  (0.0097 g, 20 µmol) and  $[Ph_3C][B(C_6F_5)_4]$  (0.0185 g, 20 µmol) in toluene (5 mL) at room temperature. The polymerization was conducted for 10 min until the polymerization had reached ca. 100% conversion. Then, a solution of *p*-DVB (0.0130 g, 0.1 mmol) in toluene was added for another 5 min. The resulting mixture was poured into a large amount of methanol to precipitate the polymer product, which was then collected by filtration, washed with methanol and dried under vacuum at 40 °C to constant weight.

**Polymer Characterization.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of polymers were determined on Bruker Avance 400 MHz NMR spectrometer in CDCl<sub>3</sub> or C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>. The differential scanning calorimeter (DSC) analysis was measured using a NETZCH DSC 204 under nitrogen atmosphere at a heating and cooling rates of 10 <sup>o</sup>C/min. The curves of the DSC analysis were recorded in the second heating cycle. The gel permeation chromatography (GPC) analysis of the obtained polymer was performed on a Viscotek TDA-350 GPC (Viscotek Corp., Houston, TX) equipped with tetra detectors [refractive index detector, UV/vis detector set at 256 nm, four bridge capillary viscosity detector and two-angle laser light scattering detector (7<sup>o</sup> and

90°)]. Two columns (T6000 M×2, Malvern) were used for polymer fractionation. HPLC-grade THF was used as the mobile phase at a flow rate of 1.0 mL/min and the column temperature of 30 °C.

run	[Bd]/[Sc]	time (min)	conv. (%)	microstructure <sup>c</sup>		NA dx10-4	NA INA d
				<i>cis</i> -1,4	1,2	<i>W</i> <sub>n</sub> *×10 <sup>+</sup>	IVI <sub>w</sub> /IVI <sub>n</sub> -
1	100	10	100	84	15	1.6	1.4
2	200	10	100	85	14	2.9	1.4
3	250	10	97	85	13	3.5	1.5
4	300	10	96	83	16	4.0	1.4
5	500	10	96	84	15	6.1	1.5
6	800	10	100	85	14	9.7	1.4
<b>7</b> <sup>b</sup>	1000	10	100	84	15	13.2	1.4

Table S1 Living polymerization of butadiene by (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF)/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>a</sup>

<sup>*a*</sup> Polymerization Conditions: [Sc], 20  $\mu$ mol, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], 20  $\mu$ mol; toluene, 6 mL; 25 °C. <sup>*b*</sup> Toluene, 12 mL. <sup>*c*</sup> Determined by <sup>13</sup>C NMR. <sup>*d*</sup> Determined by GPC in THF against polystyrene standard.



**Fig. S1** <sup>1</sup>H NMR spectra of SBR copolymer in  $CDCl_3$  ( $x_{St} = 0.31$ ).



**Fig. S2** <sup>13</sup>C NMR spectra of SBR copolymer in  $C_2D_2Cl_4$  ( $x_{st} = 0.31$ ).



**Fig. S4** GPC curves for the synthesis of star *cis*-1,4-PB at different coupling time. (a): *m*-DVB as cross-linker; (b): *p*-DVB as cross-linker.



Fig. S5 GPC curves for the synthesis of star *cis*-1,4-PB at different [*p*-DVB]/[Sc] molar ratios.



Fig. S6 GPC curves for the synthesis of star *cis*-1,4-PB at different [BD]/[Sc] molar ratios.



Fig. S7 Mark-Houwink polts of star polybutadiene (excluding the linear polymers) (run 2, 7, 10 and 11 in Table 1)



**Fig. S8** <sup>1</sup>H NMR spectra of IBR copolymer in CDCl<sub>3</sub> ( $x_{BD} = 0.56$ ). Polymerization conditions: [Sc], 20 µmol, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], 20 µmol; [BD]/[IP]/[Sc] =250/250/1; toluene, 6 mL; 25 °C.







**Fig. S11** Kinetics results of copolymerization of butadiene with styrene: conversion versus polymerization time.

The calculation of the molecular weigh  $(M_{n,LS})$  and average arm number (f) of star polybutadiene:





Figure S12 shows the GPC results of the polymer products for the formation of star polybutadiene at [p-DVB]/[Sc] = 5 and 30. As showed in Figure S12, the solid line is the GPC curve detected by RI detector and the dash line represent test result with UV detector at 254 nm. Peak 1 indicates the linear polybutadiene while peak 2 corresponding to the formation of star polybutadiene determined by RI detector. The GPC curve obtained by UV detector showed no signal with respect to linear polybutadiene, while in harmony with the star polybutadiene in the RI-detected GPC curve. By referring to the literatures, the RI detector is sensitive to both the butadiene and styrene unit, whereas the UV detector is sensitive to the styrene unit only. It turns out that, measured by RI detector, peak 1 was pure polybutadiene without *p*-DVB unit and peak 2 was star polybutadiene containing butadiene and *p*-DVB units. Therefore, molecular weight ( $M_{n,LS}$ ) and the concentration of linear polybutadiene section could be calculated by its *dn/dc* value (0.13 mL/g in our test conditions) by using the Omni SEC 4.7 software. Subsequently, the molecular weight and the *dn/dc* value of the star polybutadiene were obtained by their concentration.

The star yield  $(y_{star})$  (or the linking effciency) was calculated by the equation 1 as below:

$$y_{\text{star}} = \frac{(m_{\text{butadiene}} + m_{\text{CL}} \cdot x_{\text{CL}}) \cdot A_{\text{RI}} - m_{\text{CL}} \cdot x_{\text{CL}}}{m_{\text{butadiene}}} \quad (\text{Eq. 1})$$

Where the m(butadiene) and m(CL) are the amount of butadiene and cross linker. The conversion of cross-linker ( $x_{CL}$ ) was determined by gas chromatography analysis.  $A_{RI}$  is the area percetage of star polymer to overall polymer product determined by GPC-RI detector.

The average arm number (f) of star polybutadiene was calculated by the equation 2 as below:

$$f = \frac{m_{\text{butadiene}} \cdot y_{\text{star}}}{m_{\text{butadiene}} \cdot y_{\text{star}} + m_{\text{CL}} \cdot x_{\text{CL}}} \times \frac{M_{\text{n,star}}(\text{LS})}{M_{\text{n,arm}}(\text{LS})} \quad (\text{Eq. 2})$$

Where the absolute molecular weight of star polymer ( $M_{n,star}(LS)$ ) and polybutadiene arm ( $M_{n,arm}(LS)$ ) were determined by the GPC-LS detector.



**Fig. S13** <sup>1</sup>H NMR spectra of the polymer products obtained with the reaction of living polybutadiene arm with *p*-DVB at [p-DVB]/[Sc] = 15.

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