

## Supporting Information

### Stereoselective Copolymerization of Amino-Functionalized Styrenes with Butadiene Using a Half-Sandwich Scandium Complex

Zhenghai Shi, Fang Guo, Rui Meng, Lei Jiang, Yang Li\*

State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

Liaoning Key Laboratory of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

\* E-mail: liyang@dlut.edu.cn.

#### Experimental Section

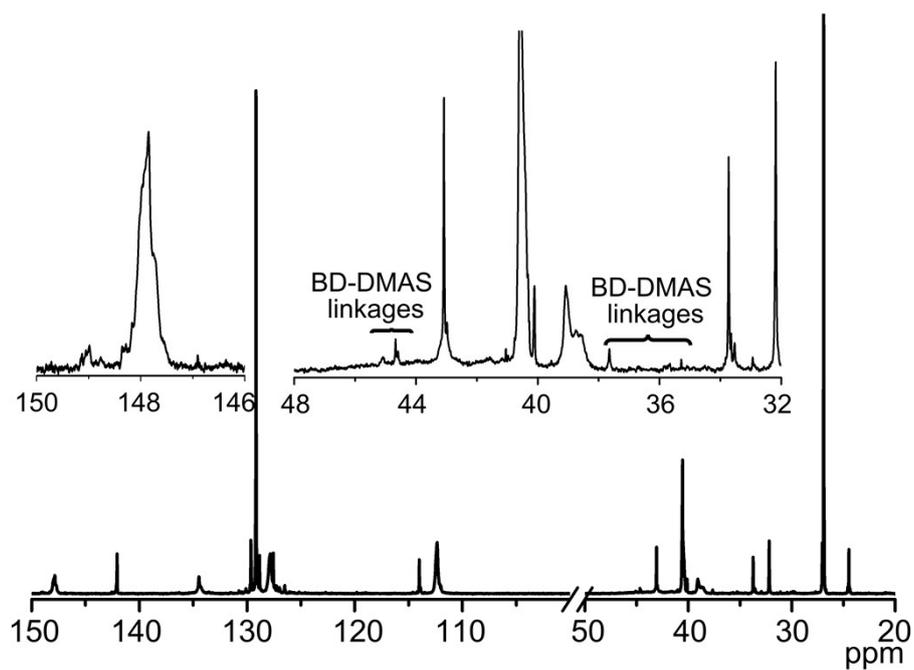
**General.** All manipulations of air or moisture-sensitive compounds were performed under a nitrogen atmosphere by use of standard Schlenk techniques or under an argon atmosphere in a Mbraun glovebox. Toluene was purified by use of a SPS-800 solvent purification system (Mbraun) and stored over fresh Na chips in the glovebox. Butadiene (Yanshan Petrochem. Co., China, polymerization grade) was treated with *n*-butyllithium twice to remove the impurities and was dissolved in dry toluene at a concentration of 3.3 mol/L prior to use. Styrenic monomers, *p*-*N,N*-dimethylaminostyrene (DMAS), *p*-*N,N*-diethylaminostyrene (DEAS) and *p*-*N,N*-diphenylaminostyrene (DPAS) were synthesized by Wittig reactions according to the literature.<sup>1</sup> A typical procedure of the synthesis of DMAS was carried out as follows: In a dry 2000 mL three-necked round-bottom flask, the methyltriphenylphosphonium bromide (218.6 g, 0.61 mol) and dry THF (750 mL) were added with stirring. Then potassium *tert*-butoxide (57.3 g, 0.51 mol) which dissolved in 250 mL dry THF was added dropwise into the flask at 0 °C under an argon atmosphere. After stirring for 30 min, 4-(Dimethylamino)benzaldehyde (50.0 g, 0.34 mol) which dissolved in 150 mL dry THF was added dropwise into the flask. The reaction was stirred for 48 h, and then 100 mL deionized water was added to the flask to terminate the reaction. The mixture was extracted with diethyl ether for 3 times (3×200 mL) and the organic layer was collected and dried with anhydrous MgSO<sub>4</sub> overnight. The solution was filtered, evaporated to remove the

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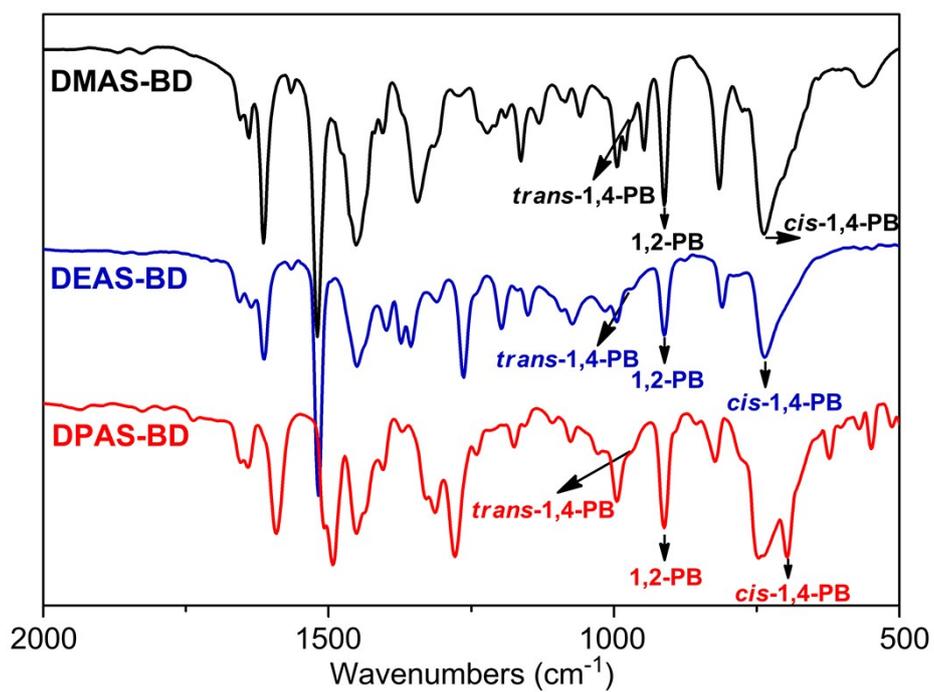
solvents, and finally distilled under reduced pressure over CaH<sub>2</sub> to obtain a colorless liquid (yield: 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) = 7.3 (d, 2H, *aromatic*), 6.7 (d, 2H, *aromatic*), 6.6 (q, 1H, -CH=CH<sub>2</sub>), 5.6 (dd, 1H, -CH=C(H)H), 5.0 (dd, 1H, -CH=C(H)H), 2.9 (s, 6H, -N(CH<sub>3</sub>)<sub>2</sub>). The scandium complex (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>2</sub> was synthesized following the literature procedures.<sup>2</sup>

**Polymerization procedure.** The copolymerization of the amino-functionalized styrenic monomers with butadiene was conducted under an argon atmosphere in a Mbraun glovebox. A typical procedure of the copolymerization of DEAS with BD was carried out as follows (Table 1, run 8): In a glovebox, a 100 mL flask equipped with a magnetic bar was charged with (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*)<sub>2</sub> (10.1 mg, 20 μmol) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (18.5 mg, 20 μmol) in toluene (5 mL) at room temperature and the flask was sealed with a rubber cock. Then a mixture of BD solution (2.73 mL, 9 mmol) and DEAS solution (175.0 mg dissolved in 1 mL toluene, 1 mmol) was added to the flask quickly by syringe under vigorous stirring. The polymerization was terminated by addition of methanol after 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 give DEAS-BD copolymer (0.63 g, 95% yield).

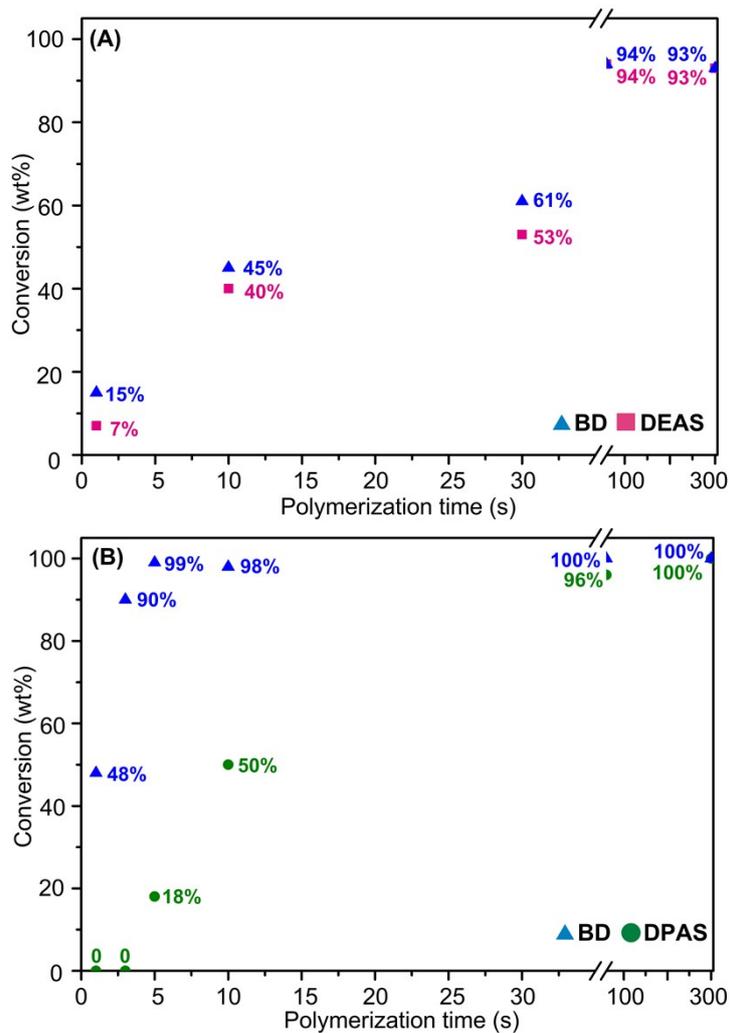
**Characterization.** <sup>1</sup>H NMR spectra of DMAS-BD and DEAS-BD copolymers were determined by Bruker Avance 400 MHz NMR spectrometer in CDCl<sub>3</sub> or C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 25 °C. <sup>1</sup>H NMR spectra of DPAS-BD copolymers were determined by Bruker Avance 500 MHz NMR spectrometer in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 120 °C. The FTIR measurements were performed on a Thermo Scientific Nicolet iS5 spectrometer using KBr pellet technique. *T<sub>g</sub>* and *T<sub>m</sub>* of the copolymers were measured using a NETZCH DSC 204 differential scanning calorimeter (DSC) under nitrogen atmosphere at a heating and cooling rates of 10 °C/min at a temperature range of -120 to 320 °C. The curves of the DSC analysis were recorded in the second heating cycle. The molecular weight (*M<sub>n</sub>*) and molecular weight distribution (*M<sub>w</sub>*/*M<sub>n</sub>*) of DMAS-BD copolymers and DEAS-BD copolymers were measured by gel permeation chromatography (GPC) on a Waters HPLC component system (2414 RI detector) at a flow rate of 1.0 mL/min in THF at 30 °C. The *M<sub>n</sub>* and *M<sub>w</sub>*/*M<sub>n</sub>* of DPAS-BD copolymers were determined by high-temperature gel permeation chromatography (HT-GPC) on a HLC-8121GPC/HT apparatus (Tosoh Corp.) at a flow rate of 1.0 mL/min in 1,2,4-trichlorobenzene at 150 °C. The calibration was made by polystyrene standard.



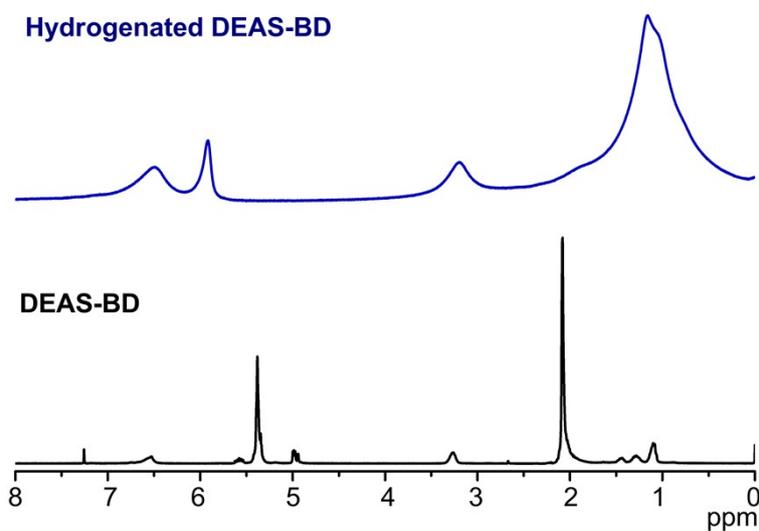
**Fig. S1**  $^{13}\text{C}$  NMR spectra of DMAS-BD copolymer ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 25  $^\circ\text{C}$ ,  $x_{\text{DMAS}} = 0.46$ ).



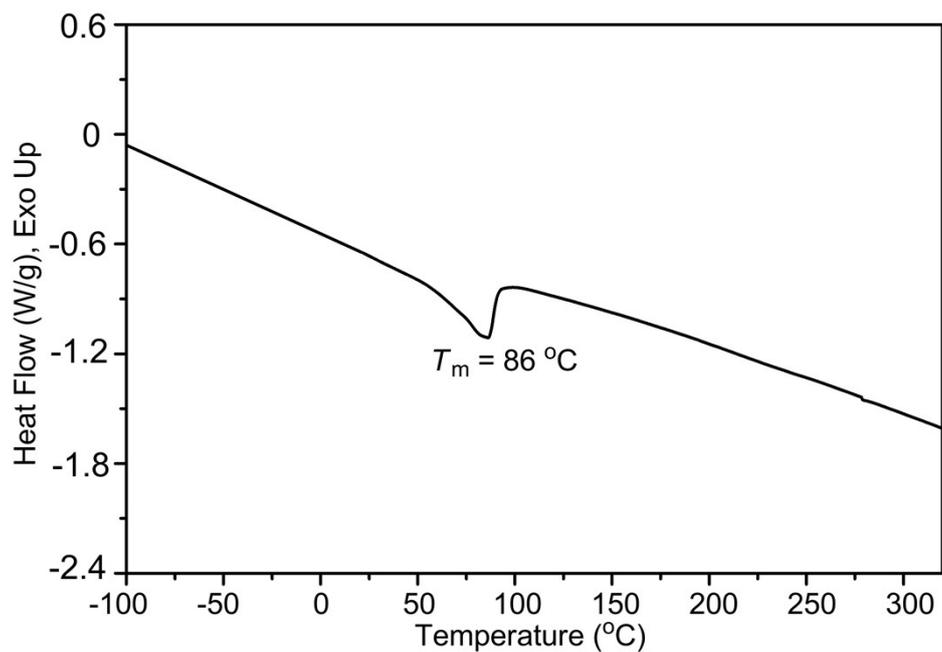
**Fig. S2** FTIR spectra of DMAS-BD, DEAS-BD and DPAS-BD copolymers.



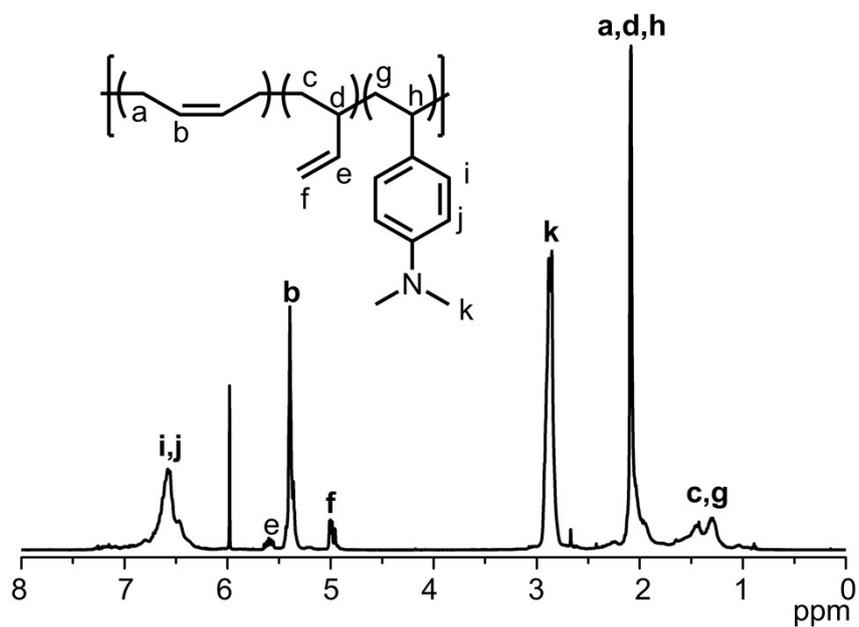
**Fig. S3** Kinetics results of copolymerization of DEAS with BD (A) and DPAS with BD (B): conversion versus polymerization time.



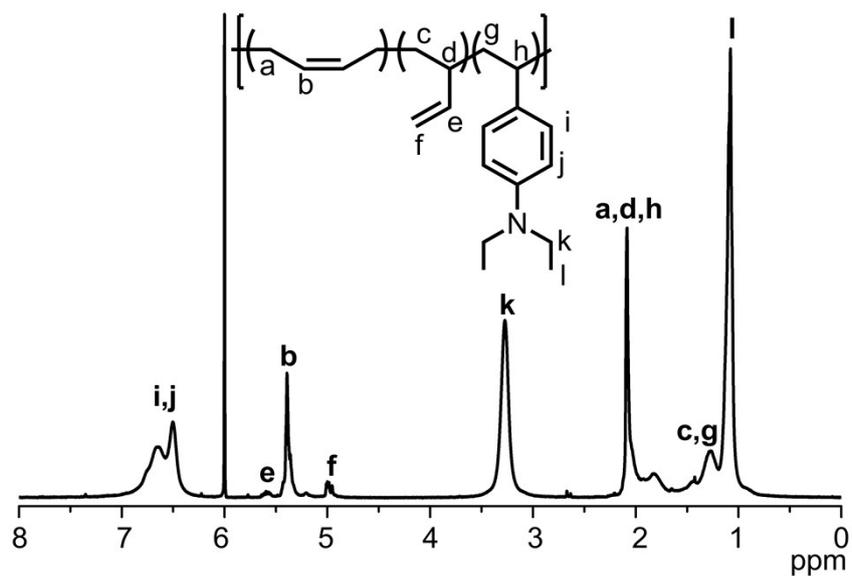
**Fig. S4** <sup>1</sup>H NMR spectra of DEAS-BD copolymer before and after hydrogenation ( $x_{\text{DEAS}} = 0.09$ ).



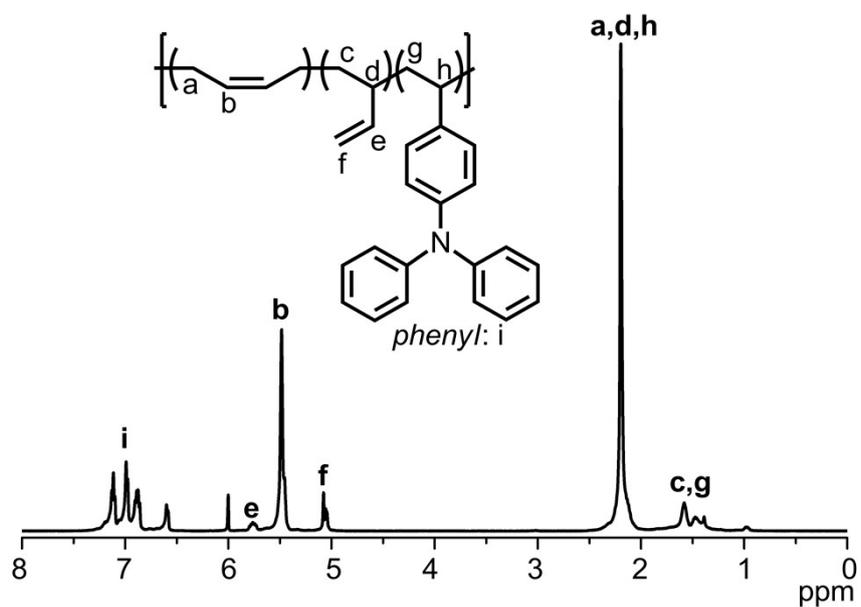
**Fig. S5** DSC curve of DEAS-BD copolymer after hydrogenation ( $x_{\text{DEAS}} = 0.09$ ).



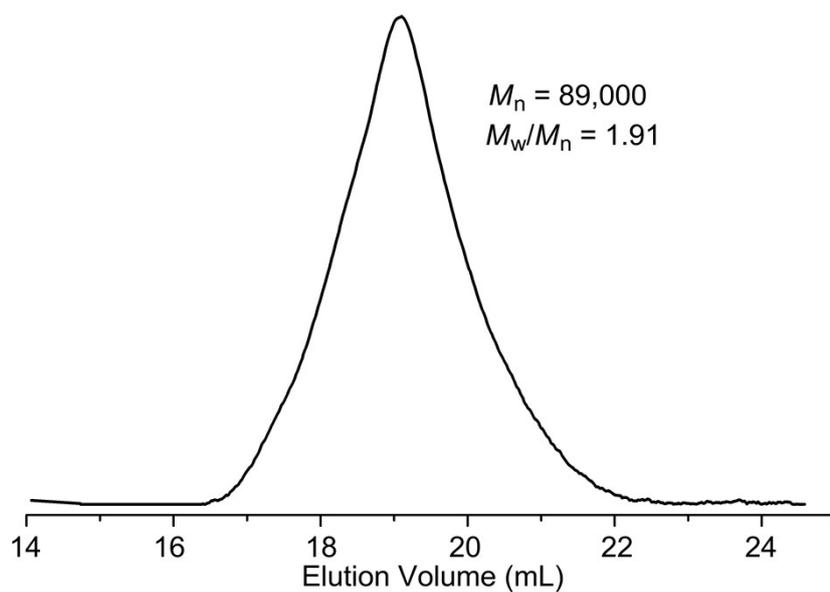
**Fig. S6**  $^1\text{H}$  NMR spectra of DMAS-BD copolymer ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $25\text{ }^\circ\text{C}$ ,  $x_{\text{DMAS}} = 0.46$ ).



**Fig. S7**  $^1\text{H}$  NMR spectra of DEAS-BD copolymer ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $25^\circ\text{C}$ ,  $x_{\text{DEAS}} = 0.59$ ).



**Fig. S8**  $^1\text{H}$  NMR spectra of DPAS-BD copolymer ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $120^\circ\text{C}$ ,  $x_{\text{DPAS}} = 0.12$ ).



**Fig. S9** GPC curve of DPAS-BD copolymer (1,2,4-trichlorobenzene, 150 °C,  $x_{\text{DPAS}} = 0.12$ ).

#### References

- 1 Y. Morishima, T. Hashimoto, Y. Itoh, M. Kamachi and S. Nozakura, *J. Polym. Sci., Part A: Polym. Chem.*, 1982, **20**, 299.
- 2 X. Li, M. Nishiura, K. Mori, T. Mashiko and Z. Hou, *Chem. Commun.*, 2007, 4137.