Supporting Information

Synthesis of Polyethylene and Polystyrene Miktoarm Star Copolymers Using an "In-Out" Strategy

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Experimental Part

*Preparation of PE Macroinitiators (MIs) by Ethylene "Living" Polymerization with **1***

The preparation of PE MIs was described in a previous publication.[S1] The detailed procedures are repeated here for the convenience of readers. The "living" polymerization of ethylene was conducted under at 5 °C and 400 psi in a 500 mL Autoclave Engineers Zipperclave reactor. Chlorobenzene (50 mL) and freshly prepared catalyst solution (0.3 mmol 1 in 20 mL chlorobenzene) were charged to the reactor under N_2. The polymerization was started with the pressurizing of ethylene to 400 psi. Ethylene was released after a certain reaction time, and the resulting polymer solution was poured into 2% acidified methanol to precipitate the polyethylene sample. The sample was redissolved in THF and passed through a 0.2 µm Teflon syringe filter to remove the Pd blacks. The filtrate was then added to a large amount of methanol to precipitate the polyethylene. The dissolution-precipitation cycle was repeated 4 times. The final polyethylene was dried under vacuum at 50 °C for 2 days. Three PE MIs with absolute number-average weights ($M_{n,LS}$) of 7.3, 10.3, and 13.7 kg/mol were prepared as shown in Table 1.

Synthesis of Homoarm Star Polymer (PE)$_n$−PDVBs

The (PE)$_n$−PDVBs were synthesized via the ATRP of DVB with the PE MI as initiator.[S2] Five (PE)$_n$-PDVB star copolymers (SMI1-SMI5, Table 1) with different PE arm numbers and lengths were prepared. Taking SMI1 as an example, MI1 (0.150 g, 0.0211 mmol), toluene (4.58 g, ca. 5.2 mL), DVB (0.417 g, 2.56 mmol, 120 equiv.), and PMDETA (49.5 mg, 0.283 mmol, 13.2 equiv.) were charged into a 20 mL Schlenk tube containing a magnetic stir bar. The tube was sealed with a rubber septum. Three freeze-pump-thaw cycles were conducted to remove the oxygen. CuBr (37.1 mg, 0.256 mmol) and CuBr$_2$ (5.61 mg, 0.0249 mmol) were then added under N_2. After the reaction solution was stirred at

room temperature under N_2 for 20 min, it was heated to 95 ºC to initiate the polymerization. The reaction was terminated after 3 h by pouring the solution into an excess amount of methanol. The precipitated polymer sample was washed with methanol three times. After drying overnight at room temperature under vacuum, 0.296 g of the sample was obtained. The conversion of DVB was determined to be 35%.

Determination of initiation efficiency (IE)

A kinetic method was provided by the Matyjaszewski group[S3] for estimating initiation efficiencies (IEs) of (poly(tert-butyl acrylate))$_n$−Poly(DVB-co-tert-butyl acrylate) SMIs. The IE values can be calculated using Eq. S1,

$$IE = \frac{[P-X]}{[P-X]_0} = \frac{k_{SMI}^{app}[1\text{-}PEBr]_0}{k_{control}^{app}[P-X]_0} \times 100\% \tag{S1}$$

where $[P–X]_0$ is theoretically initial concentration of initiation −Br groups, k_{SMI}^{app} and $k_{control}^{app}$ are the apparent propagation constants of the atom transfer radical polymerization of St using the SMI and 1-phenylethyl bromide (1-PEBr) as initiators, respectively, and $[1\text{-}PEBr]_0$ is initial 1-PEBr concentration in the control run.

The apparent propagation constant (k^{app}) is proportional to the concentration of propagating polymeric radicals in atom transfer radical polymerizations and can be estimated from the slope of semilogmarithmic kinetic plot. In the control run, the ATRP of styrene was carried out under the same experimental conditions as those in the preparation of miktoarm star polymers except using 1-PEBr instead of the SMI as initiator. The selection of 1-PEBr as initiator was due to its chemical structure and reactivity (activation and deactivation constants) comparable to the -Br groups in the crosslinked PDVB core of the SMI.[S3] Figure S1(a) shows the control run followed first-order kinetics with a $k_{control}^{app}$ of 8.25 × 10^{-6} s^{-1}. The molecular weights of PS samples in the control run determined by the GPC agree well with the theoretical values (Figure S1(b)), suggesting that all −Br groups in 1-PEBr participating in the chain propagation. From the $k_{control}^{app}$, k_{SMI}^{app}, and $[1\text{-}PEBr]_0$ values, the concentration of initiated −Br ([P−X]) can be estimated, and thus the IE.
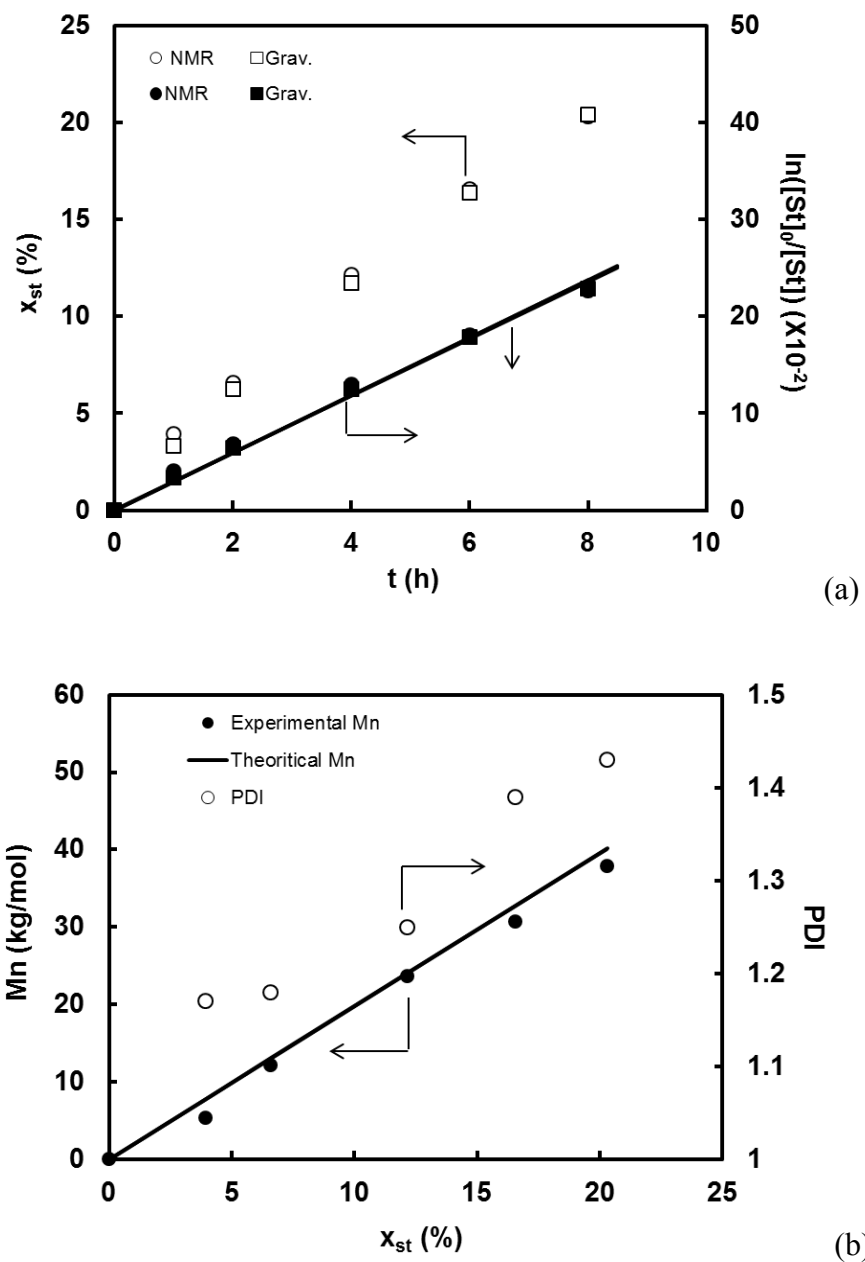
Figure S1 (a) Semi logarithmic kinetic plot of styrene conversion versus polymerization time and (b) evolution of molecular weight and PDI versus styrene conversion for control run with 1-PEBr as initiator. [1-PEBr]$_0$ = 2.3 mM; [1-PEBr]$_0$:[St]$_0$:[CuBr]$_0$:[CuBr$_2$]$_0$: [PMDETA]$_0$ = 1:2000:12:1.2:13.2, temperature = 100 ^{o}C, and toluene as solvent.

Figure S2 A deconvolution method for GPC elution traces from DRI detector): (a) Run2-0h (SMI2, $M_{n,LS}$ = 7200 kg/mol, $[MI]_0$ = 3.8 mM, $[MI]_0$:$[DVB]_0$:$[CuBr]_0$:$[CuBr_2]_0$:$[PMDETA]_0$ = 1:180:12:1.2:13.2). Peak 1 (lowest molecular weight) for the linear PE-b-PDVB, Peak 2 (middle peak) for the linear block copolymer via two PE-b-PDVB coupling, and Peak 3 (main peak) for the PE homoarm star polymers.[S4] (b) Run2-6h (SMI2 used as MI, $[SMI]_0$ = 2.2 mM, $[SMI]_0$:$[St]_0$:$[CuBr]_0$:$[CuBr_2]_0$:$[PMDETA]_0$ = 1:2000:12:1.2:13.2). Peak 1 (lowest molecular weight) and Peak 2 (middle peak) for the same linear block copolymers assigned in Run2-0h, and Peak 3 (main peak) for the miktoarm star polymers. P_s is the cutting off point to define the star polymer peak in calculation of molecular weights and intrinsic viscosities by ASTRA software.
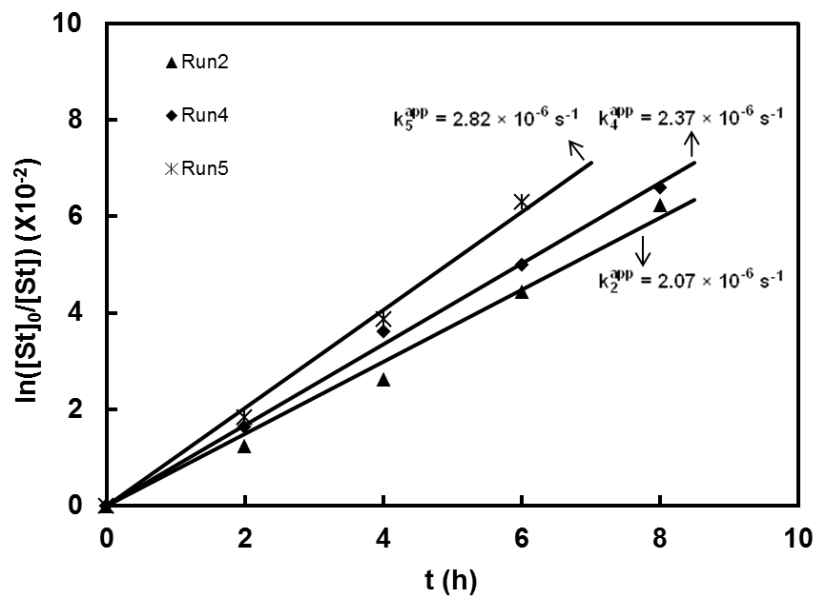
Figure S3. Semi logarithmic kinetic plot of styrene conversion versus polymerization time for Run 2 (SMI2 as macroinitiator), Run 4 (SMI4), and Run 5 (SMI5). $[SMI]_0 = 2.2$ mM; $[SMI]_0:[St]_0:[CuBr]_0:[CuBr_2]_0: [PMDETA]_0 = 1:2000:12:1.2:13.2$, temperature = 100 °C, and toluene as solvent.
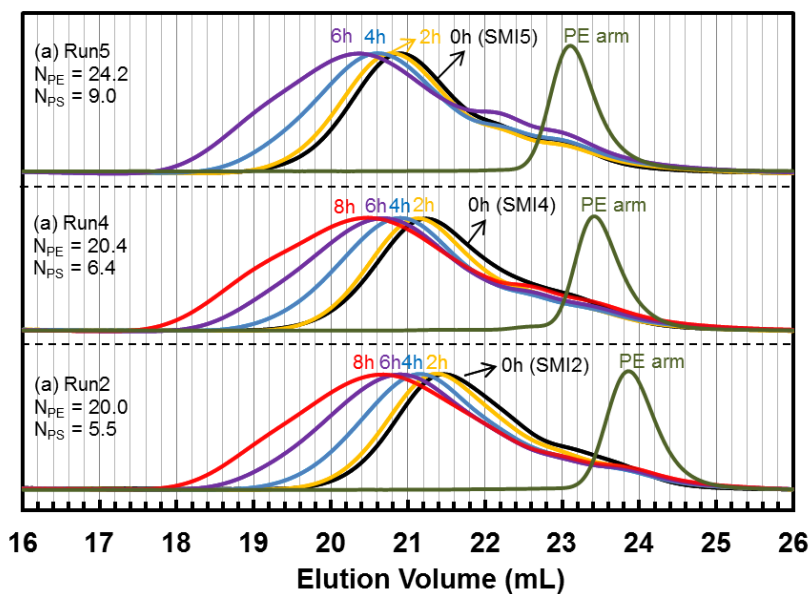
Figure S4. GPC elution traces (from DRI detector) of Run 2 (SMI2 as macroinitiator), Run 4 (SMI4), and Run 5 (SMI5).
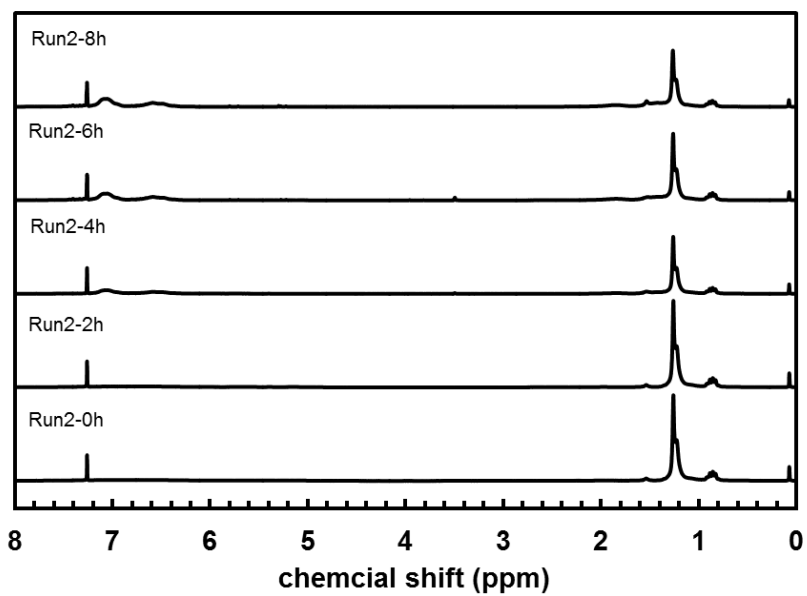
Figure S5. ^{1}H NMR spectra of the MSP samples collected at different polymerization times in Run 2 (SMI2 as macroinitiator). CDCl$_3$ was used as the deuterated solvent.
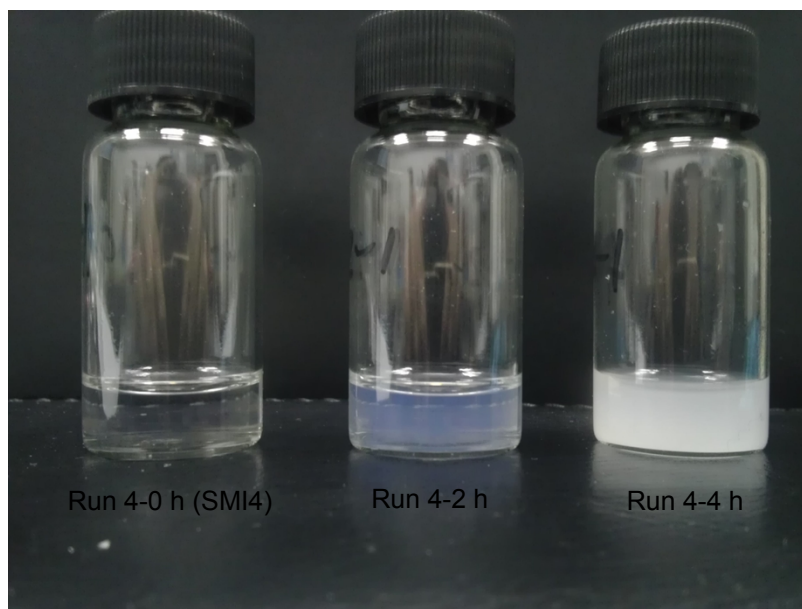
Figure S6. The appearances of Run 4-0 h (SMI4), Run 4-2 h, and Run 4-4 h samples in n-heptane at a concentration of 5 mg/mL.

Reference:

S1. Zhang, K.; Ye, Z.; Subramanian, R. *Macromolecules* 2008, **41**, 640.

S2. Liu, P.; Landry, E.; Ye, Z.; Joly, H.; Wang, W.-J.; Li, B.-G. *Macromolecules* 2011, **44**, 4125.

S3. Gao, H. F.; Matyjaszewski, K. *Macromolecules* 2006, **39**, 7216.

S4. Liu, P.; Landry, E.; Ye, Z.; Joly, H.; Wang, W.-J.; Li, B.-G. *Macromolecules* 2011, **44**, 4125.