

Supporting Information for

Synthesis of Star Polymers Using ARGET ATRP

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Experimental Section

Materials. *n*-Butyl acrylate (BA), (99%) and divinylbenzene (DVB), (80%) were purchased from Aldrich and purified by passing through a column filled with basic alumina. CuBr (Acros, 95%) was washed with glacial acetic acid in order to remove any soluble oxidized species, filtered, washed with ethanol, and dried. Anisole (Aldrich, 99%), CuBr₂ (Acros, 99%), ethyl 2-bromoisobutyrate (EBiB) (Acros, 98%), tin(II) 2-ethylhexanoate (Sn(EH)₂) (Aldrich, 95%), and tris(2-pyridylmethyl)amine (TPMA) (ATRP Solutions, Inc., 99%) were used as received.

Characterization. Monomer conversions were determined from the concentration of the unreacted monomer in the samples periodically removed from the reactions using a Shimadzu GC-14A gas chromatograph, equipped with a capillary column (DBWax, 30 m × 0.54 mm × 0.5 μm, J&W Scientific). Anisole was used as internal standard for calculation of monomer

conversions. The polymer samples were separated by GPC (Polymer Standards Services (PSS) columns (guard, 10^5 , 10^3 , and 10^2 Å), with THF eluent at 35 °C, flow rate = 1.00 mL/min and differential refractive index (RI) detector (Waters 2410)). The apparent molecular weights and molecular weight distributions (M_w/M_n) were determined with a calibration based on linear polystyrene standards using WinGPC 7.0 software from PSS. Area fractions of both star and linear polymers were determined by multipeak splitting of the GPC curve using Gaussian function in Origin 6.0 software. The obtained GPC curves with flat baseline were imported into the WinGPC software for calculation of the apparent molecular weights and molecular weight distribution of the star and linear polymers. The detectors employed to measure the absolute molecular weights ($M_{w,MALLS}$) were a triple detector system containing RI detector (Wyatt Technology, Optilab REX), viscometer detector (Wyatt Technology, ViscoStar), and a multiangle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology.

Synthesis of PBA macroinitiators. Purged BA (50 mL, 350 mmol) was transferred via a purged syringe to a dry, 100-mL nitrogen-purged Schlenk flask. A solution of CuBr_2 (7.8 mg, 0.035 mmol) and TPMA (61 mg, 0.21 mmol) in degassed anisole (3 mL) was added. The resulting mixture was stirred for 10 minutes, and then a purged solution of EBiB (514 μL , 3.5 mmol) in anisole (1 mL) was added. $\text{Sn}(\text{EH})_2$ (113.5 μL , 0.35 mmol) in purged anisole (1 mL) was added to begin polymerization. An initial sample was taken via purged syringe, and the sealed flask was placed in a thermostated oil bath at 60 °C. The polymerization was stopped after 16 hours to obtain PBA with $M_{n,\text{GPC}} = 10,300$ g/mol and $M_w/M_n = 1.11$.

Star synthesis by ATRP. PBA macroinitiator (1g), anisole (3 mL), DVB (0.17 mL) and PMDETA (16.7 μ L, 0.08 mmol) were added to a 10 mL Schlenk flask before 4 freeze-pump-thaw cycles except for CuBr. CuBr (11.1 mg, 0.08 mmol) was added to the frozen solution mixture under nitrogen (Table 1, entry 1). PBA macroinitiator (1g), anisole (3 mL), DVB (0.17 mL) and TPMA (22.6 mg, 0.08 mmol) were added to a 10 mL Schlenk flask before 4 freeze-pump-thaw cycles except for CuBr. CuBr (11.1 mg, 0.08 mmol) was added to the frozen solution mixture under nitrogen (Table 1, entry 2). PBA macroinitiator (0.85 g), anisole (2.2 mL), DVB (0.14 mL) and TPMA (0.24 mg, 0.83×10^{-3} mmol) in anisole (0.35 mL) were added to a 10 mL Schlenk flask before 4 freeze-pump-thaw cycles except for CuBr. CuBr (0.12 mg, 0.83×10^{-3} mmol) was added to the frozen solution mixture under nitrogen (Table 1, entry 3). The flask was placed in thermostated oil bath at 90 °C. Samples were withdrawn under nitrogen atmosphere at timed intervals and analyzed by GC and GPC. The reaction was stopped after 20 h.

Star synthesis by ARGET ATRP. PBA macroinitiator (1 g) was dissolved in anisole (2 mL) in a 10 mL Schlenk flask. To this solution was added a solution of CuBr₂ (0.22 mg, 0.001 mmol) and TPMA (2.9 mg, 0.01 mmol) in anisole (0.5 mL). DVB (0.17 mL, 1.2 mmol) was added next, and the flask was purged through 4 freeze-pump-thaw cycles. A solution of Sn(EH)₂ (3.24 μ L, 0.01 mmol) in anisole (0.5 mL) was added under nitrogen atmosphere, and the flask was placed in a thermostated oil bath at 90 °C.

Star synthesis by ARGET ATRP (continuous feeding). PBA macroinitiator (1 g) was dissolved in anisole (2 mL) in a 10 mL Schlenk flask. To this solution was added a solution of CuBr₂ (0.22 mg, 0.001 mmol) and TPMA (2.9 mg, 0.01 mmol) in anisole (0.5 mL). DVB (0.17 mL, 1.2 mmol) was added next, and the flask was purged through 4 freeze-pump-thaw cycles. A

solution of $\text{Sn}(\text{EH})_2$ (6.3 μL , 0.02 mmol) in anisole (0.5 mL) was added to the reaction system with a syringe pump over 20 h (0.025 mL/h rate). The flask was placed in a thermostated oil bath at 90 °C.

Star synthesis by ARGET ATRP (timed feeding). PBA macroinitiator (1 g) was dissolved in anisole (2 mL) in a 10 mL Schlenk flask. To this solution was added a solution of CuBr_2 (0.22 mg, 0.001 mmol) and TPMA (2.9 mg, 0.01 mmol) in anisole (0.5 mL). DVB (0.17 mL, 1.2 mmol) was added next, and the flask was purged through 4 freeze-pump-thaw cycles. A solution of $\text{Sn}(\text{EH})_2$ (0.32 μL , 0.001 mmol) in anisole (0.5 mL) was added under nitrogen atmosphere, and the flask was placed in a thermostated oil bath at 90 °C. Samples were withdrawn under nitrogen atmosphere at timed intervals and analyzed by GC and GPC. After 1 hour, and additional solution of $\text{Sn}(\text{EH})_2$ (0.97 μL , 0.003 mmol) in anisole (0.05 mL) was added under nitrogen atmosphere; after 2.5 hours, an additional solution of $\text{Sn}(\text{EH})_2$ (1.94 μL , 0.006 mmol) in anisole (0.1 mL) was added under nitrogen atmosphere; and after 5 hours, an additional solution of $\text{Sn}(\text{EH})_2$ (3.24 μL , 0.01 mmol) in anisole (0.17 mL) was added under nitrogen atmosphere.

The calculation of the number-average value of the number of arms per miktoarm star molecule (N_{arm}) formed during the cross-linking a mixture of two linear arm precursors (MI or MM) is shown below:¹

1. In THF 35 °C, the dn/dc values of polyBA, is 0.069 mL/g,¹ and the dn/dc value of polyDVB core is assumed to the same as that of polySt linear polymers $(\text{dn/dc})_{\text{polyDVB}} = 0.180 \text{ mL/g}$.²

2. The calculation is based on the assumption that all reacted DVB units were located in the core of star molecules.

3. The weight fraction of incorporated arms versus totally added linear arm precursors is X_{arm} :

$$\frac{\left(\frac{dn}{dc}\right)_{PBA} X_{PBA} m_1 + \left(\frac{dn}{dc}\right)_{DVB} m_{DVB} conv_{DVB}}{m_{PBA} \left(\frac{dn}{dc}\right)_{PBA} + \left(\frac{dn}{dc}\right)_{DVB} m_{DVB} conv_{DVB}} = A_{star}$$

$$\Rightarrow X_{arm} = \frac{A_{star} m_{PBA} \left(\frac{dn}{dc}\right)_{PBA} - (1 - A_{star}) m_{DVB} conv_{DVB} \left(\frac{dn}{dc}\right)_{polyDVB}}{m_{PBA} \left(\frac{dn}{dc}\right)_{PBA}}$$

in which m_{PBA} is the mass of PBA linear arm precursors in the initial mixture; m_{DVB} and $conv_{DVB}$ are the mass and conversion of added DVB cross-linker, respectively. A_{star} is the area fraction of miktoarm star polymers, determined by the multi-peak splitting of the GPC curve using Gaussian function. For the calculation, M_n of PBA was assumed to 10,000.

4. The number-average value of the number of arms per star molecule is N_{arm} :

$$N_{arm} = \frac{M_{w,MALLS}}{M_{n,arm}} \times \frac{X_{arm} m_{PBA}}{X_{arm} m_{PBA} + m_{DVB} conv_{DVB}}$$

in which, $M_{w,MALLS}$ is the weight-average molecular weight of the purified star polymers measured by THF GPC with MALLS detector.

References

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