Supporting Information

"Arm-First" Method As a Simple and General Method for Synthesis of Miktoarm Star Copolymers

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Experimental

Materials. All monomers: *n*-butyl acrylate (BA, 99%, Aldrich), *tert*-butyl acrylate (*t*BA, 98%, Aldrich), methyl acrylate (MA, 99%, Aldrich), styrene (St, 99%, Aldrich), methyl methacrylate (MMA, 99%, Aldrich) and divinylbenzene (DVB, 80%, Aldrich), were purified twice by passing through a column filled with basic alumina to remove the inhibitor. CuBr (98%, Acros) was purified using a modified literature procedure.[1] All other reagents: α-bromoisobutyryl bromide, ethyl 2-bromopropionate (EBrP), ethyl 2-bromoisobutyrate (EBiB), *2,2'*-bipyridyl (bpy), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA), $CuBr_2$ and solvents were purchased from Aldrich with the highest purity and used as received without further purification.

Poly(ethylene glycol) monomethyl ether (PEO-OH, M_n ~ 5.00 kg/mol) was purchased from Fluka.

Synthesis of polyBA-Br linear polymers by ATRP. A clean and dry Schlenk flask was charged with BA (40 mL, 0.279 mol), PMDETA (0.291 mL, 1.4 mmol), *N*,*N*-dimethylformamide (DMF, 10.0 mL). The flask was degassed by five freeze-pump-thaw cycles. During the final cycle the flask was filled with nitrogen and CuBr (0.200 g, 1.4 mmol) was quickly added to the frozen mixture. Special care was not taken to avoid moisture condensation. The flask was sealed with a glass stopper then evacuated and back-filled with nitrogen five times before it was immersed in an oil bath at 60 ^{o}C. Finally the N_2-purged initiator EBrP (0.362 mL, 2.8 mmol) was injected into the reaction system, via a syringe, through the side arm of the Schlenk flask. At timed intervals, samples were withdrawn via a syringe fitted with stainless steel needle and diluted with THF. The samples were used to measure the monomer conversions and polymer molecular weights by GC and GPC, respectively. The reaction was stopped after 2.5 h, at about 75% BA conversion, via exposure to air and dilution with THF. The solution was filtered through a column filled with neutral alumina to remove the copper complex before the polymer was dried under vacuum at 60 ^{o}C for two days. The polyBA-Br had $M_{n,GPC}$ = 9.40 kg/mol and M_w/M_n = 1.10

Synthesis of poly*t*BA-Br, polyMA-Br, polySt-Br and polyMMA-Br linear chains by ATRP. The synthesis and post-purification procedures in each ATRP reaction were similar to those in the ATRP synthesis of polyBA-Br macroinitiator (MI). Poly*t*BA-Br MI was synthesized with the initial molar ratio of reagents $[tBA]_0/[EBrP]_0/[CuBr]_0/[PMDETA]_0$ = 50/1/0.5/0.5 ($[tBA]_0$ = 3.25 M, 60 ^{o}C in anisole)

and the reaction was stopped at ca. 80% *t*BA conversion ($M_{n,GPC}$ = 6.04 kg/mol, M_w/M_n = 1.08). PolyMA-Br MI was synthesized with the initial composition as $[MA]_0/[EBrP]_0/[CuBr]_0/[PMDETA]_0$ = 120/1/0.6/0.6 ($[MA]_0$ = 5.5 M, 55 ^oC in DMF) and the reaction was stopped at ca. 60% MA conversion ($M_{n,GPC}$ = 6.20 kg/mol, M_w/M_n = 1.07). PolySt-Br MI was synthesized with the initial composition as $[St]_0/[EBrP]_0/[CuBr]_0/[PMDETA]_0$ = 150/1/0.8/0.8 ($[St]_0$ = 4.0 M, 90 ^oC in anisole) and the reaction was stopped at ca. 55 % St conversion ($M_{n,GPC}$ = 8.10 kg/mol, M_w/M_n = 1.10). PolyMMA-Br MI was synthesized with the initial composition as $[MMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[bpy]_0$ = 100/1/0.22/0.03/0.5 ($[MMA]_0$ = 4.7 M, 50 ^oC in acetone) and the reaction was stopped at ca. 60 % MMA conversion ($M_{n,GPC}$ = 6.48 kg/mol, M_w/M_n = 1.17).

Synthesis of PEO-Br linear MI. A clean, dry round-bottom flask containing 100 mL methylene chloride (dried overnight with $MgSO_4$) was cooled to 0 ^oC in ice-water bath. The solvent was purged with N_2 for 30 min before triethylamine (3.57 mL, 0.026 mol) and α-bromoisobutyryl bromide (3.16 mL, 0.026 mol) were added sequentially. The mixture was magnetically stirred for 10 min before dropwise addition of PEO-OH (M_n ~ 5000 g/mol, 25.6 g, 5.12 mmol) in 100 mL dried CH_2Cl_2 over a period of 40 min. The flask was then removed from the ice-water bath and the reaction was allowed to proceed for 24 h at room temperature. During this period, the reaction mixture slowly changed from yellowish to brown. After evaporation of 100 mL CH_2Cl_2, the reaction mixture was washed successively with 300 mL of 1 M HCl, 300 mL of 1 M NaOH and 300 mL of deionized water, and was then dried over anhydrous $MgSO_4$ overnight. After removing the solvent via rotary evaporation, the product was dissolved in 600 mL of ethanol and

purified by re-crystallization. The final product was light yellowish powder with yield 17.6 g (67%) and the structure was verified by ^{1}H NMR spectroscopy (δ, $CDCl_3$ as solvent): 4.37 ppm (t, 2H, C*H*$_2$OC(O)), 3.70 ppm (s, (C*H*$_2$C*H*$_2$O)$_n$), 3.40 ppm (s, 3H, C*H*$_3$O), 1.95 ppm (s, 6H, C(C*H*$_3$)$_2$Br).

Synthesis of miktoarm star copolymers via cross-linking two or more than two kinds of linear MIs. The synthesis and post-purification procedures in ATRP reactions were similar to those in the ATRP synthesis of polyBA-Br MI. A typical procedure for synthesis of miktoarm star copolymers containing two kinds of arms, such as polyBA and polyMA, was carried out at 110 ^{o}C with the initial ratio of reagents as [polyBA-Br (MI-1)]$_0$/[polyMA-Br (MI-2)]$_0$/[DVB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 0.5/0.5/12/ 0.8/0.8 ([polyBA-Br]$_0$ = 0.015 M in anisole). At timed intervals, samples were withdrawn for GC and GPC measurements. The reaction was stopped after 20 h via exposure to air and dilution with THF.

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 (DB-Wax, 30 m × 0.54 mm × 0.5 μm, J&W Scientific). Anisole or DMF 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 ^{o}C, flow rate = 1.00 mL/min and differential refractive index (RI) detector (Waters, 2410)). The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on linear polySt or polyMMA standards using WinGPC 6.0 software from PSS. 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 multi-angle 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. ^{1}H NMR spectra of the polymer solutions in $CDCl_3$ were collected on Bruker Avance 300 MHz spectrometer at 27 ^oC.

Liquid chromatography under the critical conditions (LCCC) of polyMA homopolymers was used to analyze the *(polyBA)$_n$-(polyMA)$_p$-polyDVB* miktoarm star copolymers by using 2 sets of Macherey & Nagel Nucleosil normal phase silica columns with pore size of 100 and 300 Å as stationary phase and 2-butanone/cyclohexane (86/14 by volume) as mobile phase (flow rate = 0.5 mL/min, 32 ^oC). By using the same columns and same solvents, the LCCC for polyMMA was established by changing the volume ratio of 2-butanone/cyclohexane to 74/26 at 32 ^oC with flow rate = 0.5 mL/min, which was used for the analysis of *(polyBA)$_n$-(polyMMA)$_p$-polyDVB* miktoarm star copolymers. Gradient polymer elution chromatography (GPEC) was used to analyze the *(polyBA)$_n$-(PEO)$_p$-polyDVB* miktoarm star copolymers by using a Waters Nova-Pak C18 column (column dimensions 150 × 3.9 mm) as stationary phase at 26 ^oC. A binary mobile phase with constant flow rate (0.8 mL/min) was employed, whose composition gradually changed from THF/MeOH (30/70 by volume) to THF/MeOH (100/0 by volume) within 15 min (Figure S1). The column was equilibrated back to initial conditions at the end of each analysis. A Waters 600 controller and pump containing a multi-solvent delivery system and an evaporative light scattering (ELS) detector (Polymer Laboratories, PL-

ELS 1000, Amherst, MA, nitrogen flow 1.2 L/min, evaporator temperature 90 ^{o}C) were used in all LCCC and GPEC analyses of the star and miktoarm star copolymers.

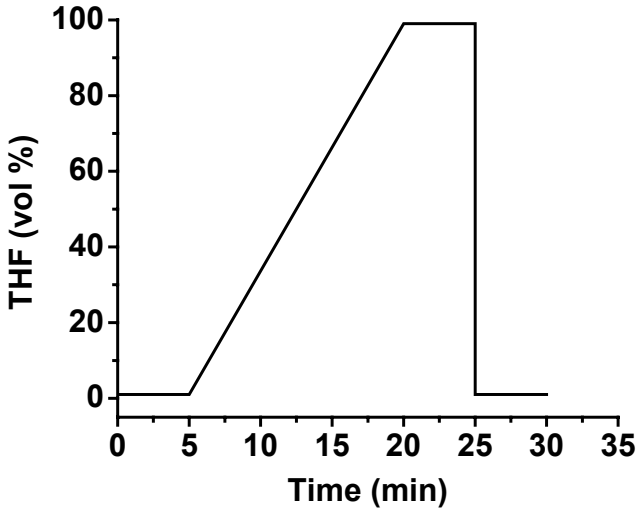

Figure S1. Gradient changing of the mobile phase as a function of time for GPEC analysis of *(polyBA)$_n$-(PEO)$_p$-polyDVB* miktoarm star copolymers.

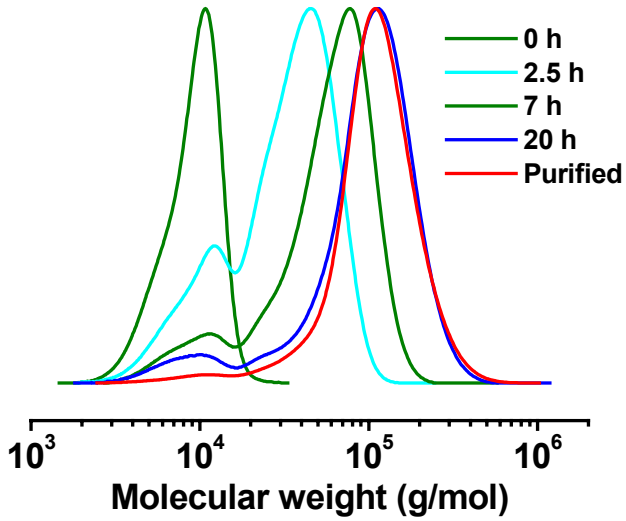

Figure S2. GPC traces during the synthesis of *(polyBA)$_n$-(polytBA)$_p$-polyDVB* miktoarm star copolymers by cross-linking two kinds of linear MIs with equal moles (M14-55, Table 3); experimental conditions: [polyBA-Br]$_0$/[poly*t*BA-Br]$_0$/[DVB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 0.5/0.5/12/0.8/0.8, [polyBA-Br] = 0.015 M, 110 ^{o}C in anisole; linear polySt standards for GPC calibration.

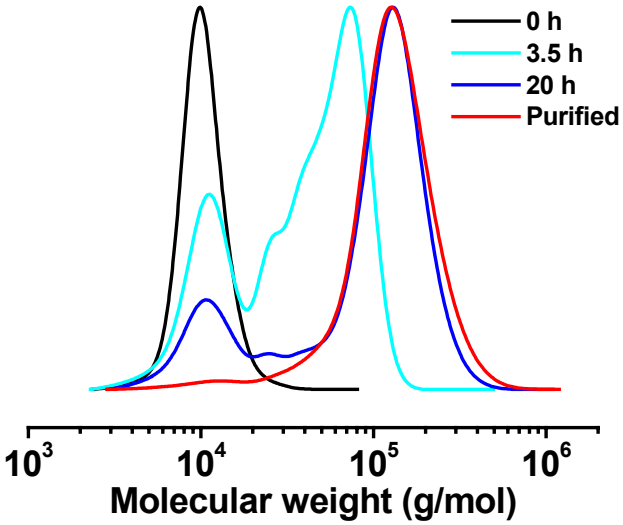

Figure S3. GPC traces during the synthesis of *(polyBA)$_n$-(polySt)$_p$-polyDVB* miktoarm star copolymers by cross-linking two kinds of linear MIs with equal moles (M15-55, Table 3); experimental conditions: [polyBA-Br]$_0$/[polySt-Br]$_0$/[DVB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 0.5/0.5/12/0.8/0.8, [polyBA-Br] = 0.015 M, 110 ^{o}C in anisole; linear polySt standards for GPC calibration.

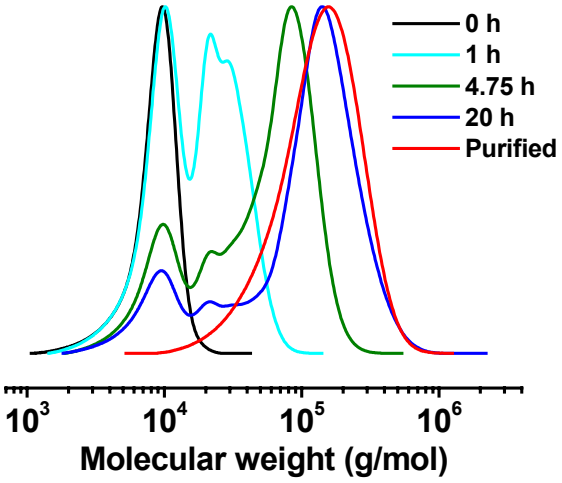

Figure S4. GPC traces during the synthesis of *(polyBA)$_n$-(polyMMA)$_p$-polyDVB* miktoarm star copolymers by cross-linking two kinds of linear MIs with equal moles (M16-55, Table 3); experimental conditions: [polyBA-Br]$_0$/[polyMMA-Br]$_0$/[DVB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 0.5/0.5/12/0.8/0.8, [polyBA-Br] = 0.015 M, 110 ^{o}C in anisole; linear polySt standards for GPC calibration.

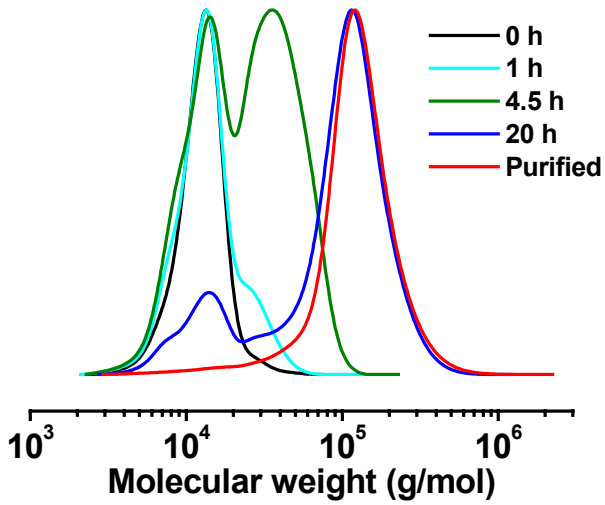

Figure S5: GPC traces during the synthesis of *(polyBA)$_n$-(PEO)$_p$-polyDVB* miktoarm star copolymers by cross-linking two kinds of linear MIs with equal moles (M17-55, Table 3); experimental conditions: [polyBA-Br]$_0$/[PEO-Br]$_0$/[DVB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 0.5/0.5/12/0.8/0.8, [polyBA-Br] = 0.014 M, 110 ^{o}C in anisole; linear polySt standards for THF GPC calibration.

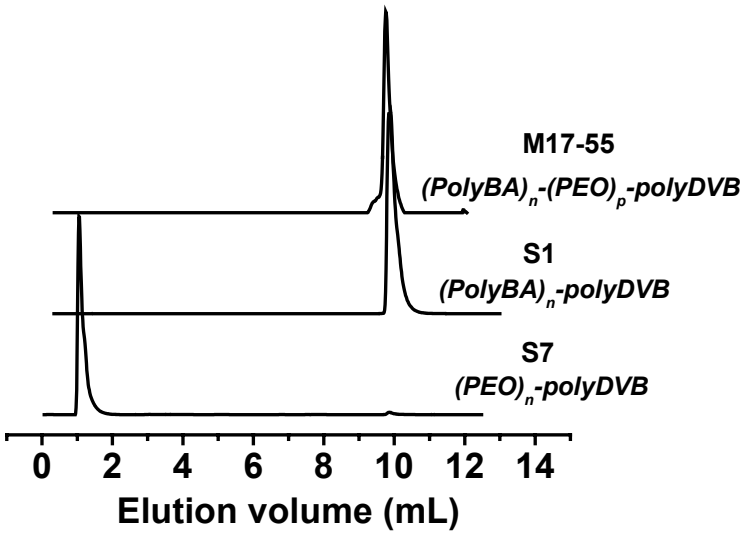

Figure S6. GPEC chromatograms of *(polyBA)$_n$-(PEO)$_p$-polyDVB* miktoarm star copolymers (M17-55, Table 3) and the corresponding homoarm star polymers: *(polyBA)$_n$-polyDVB* (S1) and *(PEO)$_n$-polyDVB* (S7); homoarm star S7 was synthesized at 110 ^{o}C with the initial ratio of reagents as [PEO-Br (MI-7)]$_0$/[DVB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 1/12/0.8/0.8 ([PEO-Br]$_0$ = 0.015 M in anisole).

In GPEC method, a binary mobile phase was used with constant flow rate (0.8 mL/min) and gradually changing composition from THF/MeOH (30/70 by volume) to THF/MeOH (100/0 by volume) within 15 min. Under this condition, the initial eluent

(MeOH-enriched solvent) was a good solvent for PEO chains but a bad solvent for polyBA chains. So *(PEO)$_n$-polyDVB* star polymers eluted at beginning with elution volume V_e = 1.54 mL (Figure S6) and the *(polyBA)$_n$-polyDVB* star polymers precipitated onto the C18 column. When the eluent composition gradually changed from MeOH-rich solvent to THF-rich solvent, the precipitated *(polyBA)$_n$-polyDVB* star polymers re-dissolved into the mobile phase and was eventually eluted at V_e = 10.1 mL. For the star product obtained by equimolar cross-linking the mixture of polyBA-Br and PEO-Br MIs, its GPEC chromatogram only showed one elution peak (V_e = 9.9 mL), indicating that a miktoarm star copolymers containing two kinds of arms in one molecule were produced. The elution volume of *(polyBA)$_n$-(PEO)$_p$-polyDVB* miktoarm star copolymers was similar to that of *(polyBA)$_n$-polyDVB* homoarm stars, indicating that the interaction of miktoarm star copolymers with the C18 column was mainly determined by the polyBA arms, instead of the PEO arms.

Calculation of the number-average value of the number of arms per star or miktoarm star molecule (N_{arm}):

1. In THF 35 ^{o}C, the dn/dc values of polyBA, poly*t*BA and polyMA linear MIs are 0.069 mL/g, dn/dc value of PEO linear MI is 0.078 mL/g, and the dn/dc value of polyDVB core is assumed to the same as that of polySt linear polymers (0.180 mL/g).[2]
2. The calculation is based on the assumption that all reacted DVB units were located in the core of star or miktoarm star molecules.
3. The average dn/dc value of the mixture of linear MIs is $\left(dn/dc\right)_{MI}$:

$$\left(dn/dc\right)_{MI} = \frac{m_{MI-1}\left(dn/dc\right)_{MI-1} + m_{MI-2}\left(dn/dc\right)_{MI-2}}{m_{MI-1} + m_{MI-2}}$$

in which, $m_{MI\text{-}i}$ and $(dn/dc)_{MI\text{-}i}$ are the mass and the dn/dc value of No. *i* linear MI, respectively.

4. The weight fraction of incorporated linear MIs versus totally added linear MIs is X_{MI}:

$$\begin{cases} \left(dn/dc\right)_{star} = \dfrac{X_{MI}m_{MI}\left(dn/dc\right)_{MI} + m_{DVB}conv_{DVB}\times\left(dn/dc\right)_{polyDVB}}{X_{MI}m_{MI} + m_{DVB}conv_{DVB}} \\ \dfrac{A_{star}}{A_{linear}} = \dfrac{A_{star}}{1-A_{star}} = \dfrac{\left(dn/dc\right)_{star}\left(X_{MI}m_{MI} + m_{DVB}conv_{DVB}\right)}{\left(dn/dc\right)_{MI}\left(1-X_{MI}\right)m_{MI}} \end{cases}$$

$$\Rightarrow \quad X_{MI} = \frac{A_{star}m_{MI}\left(dn/dc\right)_{MI} - \left(1-A_{star}\right)m_{DVB}conv_{DVB}\times\left(dn/dc\right)_{polyDVB}}{m_{MI}\left(dn/dc\right)_{MI}}$$

in which $(dn/dc)_{star}$ is the average dn/dc value of a star and/or miktoarm star polymer, $conv_{DVB}$ is the conversion of DVB and $m_{MI} = m_{MI-1} + m_{MI-2}$. The dn/dc value of a typical miktoarm star copolymer, $(polyBA)_n$-$(polyMA)_p$-$polyDVB$ (M12-55, Table 2), was determined separately by the Wyatt Optilab refractometer. The dn/dc result from the measurement was 0.092 mL/g, which is very close to the calculated result (0.090 mL/g). Such an agreement verified the accuracy of the calculated dn/dc values of the miktoarm star copolymers.

5. The average number-average molecular weight of incorporated linear MIs is $M_{n,arm}$:

$$M_{n,arm} = M_{n,MI-1} n_1 + M_{n,MI-2} n_2$$

in which, $M_{n,MI-i}$ is the number average molecular weight of *MI-i* and n_i is the molar fraction of arm *i* in the miktoarm star copolymer. Data of n_i is from Table 2, which was determined by ^{1}H NMR.

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

$$N_{arm} = \frac{M_{w,MALLS,star}}{M_{n,arm}} \times \frac{X_{MI} m_{MI}}{X_{MI} m_{MI} + m_{DVB} conv_{DVB}} \qquad \textbf{Equation S1}$$

in which, the value of $M_{w,MALLS,star}$, is from Table 2.

References

(1) Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 5995.

(2) Michielsen, S. In *Polymer Handbook*, 4th ed.; Brandup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley: New York, 1999.