Synthesis of 3-Miktoarm Stars and 1st Generation Mikto Dendritic Copolymers by 'Living' Radical Polymerization and "Click" Chemistry.

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EXPERIMENTAL

Materials

Tert-butyl acrylate (^{t}BA, 99%, Aldrich), methyl acrylate (MA, 99% Aldrich) and styrene (STY, 99%, Aldrich) were passed through a basic alumina column (activity I) to remove inhibitor. 2,2-azobis (isobutyronitrile) (AIBN, 98% Fluka) was recrystallised twice from methanol prior to use. 1-bromoethyl benzene (97%, Aldrich), ethyl-2-bromo-isobutrate (98%, Aldrich), methyl-2-bromo-propionate (97%, Fluka), CuBr (99.9%, Aldrich), $CuBr_2$ (99.9%, Aldrich), tripropargyl amine (98%, Aldrich), dimethyl 2,6-dibromoheptanedioate (DMDBHD, 97%, Aldrich) and N,N,N',N',N'' pentamethyl diethylene triamine (PMDETA, 99%, Aldrich), tetrahydrofuran (THF, 99.8%, LAB-SCAN), anisole (99%, Aldrich), dimethylformamide (DMF, A.R. Grade, Lab-Scan), Methanol (MeOH, A.R. grade, Univar) were used as received.

Synthesis of polymers with azide functionality

PSTY$_{50}$-Br (M_n = 4974, PDI = 1.09)

A typical ATRP procedure: Freshly purified styrene (13.6 g, 127 mmol), PMDETA (233 μL, 1.33 mmol), 1-bromoethyl benzene (235 μL, 1.3 mmol) and 30 mL of anisole were added to a 50 mL Schlenk flask equipped with a magnetic stirrer then degassed by four freeze-pump-thaw cycles under high vacuum. The Schlenk flask was flushed with high purity argon then $CuBr_2$ (14.2 mg, 0.060 mmol) and CuBr (186 mg, 1.3 mmol) were added. The flask was placed in an oil bath at 110^{o}C for approximately 4 h (approximately 50% conversion). The polymerization was stopped by quenching with liquid nitrogen, dilution with THF and exposure to air. The copper salts were removed by passage through an activated basic alumina column. The polymer ($PSTY_{50}$-Br) was precipitated in MeOH, filtered and dried for 24 h under high vacuum. ([STY]:[BrEB]:[CuI][CuII]:[PMDETA] = 200:1:1:0.05:1)

$PSTY_{135}$-Br **(**M_n = 13900, PDI= 1.09)

A similar procedure as above was used with the polymerization carried out in bulk at 100^{o}C for 3 h. ([STY]:[BrEB]:[CuI][CuII]:[PMDETA] = 200:1:1:1:0.05)

PMA_{65}-Br **(**M_n = 5557, PDI= 1.06)

A similar procedure as above was used, however, the polymerization was carried out using ethyl-2-bromo-isobutrate as initiator in anisole at 60^{o}C for 90 min. ([MA] : [EbiB] : [CuBr] : [PMDETA] = 200 : 1 : 0.5).

$P^{t}BA_{54}$-Br (Mn=6895 , PDI=1.08).

A similar procedure as above was used, however, the polymerization was carried out using methyl 2-bromopropionate as initiator in acetone at 60^{o}C for 5 h. ([t-BA]:[MBrP]:[CuI][CuII]:[PMDETA] = 100:1:1:.05:1.05)

$PSTY_{50}$-N_3 (M_n = 4974, PDI = 1.09) ***(Azidation)***

Azidation was as follows: 0.5 g of PSTY-Br (1.05×10^{-4} mol) was dissolved in 10 mL of DMF, and NaN_3 (65 mg, 1 mmol) was added and stirred for 24 h at room temperature. The polymer was precipitated in MeOH and exhaustively washed with water, and then

MeOH. The polymer ($PSTY_{50}$-N_3) was dried under high vacuum for 48 h at 25^{o}C and the molecular weight distribution determined by SEC. This procedure was used for the azidation of all other polymers.

N_3-PSTY$_2$-N_3 **(**M_n = 2635, PDI= 1.09)

The difunctional polystyrene (Br-PSTY-Br) was synthesized using ATRP using dimethyl 2,6-dibromoheptanedioate (DMDBHD) in bulk at 100^{o}C for 20 min ([St]:[DMDBHD]:[CuBr]:[PMDETA]= 200:1:2:1). The difunctional Br-PSTY-Br was converted to the diazide polymer using the same azidation procedure above.

Synthesis of 3-arm polystyrene stars

One pot reaction of PSTY-N_3 and tripropargylamine

$PSTY_{50}$-N_3 (0.1 g, 2.01×10^{-5} mol, 20 mM), PMDETA (42.2 μL, 2.01×10^{-4} mol, 200 mM) and 0.25 mL of a stock 26.8 mM tripropargyl amine solution in DMF was added to a Schlenk flask. The reaction mixture was then degassed by 4 freeze-thaw-pump cycles, CuBr (28.9 mg, 2.01×10^{-4} mol, 200 mM) was then added, and the reaction mixture further degassed by 4 freeze-pump-thaw cycles. The reaction mixture was purged with nitrogen and heated to 80^{o}C for 19 h. The reaction mixture was diluted with THF and passed through a basic alumina to remove the copper salts. The resulting polymer was analyzed by SEC.

Slow addition of tripropargylamine to PSTY-N_3

$PSTY_{50}$-N_3 (0.1 g, 2.01×10^{-5} mol, 20 mM) and PMDETA (42.2 μL, 2.01×10^{-4} mol, 201 mM) in 1 mL of DMF was added to a Schlenk and degassed by 4 freeze-thaw-pump cycles. CuBr (28.9 mg, 2.01×10^{-4} mol, 200 mM) was added, and the reaction mixture further degassed by 4 freeze-pump-thaw cycles. The reaction mixture was heated to 80^{o}C, and 0.25 mL of a stock 26.8 mM tripropargyl amine solution in DMF was added via a syringe pump at 0.005 mL/min for the first 30 min (approximately a 60 % stoicheometric amount of core to arms) and the rate reduced to 0.0008 mL/min for the remainder of the core. After full addition the mixture was allowed to react for a further 60min.

One pot reaction using PSTY-Br, NaN_3 and slow addition of tripropargylamine

$PSTY_{50}$-Br (0.1 g, 2.01×10^{-5} mol, 20 mM) in 1 mL of DMF was placed into a Schlenk flask, NaN_3 (2.6mg, 4.02×10^{-5} mol, 40 mM) was then added and the reaction mixture heated to 50^{o}C for 49 h. PMDETA (42.2 μL, 2.01×10^{-4} mol, 201 mM) was the added to the flask and the reaction mixture was degassed by 4 freeze-pump-thaw cycles after which CuBr (28.9 mg, 2.01×10^{-4} mol, 201 mM) was added and the mixture again degassed. The reaction mixture was heated to 80^{o}C, and 0.25 mL of a stock 26.8 mM tripropargyl amine solution in DMF was added via a syringe pump using the same feed conditions as above. Samples were withdrawn periodically for analysis via SEC. After full addition the mixture was allowed to stir for a further 60 min.

Synthesis of statistical 3-miktoarm stars

Procedure A:

A typical procedure is as follows: NaN_3 (2.6 mg, 4.02×10^{-5} mol, 40 mM) was added to a solution of $PSTY_{25}$-Br (1 Eq, 6.6×10^{-6} mol, 6.6 mM), PMA_{65}-Br (2 Eq, 1.33×10^{-5} mol, 13.3 mM) in 1 mL DMF, and the reaction was heated at 50^{o}C for 48 h. PMDETA (42.2 μL, 2.01×10^{-4} mol, 201 mM) was then added to the flask and the reaction mixture was degassed by 4 freeze-pump-thaw cycles after which CuBr (28.9 mg, 2.01×10^{-4} mol, 201 mM) was added and the mixture again degassed. The reaction mixture was heated to

80^{o}C, and 0.25 mL of a stock 26.8 mM tripropargyl amine solution was added via a syringe pump using the same feed conditions as above.

Procedure B:

0.092 g of PSTY$_{135}$-Br (6.62×10^{-6} mol, 6.26 mM) and 0.092 g of PtBA$_{54}$-Br (1.33×10^{-5} mol, 13.3 mM) was dissolved in 1 mL of DMF in a 10 mL Schlenk flask with a magnetic stirrer. This gave a molar ratio of Sty:MA of approximately 1:2. To the stirred solution was added NaN$_3$ (2.6 mg, 4.02×10^{-5} mol, 40 mM). The solution was stirred for 48hrs at 50^{o}C. Formation of mikto arm stars was achieved in a similar fashion to that used in procedure B above.

Synthesis of well-defined 3-miktoarm stars

PSTY$_{50}$-Br (0.5 g, 1.01×10^{-4} mol, 10 mM,) was dissolved in 10 mL of DMF. NaN$_3$ (65 mg, 1.01×10^{-3} mol, 103 mM) was then added to the solution and stirred at room temperature for 24 h. The resulting PSTY$_{50}$-N$_3$ was precipitated in MeOH and dried in a vacuum oven at 25^{o}C for 48 h. PSTY$_{50}$-N$_3$ (0.3 g, 6.03×10^{-5} mol, 20 mM) was dissolved in 3 mL of DMF. PMDETA (126.6 μL, 6.03×10^{-4} mol, 201 mM) and tripropargylamine (170.6 μL, 1.21×10^{-3} mol, 403 mM) were added to the solution and degassed by 4 successive freeze-thaw-pump cycles. CuBr (86.7 mg, 6.03×10^{-4} mol, 201 mM) was added, and the reaction mixture further degassed by 4 successive freeze-thaw-pump cycles. The reaction was then heated to 80^{o}C for 60 min. The mixture was diluted with THF, and the copper salts removed by passing through a basic alumina column. The PSTY$_{50}$-(-≡)$_2$ was then precipitated in and washed with MeOH, and dried in a vacuum oven at 25^{o}C for 48 h. A solution of P^{t}BA$_{54}$-N$_3$ (1.34×10^{-5} mol, 13.4 mM) in 1 mL of DMF (prepared using the same methodology as above) and PMDETA (28.1 μL, 1.34×10^{-}

^{4} mol, 134 mM) was degassed by 4 successive freeze-thaw-pump cycles, CuBr (19.2 mg, 1.34×10^{-4} mol, 134 mM) was then added and the reaction mixture further degassed by 4 successive freeze-thaw-pump cycles. Then 0.25 mL of a 26.7 mM solution of PSTY$_{50}$-(-≡)$_2$ in DMF was then fed in using a syringe pump at a rate of 0.0008 mL/min. Samples were withdrawn periodically for analysis by SEC. After full addition the mixture was allowed to stir for a further 60 min.

Annotations to above experimental procedures

P^{t}BA$_{54}$-N$_3$ and PMA$_{65}$-N$_3$ were prepared as detailed above for PSTY$_{50}$-N$_3$ but were purified by extraction from chloroform/water. P^{t}BA$_{54}$-(-≡)$_2$ and PMA$_{65}$-(-≡)$_2$ were prepared as for PSTY$_{50}$-(-≡)$_2$ above but were purified by precipitation in a cold 50/50 methanol/water solution. The 3-miktoarm stars, P[(MA$_{65}$)$_2$-(STY$_{50}$)$_1$], P[(MA$_{65}$)$_2$-(^{t}BA$_{54}$)$_1$], P[(STY$_{50}$)$_2$-(^{t}BA$_{54}$)$_1$], and P[(^{t}BA$_{54}$)$_2$-(MA$_{65}$)$_1$] were prepared as detailed above for P[(^{t}BA$_{54}$)$_2$-(STY$_{50}$)$_1$].

1st Generation 4-arm Dendrimer

(≡-)$_2$-PSTY$_{25}$-(-≡)$_2$: 0.3 g of PSTY$_{25}$-(N$_3$)$_2$ prepared above (1.14×10^{-4} mol, 38 mM) was dissolved in 3 mL DMF. To this solution was added PMDETA (476 μL, 2.28×10^{-3} mol, 760 mM) and tripropargyl amine (645 μL, 4.56×10^{-3} mol, 1.52 M). The solution was then degassed by 4 freeze-thaw-pump cycles. The Schenk flask was carefully opened and CuBr (328 mg, 2.28 ×10^{-3} mol, 760 mM) was quickly added after which the flask was sealed and degassed again with 4 freeze-pump-thaw cycles. After the final cycle the Schlenk flask was purged with nitrogen and heated to 80^{o}C in a temperature controlled oil bath for 60 min. The flask was then opened and the solution diluted with THF.

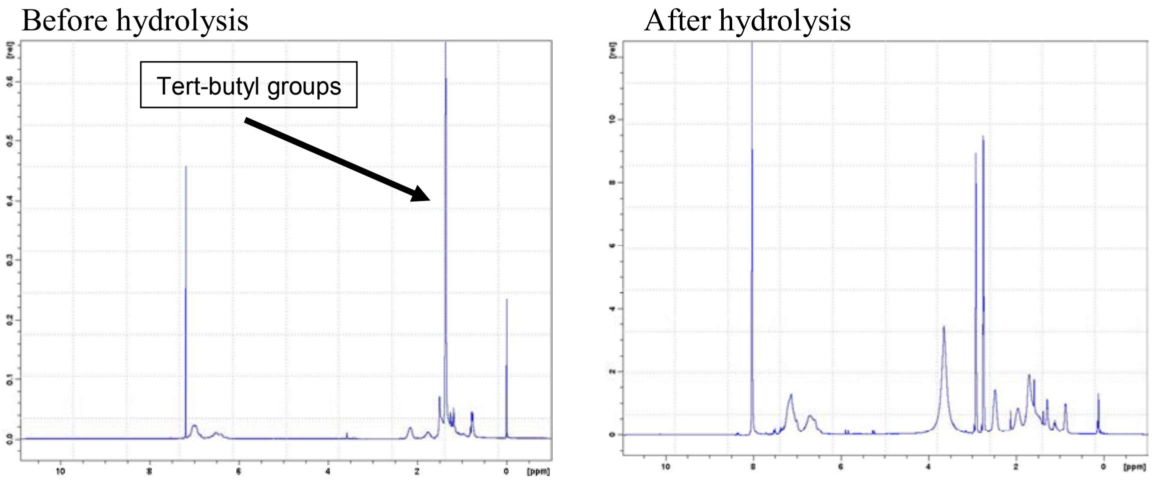
Copper salts were removed via passage through a basic alumina column. The polymer $PSTY_{25}$-(-≡)$_4$ was precipitated in methanol and recovered by filtration after exhaustive washing with methanol. The polymer was dried for 48 h under high vacuum at 25^oC.

P[(STY$_{25}$)$_1$-(^{t}BA$_{54}$)$_4$] **:** A solution of P^tBA_{54}-N_3 (1.34×10^{-5} mol, 13.4 mM) in 1 mL of DMF (prepared using the same methodology as above) and PMDETA (28.1 μL, 1.34×10^{-4} mol, 134 mM) was degassed by 4 successive freeze-thaw-pump cycles, CuBr (19.2 mg, 1.34×10^{-4} mol, 134 mM) was then added and the reaction mixture further degassed by 4 successive freeze-thaw-pump cycles. Then 0.24 mL of a 13.9 mM solution of $PSTY_{25}$-(-≡)$_4$ in DMF was then fed in using a syringe pump at a rate of 0.0008 mL/min.

P[(STY$_{50}$)$_2$-(STY$_{25}$)$_1$-(^{t}BA$_{54}$)$_2$]: A solution of $PSTY_{50}$-N_3 (1.01×10^{-5} mol, 10 mM), P^tBA_{54}-N_3 (1.01×10^{-5} mol, 10 mM) in 1 mL of DMF (prepared using the same methodology as above) and PMDETA (42.2 μL, 2.01×10^{-4} mol, 201 mM) was degassed by 4 freeze-pump-thaw cycles after which CuBr (28.9 mg, 2.01×10^{-4} mol, 201 mM) was added and the mixture again degassed. A 1st generation dendrimer with $PSTY_{50}$ and P^tBA_{54} arms was achieved in a similar fashion to that used in procedure above.

Hydrolysis of P^{t}BA to PAA

A typical hydrolysis reaction is as follows: hydrolysis of the well-defined 3-miktoarm star polymer, P[(^{t}BA$_{54}$)$_2$-(Sty$_{50}$)$_1$]: to a stirred solution of 20 mg of polymer was dissolved into 1 mL of DCM (1.14×10^{-4} mol. ^{t}BA groups) was added TFA (65 mg, 5.70×10^{-4} mol). The solution was stirred overnight at 25^oC after which the solution was dried with a nitrogen stream. The hydrolysed material was then further dried for 48 h at 25^oC in a high vacuum oven. Hydrolysis of the ^{t}BA groups was confirmed by the loss of the tert-butyl groups in the ^1H spectrum situated at 1.35 ppm.


Before hydrolysis

After hydrolysis

Figure S1: ^{1}H spectrum of P[(^{t}BA$_{54}$)$_2$-(Sty$_{50}$)$_1$] before and after hydrolysis with TFA.

Size Exclusion Chromatography (SEC):

Size Exclusion Chromatography (SEC) measurements of the star and cleaved arms were also performed using a Waters Alliance 2690 Separations Module equipped with an autosampler, column heater, differential refractive index detector and a Photo Diode Array (PDA) connected in series. HPLC grade tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1}. The columns consisted of three 7.8*300 mm Waters Styragel SEC columns connected in series, comprising 2 linear Ultrastyragel and one Styragel HR3 columns. Polystyrene standards ranging from 2000000 - 517 g mol^{-1} were used for calibration.

Table S1: Size exclusion chromatographic data for 3-arm homopolymer stars using ATRP and ‘click’ chemistry.

Experiment	**Starting arms**	**3-arm stars**	**M_n**	**PDI**	**Yield[d] %**
3-homoarm stars					
S1[a]	STY_{50}-N_3 (M_n=4974, PDI=1.09)	$(PSty_{50})_3$	13192	1.05	75 (19 h)
S2[b]	STY_{50}-N_3 (M_n=4974, PDI=1.09)	$(PSty_{50})_3$	13873	1.04	78 (3.5 h)
S3[c]	STY_{50}-N_3 (M_n=4974, PDI=1.09)	$(PSty_{50})_3$	14211	1.04	69 (0.5 h)
			13928	1.04	80 (1.5 h)
			14906	1.03	86 (3.5 h)
S4	P^tBA_{54}-N_3 (M_n=6895, PDI=1.08)	$(P^tBA_{54})_3$	18775	1.04	75 (0.5 h)
			18815	1.04	83 (1.5 h)
			19943	1.05	87 (3.5 h)
S5	PMA_{65}-N_3 (Mn=5557, PDI=1.06)	$(PMA_{65})_3$	14567	1.05	45 (0.5 h)
			14780	1.05	71 (1.5 h)
			15539	1.04	88 (3.5 h)

a) one shot addition of tripropargyl amine to $PSTY_{50}$-N_3
b) slow addition of tripropargyl amine to $PSTY_{50}$-N_3
c) slow addition of tripropargyl amine to *in situ* generated $PSTY_{50}$-N_3
d) estimated from cumulative weight fraction

Table S2: Size exclusion chromatographic data for well-defined 3-miktoarm stars using ATRP and ‘click’ chemistry.

Experiment	**Starting arms**		**3-arm stars**	**M_n**	**PDI**	**Yield^a %**
3-miktoarm stars	**1 Eq.**	**2 Eq.**				
S6	$PSTY_{50}\text{-}(\equiv)_2$ (M_n=4974, PDI=1.09)	$P^tBA_{54}\text{-}N_3$ (M_n=6895, PDI=1.08)	$P[({}^{t}BA_{54})_2\text{-}(Sty_{50})_1]$	18239	1.03	28 (1 h)
				18243	1.04	54 (2 h)
				17995	1.04	66 (3 h)
				18092	1.04	81 (4 h)
				17772	1.04	88 (6 h)
				18415	1.03	92 (19 h)
S7	$PSTY_{50}(\equiv)_2$ (M_n=4974, PDI=1.09)	$PMA_{65}\text{-}N_3$ (M_n=5557, PDI=1.06)	$P[(MA_{65})_{2\text{-}}(STY_{50})_1]$	15188	1.04	23 (1h)
				15045	1.04	50 (2h)
				14799	1.04	63 (3h)
				14740	1.05	82 (5h)
S8	$P^tBA_{54}\text{-}(\equiv)_2$ (M_n=6895, PDI=1.08)	$PSTY_{50}\text{-}N_3$ (M_n=4974, PDI=1.09)	$P[(STY_{50})_{2\text{-}}({}^{t}BA_{54})_1]$	15484	1.05	43 (1h)
				15367	1.05	75 (2h)
				16541	1.05	80 (3h)
				16365	1.04	88 (5h)
S9	$P^tBA_{54}\text{-}(\equiv)_2$ (M_n=6895, PDI=1.08)	$PMA_{65}\text{-}N_3$ (M_n=5557, PDI=1.06)	$P[(MA_{65})_{2\text{-}}({}^{t}BA_{54})_1]$	16603	1.02	32 (1h)
				15675	1.05	76 (2h)
				15876	1.05	78 (3h)
				15869	1.05	82 (5h)
S10	$PMA_{65}\text{-}(\equiv)_2$ (M_n=5557, PDI=1.06)	$P^tBA_{54}\text{-}N_3$ (M_n=6895, PDI=1.08)	$P[(MA_{65})_{1\text{-}}({}^{t}BA_{54})_2]$	16059	1.07	75 (5 h)

Table S3: Size exclusion chromatographic data for the 1st generation dendrimer using ATRP and 'click' chemistry.

Experiment	**Starting arms**		**3-arm stars**	**M_n**	**PDI**	**Yield[a] %**
1st Generation Dendrimer	**Core**	**Arms**				
S11	$(\equiv)_2$-PSTY$_{25}$-$(\equiv)_2$ (M_n=2639, PDI=1.09)	P^{t}BA-N$_3$ (M_n=6895, PDI=1.08)	P[(STY$_{25}$)$_1$-(^{t}BA$_{54}$)$_4$]	29222	1.04	35 (2 h)
				28792	1.04	51 (3 h)
				27012	1.08	70 (4 h)
				26628	1.08	80 (6 h)
S12	$(\equiv)_2$-PSTY$_{25}$-$(\equiv)_2$	P^{t}BA$_{54}$-N$_3$ (M_n=6895, PDI=1.08)	P[(STY$_{50}$)$_2$-(STY$_{25}$)$_1$-(^{t}BA$_{54}$)$_2$]	24028	1.08	37 (2 h)
	(M_n=2639, PDI=1.09)	STY$_{50}$-N$_3$ (M_n=4974, PDI=1.09)		23246	1.09	54 (3 h)
				22500	1.10	65 (4 h)
				22497	1.10	70 (6 h)

a) estimated from cumulative weight fraction

Table S4: Size exclusion chromatographic data for statistical 3-miktoarm stars using ATRP and 'click' chemistry.

Experiment	**Starting arms**		**3-arm stars**	**M_n**	**PDI**	**Yield[a] %**
3-miktoarm stars	**1 Eq.**	**2 Eq.**				
S13	P^{t}BA$_{54}$-N$_3$ (M_n=6895, PDI=1.08)	PMA-N$_3$ (M_n=5557, PDI=1.06)	P[(MA$_{65}$)$_2$-(^{t}BA$_{54}$)$_1$]	16047	1.04	58 (0.5 h)
				15780	1.05	76 (1.5 h)
				15559	1.06	85 (3.5 h)
S14	STY$_{50}$-N$_3$ (M_n=4974, PDI=1.09)	P^{t}BA$_{54}$-N$_3$ (M_n=6895, PDI=1.08)	P[(^{t}BA$_{54}$)$_2$-(Sty$_{50}$)$_1$]	18002	1.04	58 (0.5 h)
				17488	1.05	70 (1.5 h)
				17141	1.06	76 (3.5 h)
S15	STY$_{50}$-N$_3$ (M_n=4974, PDI=1.09)	PMA-N$_3$ (M_n=5557, PDI=1.06)	P[(MA$_{65}$)$_2$-(Sty$_{50}$)$_1$]	14386	1.06	70 (3.5 h)
S16	STY$_{135}$-N$_3$ (M_n=13900, PDI=1.07)	P^{t}BA$_{54}$-N$_3$ (M_n=6895, PDI=1.08)	P[(^{t}BA$_{54}$)$_2$-(Sty$_{135}$)$_1$]	27000	1.11	85 (6 h)

a) estimated from cumulative weight fraction

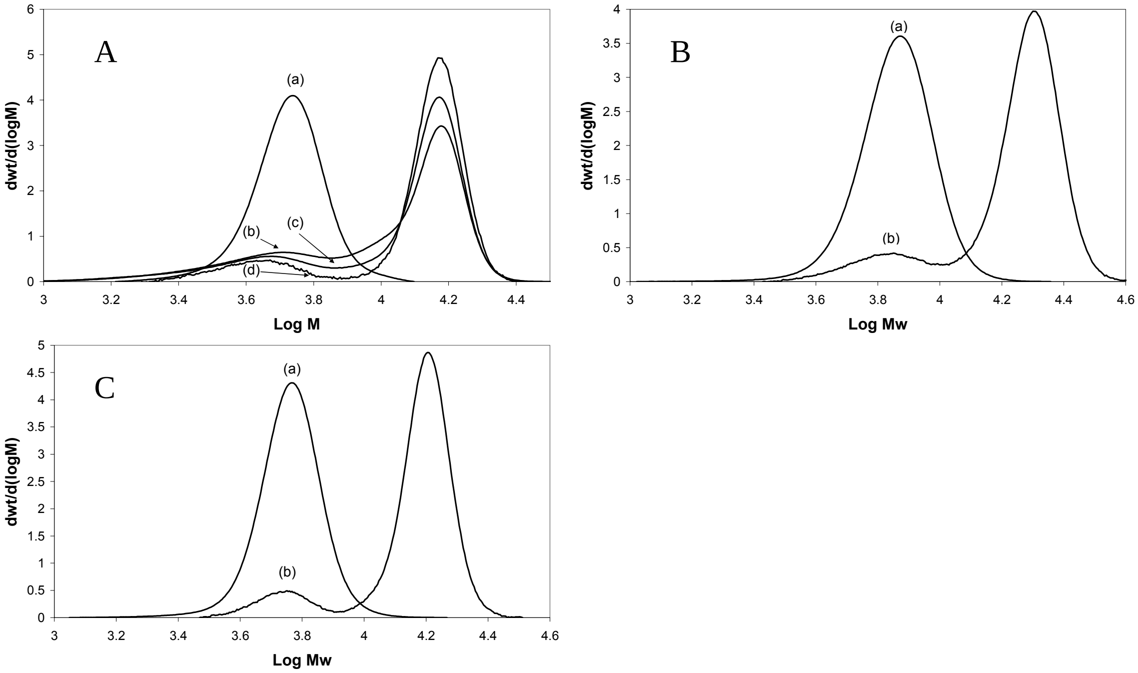


Figure S2: Size exclusion chromatograms of 3-homoarm stars (A) P(STY$_{50}$)$_3$ (Expt. S1): curve (a) PSTY$_{50}$-N$_3$, (b) Exp S1 single shot addition to PSTY$_{50}$-N$_3$, (c) slow addition of tripropargylamine to PSTY$_{50}$-N$_3$, and (d) in situ azidation of PSTY$_{50}$-Br with slow addition of tripropargylamine. (B) synthesis of P(^{t}BA$_{54}$)$_3$ 3-arm stars (Expt S4): curve (a) P^{t}BA$_{54}$-Br, (b) P(^{t}BA$_{54}$)$_3$ after 3.5 h reaction with tripropargylamine. (C) synthesis of P(MA$_{65}$)$_3$ 3-arm stars (Expt. S5): curve (a) PMA$_{64}$-Br, and (b) P(MA$_{65}$)$_3$ after 3.5 h reaction time.

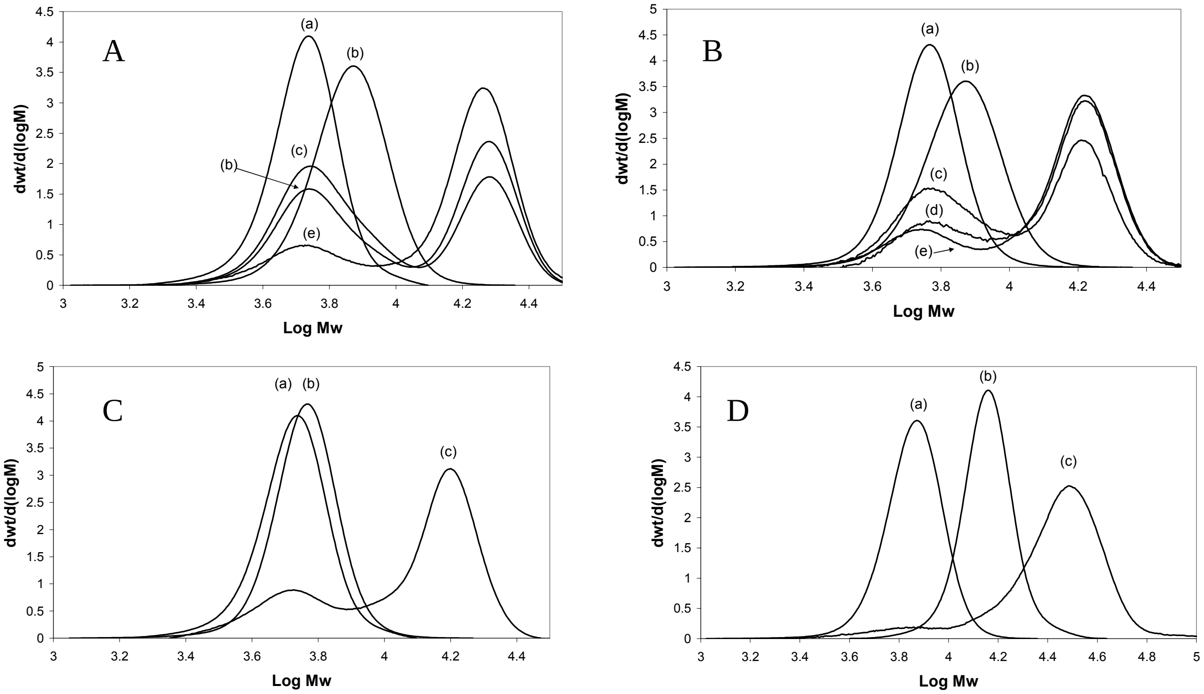


Figure S3: Size exclusion chromatograms of statistical 3-mitkoarm stars. (A) P[(^{t}BA$_{54}$)$_2$-(Sty$_{50}$)$_1$] stars (Expt. S14): curve (a) PSTY$_{50}$-Br (M_n=4974, PDI=1.09), (b) P^{t}BA$_{54}$-Br (M_n=6895, PDI=1.08), (c) 30 min, (d) 90 min and (c) 210 min reaction times with tripropargylamine. (B) P[(MA$_{65}$)$_2$-(^{t}BA$_{54}$)$_1$] (Expt. S13): curve (a) PMA$_{65}$-Br, (b) PtBA$_{54}$-Br , (c) 30 min, (d) 90 min, and (e) 210 min reaction time with tripropargylamine. (C) P[(MA$_{65}$)$_2$-(Sty$_{50}$)$_1$] (Expt. S15): curve (a) PSTY$_{50}$-Br, (b) PMA$_{65}$-Br, and (c) 3.5 h reaction time with tripropargylamine. (D) P[(^{t}BA$_{54}$)$_2$-(Sty$_{135}$)$_1$] (Expt. S16): curve (a) PSTY$_{135}$-Br (M_n=13900, PDI=1.07), (b) P^{t}BA$_{54}$-Br (M_n=6895, PDI=1.08), (c) after 6 h reaction time.

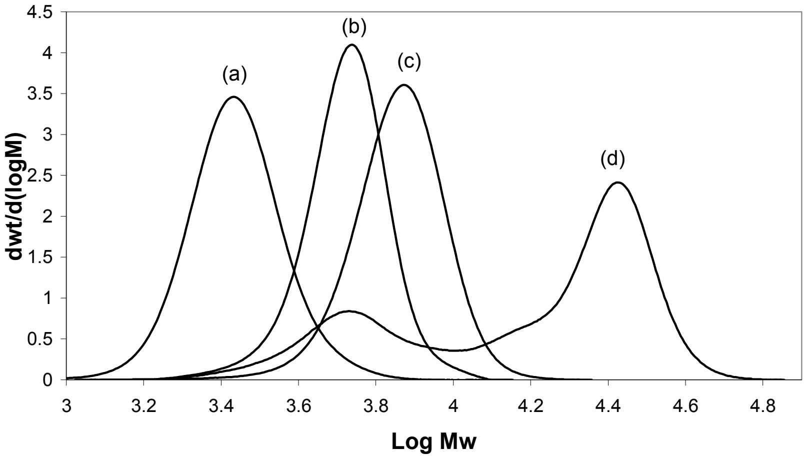


Figure S4: Size exclusion chromatograms: the evolution for the formation of P[$(STY_{50})_2$-$(STY_{25})_1$-$(^tBA_{54})_2$] (Expt. S12): curve (a) $(\equiv\text{-})_2$-$PSTY_{25}$-$(\text{-}\equiv)_2$, (b) $PSTY_{50}$-Br , (c) P^tBA_{54}-Br, and (d) P[$(STY_{50})_2$-$(STY_{25})_1$-$(^tBA_{54})_2$] after 6 h reaction time.

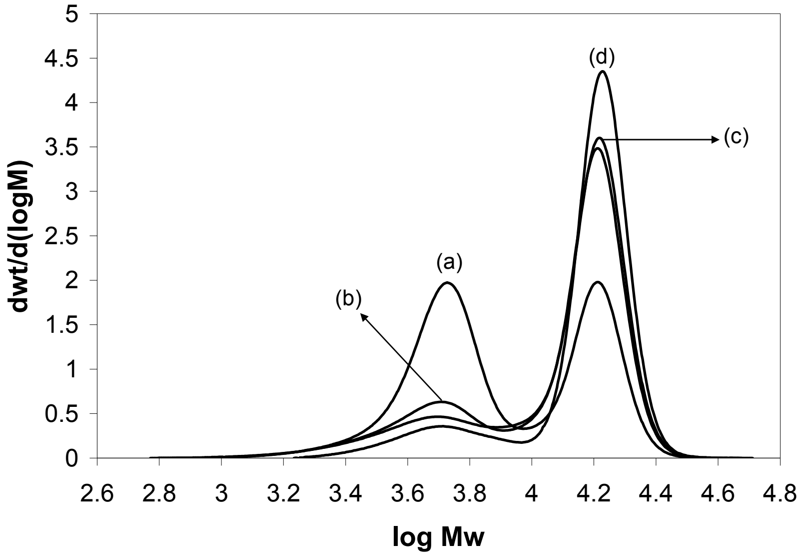


Figure S5: Size exclusion chromatograms of well-defined 3-miktoarm stars P[(STY$_{50}$)$_2$-(^{t}BA$_{54}$)$_1$] (Expt. S8): curve (a) 1 h, (b) 2 h, (c) 3 h, and (d) 5 h reaction time.

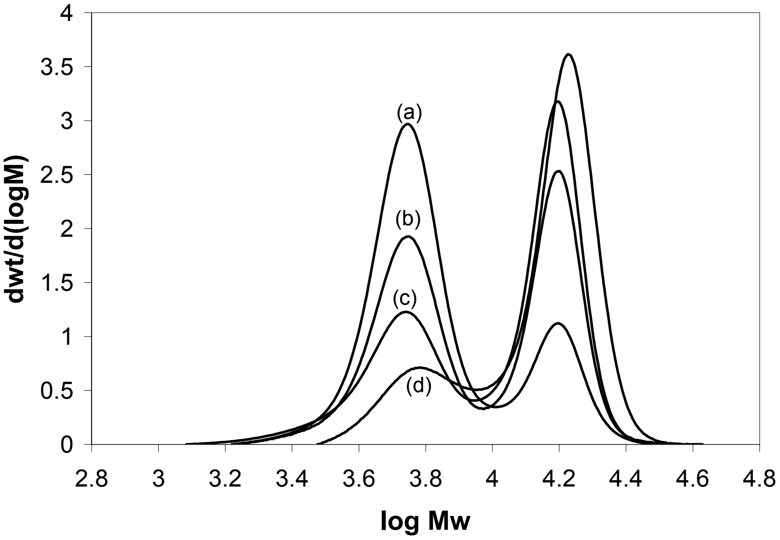


Figure S6: Size exclusion chromatograms of well-defined 3-miktoarm stars P[(STY$_{50}$)$_1$-(MA$_{54}$)$_2$] (Expt. S7): curve (a) 1 h, (b) 2 h, (c) 3 h, and (d) 5 h reaction time.

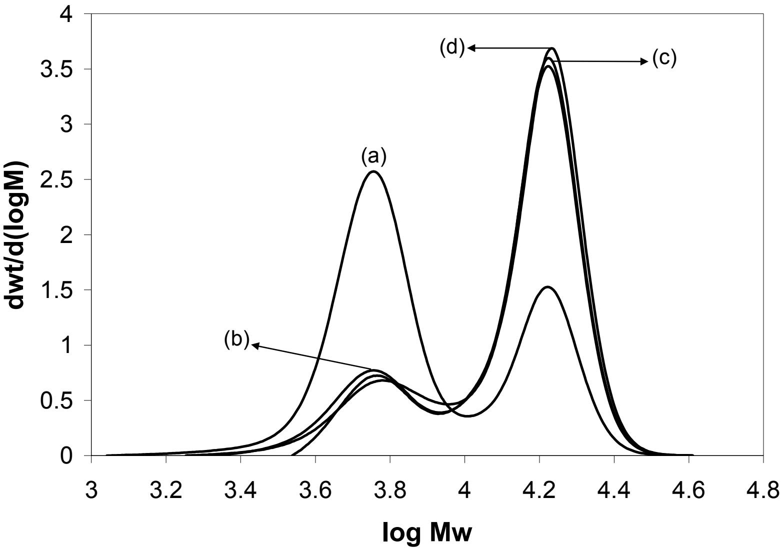


Figure S7: Size exclusion chromatograms of well-defined 3-miktoarm stars P[$(MA_{65})_2$-$(^tBA_{54})_1$] (Expt. S9): curve (a) 1 h, (b) 2 h, (c) 3 h, and (d) 5 h reaction time.